Chapter Two

Preparation

Of

Organotin Compounds

2.1 Main methods of synthesis

Organotin compounds (OTCs) can be prepared by four main methods.

These methods are:

1. Grignard reaction

2. Wurtz reaction

3. Reaction by organoaluminium

4. Direct synthesis.

2.1.1 Grignard reaction

The tetraorganotins, R_4Sn can be prepared by this method by first forming the Grignard reagent of RMgBr derived from the reaction between Mg turning and an organic bromide, RBr. Subsequent reaction of the Grignard reagent with stannic chloride, $SnCl_4$ afforded R_4Sn. R_3SnX, R_2SnX_2 and R_3SnX_3 are prepared from the tetraorganotin by comproportionantion reaction between R_4Sn and stannic chloride at ca. $200C^o$ for several hours. Redistribution reactions have also been used for preparation of asymmetric OTCs.

$$4RMgX + SnX_4 \longrightarrow R_4Sn + 4MgX_2 \qquad (2\text{-}1)$$

2.1.2 Wurtz method:

This method is based on *in situ* reaction of Na, alkyl halide with SnX_4 (Reaction 2.2).

$$SnX_4 + 4RX + 8Na \longrightarrow R_4Sn + 8NaX \qquad (2\text{-}2)$$

One of the disadvantages of this method is that large amount of solvent should be used.

This method proceeds by following steps:

$$SnX_4 \xrightarrow[-2NaX]{RX + 2Na} RSnX_3 \xrightarrow[-2NaX]{RX + 2Na} R_2SnX_2 \xrightarrow[-2NaX]{RX + 2Na} R_3SnX \xrightarrow[-2NaX]{RX + 2Na} R_4Sn \qquad (2\text{-}3)$$
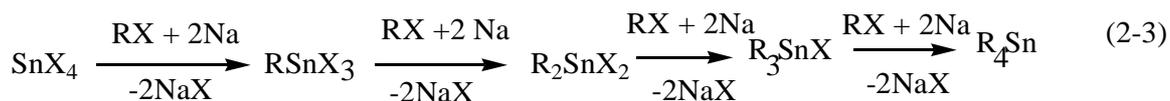
2.1.3 Organoaluminium method:

This reaction is also accompanied with the formation of R_3SnX, R_2SnX_2 and $RSnX_3$

2.1.4 Direct synthesis:

Sir Edward Frankland (1825-1899) was the first person who prepared OTCs by direct method (Frankland,1854).

$$2EtI + Sn \longrightarrow Et_2SnI_2 \qquad\qquad (2\text{-}4)$$

The order of reactivity is RI > RBr > RCl and for a given halogen MeX >EtX > PrX

2.1.5 Rochow method:

The direct reaction of organosilicon compounds discovered by Rochow in 1944 and was applied for the preparation of methyltin and phenyltin.

$$Sn + CH_3Cl \xrightarrow[Cu]{300\text{-}400^{o}C} CH_3SnCl \qquad\qquad (2\text{-}5)$$

Cu or Zn can be used as catalyst.

2.1.6 Sisido method:

In 1953 Sisido and his coworkers found that dibenzyltin chloride, tribenzyltin chloride and diallyltin dibromide were prepared in high yield by refluxing reactive halides such as benzyl chloride and allyl chloride or allyl bromide with tin powder in water or toluene in the presence of a trace amount of water. The reaction in a strongly polar solvent gives

triorganotin compounds on the other hand, in a weakly polar solvent gives diorganotin compounds.

$$2PhCH_2Cl + Sn \xrightarrow[\text{toluene}]{110\,^{o}C\ 88\%} (PhCH_2)_2SnCl_2 \qquad (2\text{-}6)$$

$$3PhCH_2Cl + 2Sn \xrightarrow[\text{water}]{100\,^{o}C\ 94\%} (PhCH_2)_3SnCl + SnCl_2 \qquad (2\text{-}7)$$
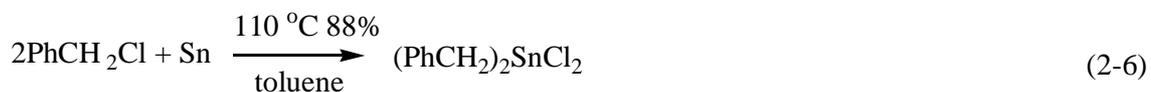
2.1.7 Redistribution reaction (Kocheskov Reaction):

