

2.1 INTRODUCTION

This chapter focuses on the preparations of the organotin starting materials which were subsequently used to prepare the organotin complexes. The tetraorganotin compounds were prepared using the Grignard method. Subsequently, the tetraorganotins were converted to diorganotins *via* a comproportionation reaction. Comproportionation usually refers to a chemical reaction whereby two reactants, each containing the same element but with different oxidation number, form a product with an oxidation number intermediate between those of the two reactants. However, as the yield of the diorganotins obtained from the comproportionation reaction was rather low, due to the formation of numerous side-products, such as magnesium bromide, magnesium chloride, stannous chloride, stannic chloride, a bromination reaction had been suggested for the preparation of the diorganotin derivatives. The use of a mild brominating agent will therefore be the focus of the study in order to obtain the diorganotin compounds in higher yield.

In addition to the conventional comproportionation reaction for the preparation of diorganotin compounds, a section of this chapter will report on the bromination reaction of some tetraorganotin compounds using suitable mild brominating agent. Several brominating agents such as bromine, *N*-bromosuccinimide (NBS), 1,3-dibromo-5,5-dimethylhydantoin (DBMDH), 4-dimethylaminopyridine hydrobromide perbromide and pyridinium tribromide have been used in various bromination reactions. Bromine was not favourable as brominating agent as it was a strong brominating agent and the products obtained were not selective. Also, it was very toxic and hazardous upon direct exposure. *N*-Bromosuccinimide (NBS) was a brominating and oxidizing agent that is often used as a source of bromine in various radical reactions and electrophilic

additions. 1,3-Dibromo-5,5-dimethylhydantoin (DBMDH) was a cheaper and convenient alternative to NBS for the bromination of electron-rich arenes while pyridinium tribromide was often used in the bromination of stilbene.

For the current bromination reaction, 4-(dimethylamino)pyridine hydrobromide perbromide was used as it was a mild brominating agent whereby the reaction should be more selective and the yield obtained for the diorganotin derivatives could be higher. A number of bromination products using 4-dimethylaminopyridine hydrobromide perbromide such as 4-(dimethylamino)pyridinium dibromidotriphenylstannate(IV) [Norshafiza *et al.*, 2008], *bis*[4-(dimethylamino)-pyridinium] tetrabromidodiphenylstannate(IV) [Yap *et al.*, 2008a], *bis*[4-(dimethylamino)pyridinium] tetrabromidobis(3,4-dichlorophenyl)stannate(IV)-1-bromo-3,4-dichlorobenzene (1/1) [Koon *et al.*, 2009], *bis*[4-(dimethylamino)pyridinium] tribromidochloridodimethylstannate(IV) [Lo and Ng 2008] have been reported.

The dibenzyltin and chloro-substituted dibenzyltin derivatives were synthesized according to the preparation method reported in the literature [Sisido *et al.*, 1961]. In this report, the tin powder and benzyl chloride or chloro-substituted benzyl chloride reacted when the reaction mixture reached a temperature of 110-120°C with a trace amount of water.

2.2 SYNTHESIS

The following commercial chemicals of reagent grade were used in the synthesis: benzyl chloride, 2-chlorobenzyl chloride, 4-chlorobenzyl chloride, tin powder, magnesium, bromocyclohexane, *p*-bromochlorobenzene, 4-bromotoulene anhydrous stannic chloride, ammonium chloride and sodium hydroxide. 4-(dimethylamino)pyridine tribromide was used as the bromination agent in the bromination reaction of the tetraorganotins.

The solvents used in the preparation of the organotin starting materials were toluene, chloroform, tetrahydrofuran, acetone, petroleum ether and absolute ethanol. These solvents were distilled before use.

2.2.1 Preparation of Organotin Compounds

Preparation of dibenzyltin dichloride and its derivatives

Three or four drops of distilled water were added into a flat-bottom flask which contained tin powder (17.8 g, 0.15 mol) in a toluene suspension. The mixture was mixed thoroughly, stirred well and efficiently; and heated to about 110°C, which was the boiling-point of toluene. Then, 19.2 g (0.15 mol) of benzyl chloride were added dropwise into the suspension mixture and refluxed for 3 hours.

After refluxing, fine colourless crystals started to appear on the surface of the solution. The mixture was filtered while it was hot. The grayish residue which remained at the bottom of the flask was dissolved, extracted with acetone and filtered. The second filtrate was mixed together with the first filtrate and the solution was

evaporated under diminished pressure to give a yellow solid. Yield: 38.41 g (68.8%), m.p. 161-164 °C

The other derivatives of dibenzytin dichloride; di(*o*-chlorobenzyl)tin dichloride [Yield: 41.50 g (62.8%), m.p. 190-192°C] and di(*p*-chlorobenzyl)tin dichloride [Yield: 39.91 g (60.3%), m.p. 200-202°C] were prepared using similar method.

Preparation of tetracyclohexyltin(IV)

12.16 g (0.5 mol) of magnesium was added to 500 mL of dry tetrahydrofuran. After that, about 5 mL of the 62 mL (0.5 mol) of bromocyclohexane was added slowly through a dropping funnel into the magnesium suspension. The mixture was stirred and heated until the reaction started and a dark brown solution was obtained. Then, the remaining bromocyclohexane was added dropwise and upon completion, the mixture was refluxed for two hours. After cooling the mixture, 10 mL (0.125 mol) of anhydrous stannic chloride (SnCl₄) in 90 mL of toluene was added dropwise into the mixture. Upon completion, the mixture was refluxed for another two hours, followed by stirring overnight. The reaction mixture was hydrolyzed with 10% ammonium chloride in order to remove the excess stannic chloride and Grignard reagent. The organic layer which was separated was concentrated by rotary evaporation. A white solid was formed upon removal of solvent. The solid was recrystallized from chloroform. Yield: 39.53 g (70.2 %); m.p. 261-264°C.

Preparation of dicyclohexyltin(IV) dichloride

Tetracyclohexyltin (11.30 g, 0.025 mol) and anhydrous stannic chloride (6.51 g, 0.025 mol) were heated in an oil-bath at 230°C for 3 hours with stirring. Then, the viscous liquid was extracted with hot chloroform. After that, the chloroform extract

was concentrated to a small volume and petroleum ether (b.p. 60-80°C) was added to it to obtain the product. The pure product was obtained by recrystallization of the crude product from petroleum ether. Yield: 9.11 g (51.0 %); m.p. 108-110°C

Preparation of dicyclohexyltin(IV) oxide

10% sodium hydroxide was slowly added dropwise into a stirring solution of dicyclohexyltin dichloride (5.34 g, 0.015 mol) which was dissolved in acetone. The fine white powder that was precipitated after the addition of 10% sodium hydroxide solution was then filtered and vacuum-dried. The starting material was used without further purification. Yield: 2.32 g (51.3 %); m.p. > 350°C (dec.)

Preparation of tetra(4-chlorophenyl)tin(IV)

Firstly, *p*-bromochlorobenzene (95.73 g, 0.5 mol) was dissolved in dried tetrahydrofuran. Then, 12.16 g (0.5 mol) of magnesium was added to 500 mL of dry tetrahydrofuran. After that, about 5 mL of *p*-bromochlorobenzene was added slowly through a dropping funnel into the magnesium suspension. The mixture was stirred and heated until the reaction started and a dark brown solution was obtained. Then, the remaining *p*-bromochlorobenzene was added dropwise and upon completion, the mixture was refluxed for two hours. After cooling the mixture, 10 mL (0.125 mol) of anhydrous stannic chloride (SnCl₄) in 90 mL of toluene was added dropwise into the mixture. Upon completion, the mixture was refluxed for another two hours, followed by stirring overnight. The reaction mixture was hydrolyzed with 10% ammonium chloride in order to destroy the excess stannic chloride and Grignard reagent. The organic layer was separated and concentrated by rotary evaporation. A white solid was formed upon removal of solvent. The solid was recrystallized from chloroform.

Yield : 51.70 g (73.2 %); m.p. 193-195°C [Lit: 197-199°C, Stern and Becker 1964].

Preparation of tetra(4-methylphenyl)tin(IV)

12.16 g (0.5 mol) of magnesium was added to 500 mL of dry tetrahydrofuran. Next, about 5 mL of the 62 mL (0.5 mol) of 4-bromotoluene was added slowly through a dropping funnel into the magnesium suspension. The mixture was stirred, refluxed until the reaction began and a dark brown solution was obtained. Then, the remaining 4-bromotoluene was added dropwise and upon completion, the mixture was further refluxed for two hours. After cooling for an hour, 10 mL (0.125 mol) of anhydrous stannic chloride (SnCl_4) in 90 mL of toluene was added dropwise into the mixture. Upon completion, the mixture was refluxed for another two hours, followed by stirring overnight. The reaction mixture was hydrolyzed with 10% ammonium chloride in order to remove the excess stannic chloride and Grignard reagent. The organic layer which was separated was concentrated by rotary evaporation. A white solid was formed upon removal of solvent and was recrystallized from chloroform.

Yield : 39.51 g (65.4 %); m.p. 241-243°C.

2.2.2 Bromination of tetraorganotins

Dicyclohexyltin bromide, C1

Tetracyclohexyltin (0.45 g, 1 mmol) and 4-(dimethylamino)pyridine hydrobromide perbromide (0.72 g, 2 mmol) were dissolved separately in absolute ethanol (25 ml) and refluxed for six hours. The solution was filtered and colourless crystals were isolated upon cooling to room temperature. Yield: 0.20 g (51.3 %); m.p. 195-197°C. Anal. Calc for $\text{C}_{12}\text{H}_{22}\text{Br}_2\text{Sn}$: C, 32.42; H, 4.95%. Found: C, 32.80; H, 4.68% **IR** (cm^{-1}): **^1H NMR (ppm)**: 1.23-2.00 (m, 22H), [s=singlet, m = multiplet], **^{13}C NMR (ppm)**: 26.2, 28.6, 30.0, 40.2 δ (Sn-Cyh)

Bis[4-(dimethylamino)pyridinium]tetrabromidobis(4-chlorophenyl)stannate(IV).4-bromochlorobenzene (1/1), C2

An ethanolic solution of tetra(4-chlorophenyl)tin (0.57 g, 1 mmol) was added to 4-(dimethylamino)pyridine hydrobromide perbromide (0.72 g, 2 mmol) which was also dissolved in absolute ethanol (25 ml). The mixture was refluxed for six hours; filtered and colourless crystals were isolated upon cooling to room temperature. Yield: 0.60 g (54.5 %); m.p. 182-184°C. Anal. Calc for C₃₂H₃₄N₄Cl₃Br₅Sn: C, 34.97; H, 3.09; N, 5.09%. Found: C, 35.17; H, 3.48; N, 5.18% **IR** (cm⁻¹): 3434 ν (N-H), 1648 ν (C=N), **¹H NMR (ppm)**: 2.33-2.40 (m, 6H), 6.76-8.14 (m, 12H), 11.10 (s, 1H) [s=singlet, m = multiplet], **¹³C NMR (ppm)**: 21.5, 40.2, 106.5, 128.2, 129.0, 129.4, 129.7, 130.4, 130.6, 133.4, 134.4, 135.7, 136.1, 136.8, 137.1, 137.4, 138.3, 138.7, 140.3, 140.4, 157.4 δ (Ar), **¹¹⁹Sn NMR (ppm)**: -130.6

Bis[4-(dimethylamino)pyridinium]tetrabromidobis(4-methylphenyl)stannate(IV), C3

Tetra(4-methylphenyl)tin (0.49 g, 1 mmol) and 4-(dimethylamino)pyridine hydrobromide perbromide (0.72 g, 2 mmol) were dissolved in absolute ethanol (50 ml) and refluxed for six hours. The solution was filtered and colourless crystals were isolated upon cooling to room temperature. Yield: 0.44 g (50.9 %); m.p. 188-190°C Anal. Calc for C₂₈H₃₆N₄Br₄Sn: C, 38.79; H, 4.15; N, 6.46%. Found: C, 39.10; H, 4.41; N, 6.08% **IR** (cm⁻¹): 3422 ν (N-H), 1639 ν (C=N), **¹H NMR (ppm)**: 2.34-2.41 (m, 12H), 3.25 (s, 2H), 6.80-8.15 (m, 17H) [s=singlet, m = multiplet], **¹³C NMR (ppm)**: 21.5, 23.4, 40.3, 106.7, 128.0, 129.1, 129.4, 129.8, 130.5, 130.9, 133.3, 134.5, 135.5, 136.1, 136.7, 137.0, 137.4, 138.3, 138.6, 140.3, 140.5, 157.7 δ (Ar), **¹¹⁹Sn NMR (ppm)**: -124.7

2.3 PHYSICAL MEASUREMENTS OF ORGANOTIN COMPOUNDS

The melting points of the compounds were determined on 'Electrothermal' digital melting point apparatus and were uncorrected. Elemental analyses of the complexes were carried out on a Perkin Elmer EA2400 CHNS Elemental Analyzer in the University of Malaya.

The infrared spectra for the compounds were recorded in the region 400-4000 cm^{-1} with a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and a Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer. The samples were prepared as nujol mull or KBr pellet.

The ^1H and ^{13}C NMR spectra for the compounds were recorded in CDCl_3 at ambient temperature on a JEOL JNM-GSX270 FT NMR SYSTEM spectrometer operating at 270.05 MHz for ^1H NMR and 67.80 MHz for ^{13}C NMR. The ^{119}Sn NMR spectra were recorded on a JEOL ECA-400MHz. The chemical shifts were recorded in ppm with reference to Me_4Si for ^1H NMR, CDCl_3 for ^{13}C NMR and Me_4Sn for ^{119}Sn NMR.

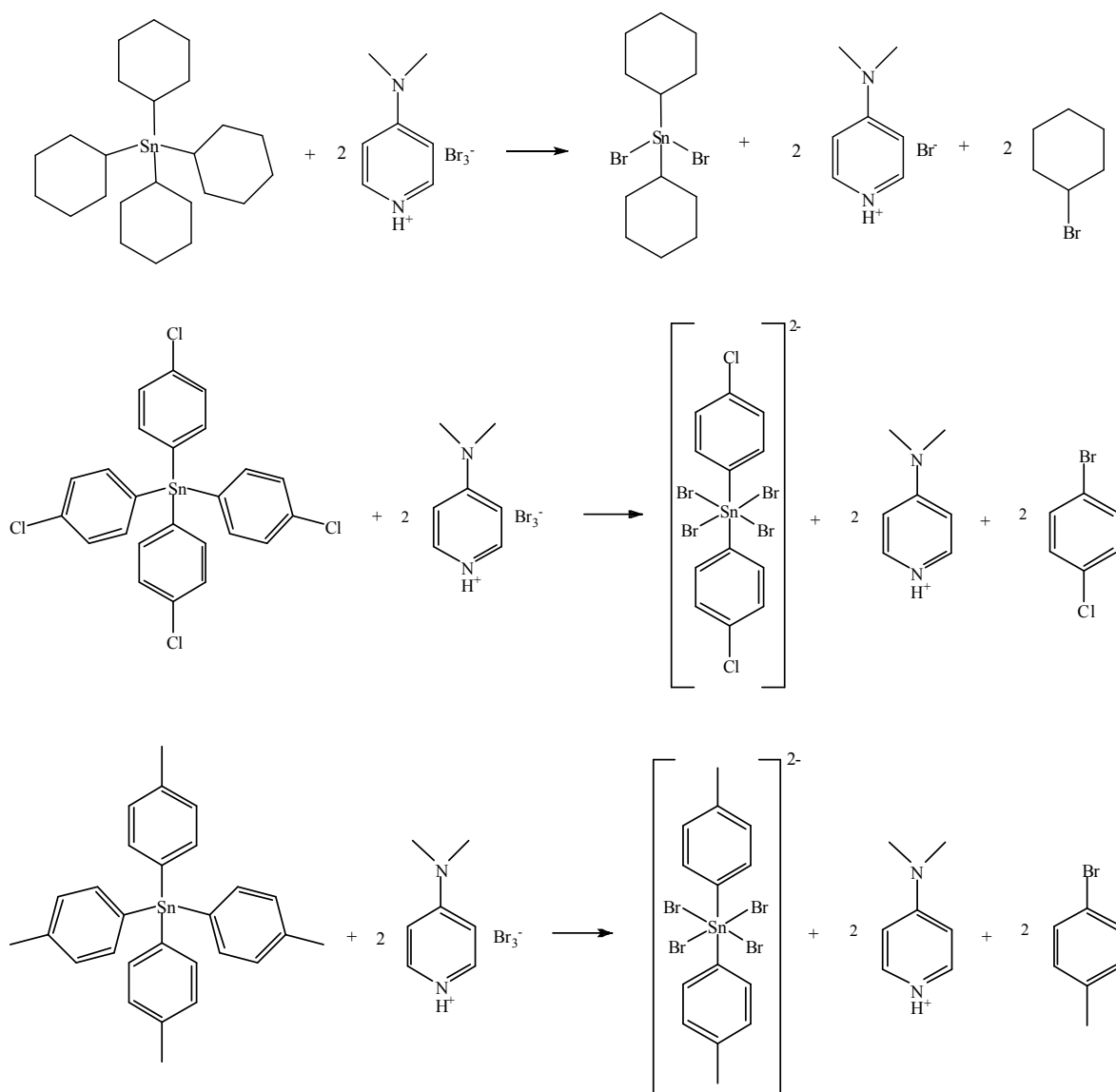
The X-ray crystallographic intensity data were measured using Mo-K_α radiation graphite-crystal monochromator ($\lambda = 0.71073 \text{ \AA}$) radiation on a Bruker SMART APEX2 CCD diffractometer in University of Malaya. The structure of the compounds were solved by the direct method and refined by the full-matrix least-squares procedure based on F^2 using the SHELXL programme (Sheldrick 1993, Sheldrick 1997). Supplementary data including observed and calculated structure factors for the complexes are available from the author on request.

2.4 RESULTS AND DISCUSSION

2.4.1 Analytical Data

Several organotin starting materials were prepared in this project, namely dicyclohexyltin dichloride, dicyclohexyltin oxide, dibenzyltin dichloride, di(*o*-chlorobenzyl)tin dichloride and di(*p*-chlorobenzyl)tin dichloride. The reaction scheme of the bromination reaction of the tetraorganotins shows a summary of the preparation of the diorganotin compounds.

Scheme 2.3.1 Reaction scheme for the bromination reaction of the tetraorganotins



The products obtained were six-coordinated diorganotin anionic complexes, except for the reaction between tetracyclohexyltin with 4-(dimethylamino)pyridine hydrobromide perbromide whereby dicyclohexyltin dibromide was obtained.

2.4.2 IR Spectral data

In the IR spectra for **C2** and **C3**, the presence of a sharp peak around the 3400 cm^{-1} region showed the possibility of the presence of the N-H stretching frequency. The peak in the 1600-1650 cm^{-1} region was assigned to the C=N stretching frequency. The presence of both the N-H and C=N stretching frequency peaks for the complexes indicated the presence of the dimethylamino pyridinium cation in the organotin compounds.

2.4.3 NMR Spectral Data

The ^1H and ^{13}C NMR chemical shift values of the aromatic and aliphatic protons of the complexes were located in the expected region of the spectra. These chemical shifts were useful for the confirmation of the presence of the alkyl and aryl groups in the complexes.

The proton chemical shifts for the methyl groups of the 4-(dimethylamino)pyridinium cation were located between 2.3-2.4 ppm. The aromatic protons of the pyridinium cation and phenyl rings were found between 6.7-8.2 ppm. The ^{13}C chemical shift values corresponded with those of the predicted structures.

2.4.4 X-Ray Structures

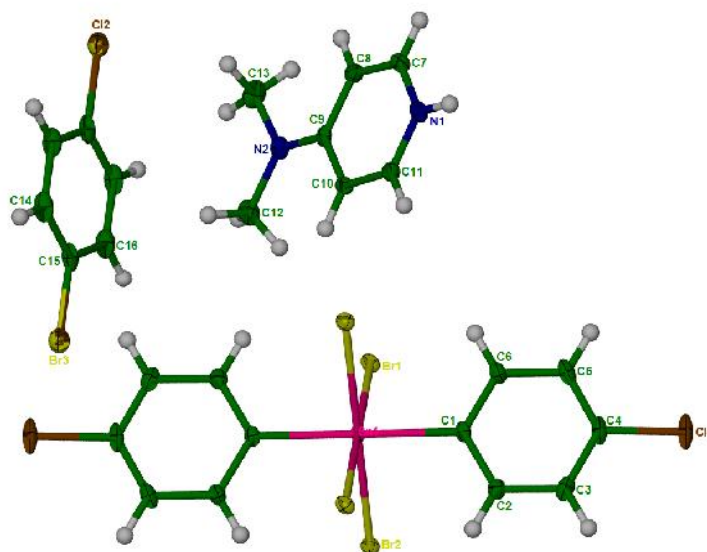
Bis[4-(dimethylamino)pyridinium] tetrabromidobis(4-chlorophenyl)stannate(IV)

.4-bromochlorobenzene (1/1), C2

Bis[4-(dimethylamino)pyridinium] tetrabromidobis(4-chlorophenyl)stannate(IV) .4-bromochlorobenzene (1/1), **C2** crystallizes in triclinic, $P\bar{1}$ space group. The crystallographic data, selected bond lengths and angles for **C2** are tabulated in tables 2.4.1 and 2.4.2 respectively while the molecular structure of complex **C2** is shown in figure 2.4.1.

The crystal structure of **C2** contained a cleavage product from the bromination reaction of the tetra(4-chlorophenyl)tin, which was 4-bromochlorobenzene. The tin atom in the tetrabromidobis(4-chlorophenyl)stannate(IV) anion lies on a centre of inversion. The bond distances between the 4-(dimethylamino)pyridinium nitrogen atom (N1) with Br atoms of the anion were 3.450 and 3.452 Å, respectively, suggesting weak hydrogen-bonding. The 4-bromochlorobenzene molecule, which was a bromination by-product from the reaction, was disordered about a two-fold rotation axis with approximately equal occupancy. The overall complex structure was stabilized by the weak hydrogen-bonding between the *bis*[4-(dimethylamino)pyridinium] cation with the anion *via* N—H---Br hydrogen bonds.

Figure 2.4.1
Molecular plot of *bis*[4-(dimethylamino)pyridinium]tetrabromido*bis*(4-chlorophenyl)stannate(IV).4-bromochlorobenzene (1/1), **C2**



***Bis*[4-(dimethylamino)pyridinium]tetrabromido*bis*(4-methylphenyl)stannate(IV),**

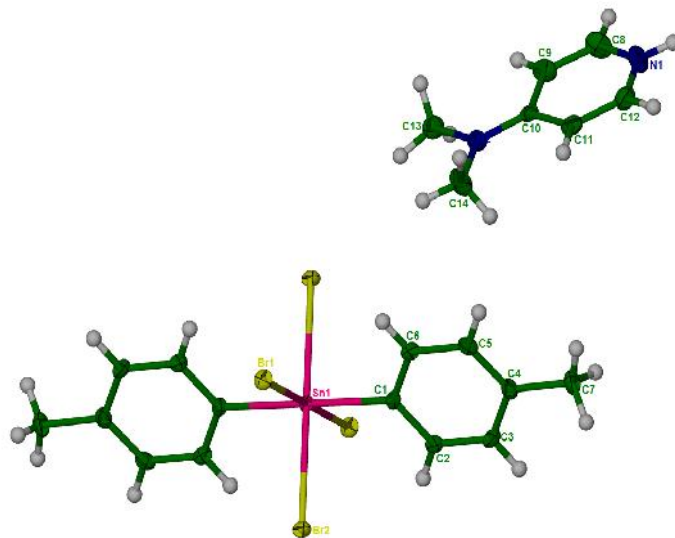
C3

The crystallographic data and selected bond lengths and angles of *bis*[4-(dimethylamino)pyridinium]tetrabromido*bis*(4-methylphenyl)stannate(IV), **C3** are tabulated in tables 2.4.3 and 2.4.4, respectively. The molecular structure is shown in figure 2.4.2.

C3 crystallized in the monoclinic, $P2_1/n$ space group and as similar to **C2**, the tin atom was six-coordinated and the equatorial plane was occupied by four bromides ions. The tetrabromido*bis*(4-methylphenyl)stannate(IV) anion possessed a centre of inversion at the tin atom. The bond distance between 4-(dimethylamino)pyridinium nitrogen atom (N1) with Br atoms of the anion (3.448 and 3.517 Å) suggested an unfavourable possibility of weak hydrogen-bonding between the two inversion-related *bis*[4-(dimethylamino)pyridinium] cation with the anion *via* N—H----Br hydrogen

bonds. Unlike **C2**, **C3** did not consist of a cleavage product from the bromination reaction.

Figure 2.4.2
Molecular plot of *bis*[4-(dimethylamino)pyridinium]tetrabromidobis(4-methylphenyl)stannate(IV), **C3**



Summary of the bromination reaction

The main objective of the bromination reaction was to obtain diorganotin compounds. 4-(dimethylamino)pyridine hydrobromide perbromide was used as the brominating agent as it was a mild brominating reagent and the bromination reaction should be selective. The ratio of the 4-(dimethylamino)pyridine hydrobromide perbromide and tetraorganotin used in the reaction were 1:2. From the bromination reactions, only tetracyclohexyltin yielded the diorganotin dibromide. However, this reaction was not further pursued as the yield obtained was relatively low with many side products which include bromocyclohexane. Although the yield obtained from the bromination reactions with tetra(4-chlorophenyl)tin(IV) and tetra(4-methylphenyl)tin were higher, the desired diorganotin compounds were not obtained. Instead, an ionic diorganotin compound which consisted of tetrabromidodiorganotin anion and 4-(dimethylamino)pyridinium cation was obtained. Both the anion and cation were held together by strong hydrogen-bonding which stabilized the overall structures. Therefore, a higher activation energy would be needed in order to break this hydrogen bonding and also the tetrabromido bonds in the diorganotin compounds. These ionic compounds were not favourable starting materials for further reactions with Schiff base ligands.

Table 2.4.1
 Crystal data and structure refinement for *bis*[4-(dimethylamino)pyridinium]tetrabromido*bis*(4-chlorophenyl)stannate(IV).4-bromochlorobenzene (1/1), **C2**

Empirical formula	C ₃₂ H ₃₄ Br ₅ Cl ₃ N ₄ Sn
Formula weight	1099.22
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
	<i>a</i> (Å) = 8.7692(18) <i>b</i> (Å) = 10.128(2) <i>c</i> (Å) = 11.407(2) α (°) = 111.16(3) β (°) = 93.38(3) γ (°) = 92.85(3)
Volume	940.4(3)
Z	1
Calculated density D_{calc} (Mgm ⁻³)	1.941
Absorption coefficient, μ (mm ⁻¹)	6.233
F(000)	530
Crystal size (mm)	0.45 x 0.26 x 0.19
Limiting indices	-11 ≤ <i>h</i> ≤ 8, -13 ≤ <i>k</i> ≤ 13, -14 ≤ <i>l</i> ≤ 13
Reflections collected / unique	7255 / 4265 [R(int) = 0.0192]
Max. and min. transmission	0.3839 and 0.1658
Data / restraints / parameters	4265 / 0 / 207
Goodness-of-fit on F ²	1.050
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.0229, wR ₂ = 0.0611
R indices (all data)	R ₁ = 0.0259, wR ₂ = 0.0624
Largest diff. peak and hole (eÅ ⁻³)	0.774 and -1.124

Table 2.4.2.

Bond lengths (Å) and angles (°) with estimated standard deviation for *bis*[4-(dimethylamino)pyridinium]tetrabromidobis(4-chlorophenyl)stannate(IV).4-bromochlorobenzene (1/1), **C2**

Sn(1)-C(1)	2.148(3)	Br(1)-Sn(1)-Br(1)#1	180.0
Sn(1)-C(1)#1	2.148(3)	Br(2)-Sn(1)-Br(1)	88.45(3)
Sn(1)-Br(1)	2.7319(7)	Br(2)-Sn(1)-Br(1)#1	91.55(3)
Sn(1)-Br(1)#1	2.7319(7)	Br(2)#1-Sn(1)-Br(1)	91.55(3)
Sn(1)-Br(2)	2.7172(8)	Br(2)#1-Sn(1)-Br(2)	180.0
Sn(1)-Br(2)#1	2.7172(9)	Br(2)#1-Sn(1)-Br(1)#1	88.45(3)
Br(3)-C(15)	1.807(3)	C(1)-Sn(1)-Br(1)	90.12(7)
Cl(1)-C(4)	1.744(3)	C(1)-Sn(1)-Br(2)	89.62(7)
N(1)-C(7)	1.346(3)	C(1)-Sn(1)-Br(1)#1	89.88(7)
N(1)-C(11)	1.344(3)	C(1)-Sn(1)-Br(2)#1	90.38(7)
N(2)-C(9)	1.337(3)	C(1)#1-Sn(1)-Br(1)	89.88(7)
N(2)-C(12)	1.465(4)	C(1)#1-Sn(1)-Br(2)	90.38(7)
N(2)-C(13)	1.460(4)	C(1)#1-Sn(1)-Br(1)#1	90.12(7)
C(1)-C(2)	1.386(4)	C(1)#1-Sn(1)-Br(2)#1	89.62(7)
C(1)-C(6)	1.392(4)	C(1)#1-Sn(1)-C(1)	180.0
C(2)-C(3)	1.392(4)	C(1)-C(2)-C(3)	120.5(3)
C(3)-C(4)	1.382(4)	C(2)-C(1)-C(6)	119.5(2)
C(4)-C(5)	1.383(4)	C(2)-C(1)-Sn(1)	120.03(18)
C(5)-C(6)	1.391(4)	C(3)-C(4)-Cl(1)	118.7(2)
C(7)-C(8)	1.357(4)	C(3)-C(4)-C(5)	121.8(3)
C(8)-C(9)	1.418(4)	C(4)-C(3)-C(2)	118.9(3)
C(9)-C(10)	1.420(3)	C(4)-C(5)-C(6)	118.6(3)
C(10)-C(11)	1.357(4)	C(5)-C(4)-Cl(1)	119.5(2)
C(14)-C(15)	1.389(4)	C(5)-C(6)-C(1)	120.6(3)
C(14)-C(16)#2	1.378(5)	C(6)-C(1)-Sn(1)	120.51(19)
C(15)-C(16)	1.379(4)	C(7)-C(8)-C(9)	120.5(2)
C(16)-C(14)#2	1.378(5)	C(8)-C(9)-C(10)	116.2(2)
		C(9)-N(2)-C(12)	122.5(2)
		C(9)-N(2)-C(13)	120.7(2)
		C(11)-C(10)-C(9)	120.2(2)
		C(11)-N(1)-C(7)	120.7(2)
		C(13)-N(2)-C(12)	116.4(2)
		C(14)-C(15)-Br(3)	119.0(2)
		C(14)#2-C(16)-C(15)	119.7(3)
		C(16)-C(15)-Br(3)	119.9(2)
		C(16)-C(15)-C(14)	121.1(3)
		C(16)#2-C(14)-C(15)	119.1(3)
		N(1)-C(7)-C(8)	121.0(2)
		N(1)-C(11)-C(10)	121.3(2)
		N(2)-C(9)-C(8)	121.3(2)
		N(2)-C(9)-C(10)	122.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z+2

Table 2.4.3

Crystal data and structure refinement for *bis*[4-(dimethylamino)pyridinium]tetrabromido-*bis*(4-methylphenyl)stannate(IV), **C3**

Empirical formula	C ₂₈ H ₃₆ Br ₄ N ₄ Sn
Formula weight	866.94
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
	<i>a</i> (Å) = 10.2178(3) <i>b</i> (Å) = 10.4808(3) <i>c</i> (Å) = 14.5833(3) α (°) = 90 β (°) = 95.063(1) γ (°) = 90
Volume (Å ³)	1555.64(7)
Z	2
Calculated density <i>D</i> _{calc} (Mgm ⁻³)	1.851
Absorption coefficient, μ (mm ⁻¹)	5.982
F(000)	844
Crystal size (mm)	0.35 x 0.30 x 0.22
Limiting indices	-13 ≤ <i>h</i> ≤ 10, -13 ≤ <i>k</i> ≤ 8, -18 ≤ <i>l</i> ≤ 18
Reflections collected / unique	11555 / 3569 [<i>R</i> _(int) = 0.0193]
Max. and min. transmission	0.3528 and 0.2286
Data / restraints / parameters	3569 / 0 / 172
Goodness-of-fit on F ²	1.047
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0176, <i>wR</i> ₂ = 0.0438
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0216, <i>wR</i> ₂ = 0.0452
Largest diff. peak and hole (eÅ ⁻³)	0.444 and -0.452

Table 2.4.4
Bond lengths (Å) and angles (°) with estimated standard deviation for *bis*[4-(dimethylamino)pyridinium]tetrabromidobis(4-methylphenyl)stannate(IV), **C3**

Sn(1)-Br(1)	2.76515(18)	Br(1)-Sn(1)-Br(1)#1	180.000(10)
Sn(1)-Br(1)#1	2.76515(18)	Br(2)-Sn(1)-Br(1)#1	91.340(6)
Sn(1)-Br(2)	2.7349(2)	Br(2)-Sn(1)-Br(1)	88.660(6)
Sn(1)-Br(2)#1	2.7349(2)	Br(2)#1-Sn(1)-Br(1)	91.340(6)
Sn(1)-C(1)	2.1424(18)	Br(2)#1-Sn(1)-Br(2)	180.000(12)
Sn(1)-C(1)#1	2.1424(18)	Br(2)#1-Sn(1)-Br(1)#1	88.660(6)
N(1)-C(8)	1.346(3)	C(1)-Sn(1)-Br(1)	90.78(5)
N(1)-C(12)	1.346(3)	C(1)-Sn(1)-Br(1)#1	89.22(5)
N(2)-C(10)	1.335(2)	C(1)-Sn(1)-Br(2)	89.88(5)
N(2)-C(13)	1.462(3)	C(1)-Sn(1)-Br(2)#1	90.12(5)
N(2)-C(14)	1.459(3)	C(1)#1-Sn(1)-Br(1)	89.22(5)
C(1)-C(2)	1.391(3)	C(1)#1-Sn(1)-Br(1)#1	90.78(5)
C(1)-C(6)	1.388(3)	C(1)#1-Sn(1)-Br(2)	90.12(5)
C(2)-C(3)	1.388(3)	C(1)#1-Sn(1)-Br(2)#1	89.88(5)
C(3)-C(4)	1.396(3)	C(1)#1-Sn(1)-C(1)	180.00(13)
C(4)-C(5)	1.394(3)	C(1)-C(6)-C(5)	120.63(18)
C(4)-C(7)	1.504(3)	C(2)-C(3)-C(4)	121.28(18)
C(5)-C(6)	1.393(3)	C(2)-C(1)-Sn(1)	121.04(13)
C(8)-C(9)	1.356(3)	C(3)-C(2)-C(1)	120.37(17)
C(9)-C(10)	1.422(3)	C(3)-C(4)-C(7)	120.66(18)
C(10)-C(11)	1.424(3)	C(5)-C(4)-C(3)	117.91(17)
C(11)-C(12)	1.359(3)	C(5)-C(4)-C(7)	121.42(17)
		C(6)-C(1)-C(2)	118.88(17)
		C(6)-C(1)-Sn(1)	119.98(13)
		C(6)-C(5)-C(4)	120.90(17)
		C(8)-C(9)-C(10)	120.1(2)
		C(9)-C(10)-C(11)	116.47(18)
		C(10)-N(2)-C(14)	120.81(17)
		C(10)-N(2)-C(13)	121.38(17)
		C(12)-C(11)-C(10)	120.16(19)
		C(12)-N(1)-C(8)	120.94(19)
		C(14)-N(2)-C(13)	117.71(17)
		N(1)-C(8)-C(9)	121.3(2)
		N(1)-C(12)-C(11)	121.0(2)
		N(2)-C(10)-C(9)	121.88(18)
		N(2)-C(10)-C(11)	121.65(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z