As mentioned already, R_4Sn is the starting material for the preparation of R_3SnX, R_2SnX_2, and $RSnX_3$, this reaction also named comproportionation reactions.

$$R_4Sn + SnX_4 \longrightarrow 2R_2SnX_2 \qquad (2\text{-}8)$$

$$3R_4Sn + SnX_4 \longrightarrow 4R_3SnX \qquad (2\text{-}9)$$

$$R_4Sn + 3SnX_4 \longrightarrow 4RSnX_3 \qquad (2\text{-}10)$$

The commercial production of OTCs starts with the conversion of metallic tin into $SnCl_4$ and then convert to R_4Sn by Grıgnard reagent , R_4Sn serves as starting material for the synthesis of other organotin halides that can be generated through redistribution reaction with $SnCl_4$. In the final step the remaining chloride anions can be substituated by the desired anion (e.g. oxide, hydroxide, thioglycolate, carboxylate trizolite, (Poller, 1970; Sander et al., 2004).

2.2 Organotin carboxylates:

One of the categories of OTCs that recently attention has been paid to that is organotin carboxylates. This is because of the potential biological activities of these compounds, such

as antitumor activity and was found to be active against various types of cancers. There are several methods for prepration of organotin carboxylates (Yip Foo et al., 2006).

1. Synthesis by reaction of carboxylic acid and dibutyltin oxide (DBTO).

2. Synthesis by reaction of salt of carboxylic acid with TBTCl.

3. Synthesis by reaction of silver salt of carboxylic acid.

4. Synthesis by using amines.

5. Synthesis by reaction of carboxylic acid with $SnCl_4$.

Some of the dibutyltin caboxylates were prepared by heating dibutyltin oxide (Bu_2SnO) with the respective acid (1:1) in mixture of toluene to produce carboxylate (Szoresik et al., 2003). Usually the preparation required the use of Dean-Stark apparatus for the separation of the water.

$$Bu_2SnO + 2RCOOH \longrightarrow H_2O + Bu_2 Sn(OCOR)_2 \qquad (2\text{-}11)$$
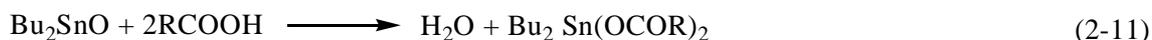
The carboxylate ligand can be bonded to metal ion in different modes as shown below:
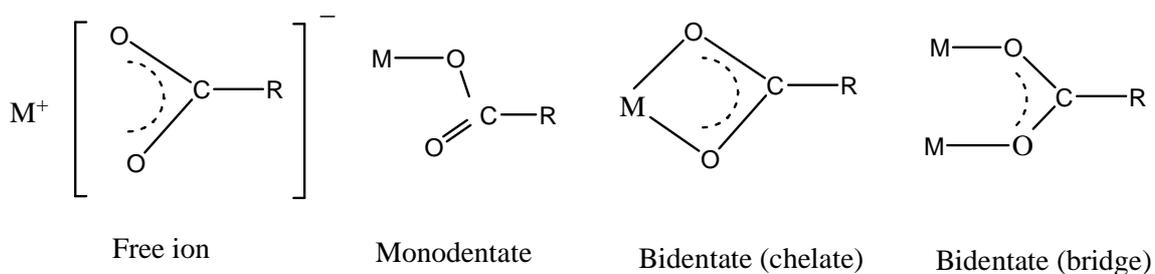
Figure 2.1 Different bonding modes of carboxylate ligand to metal

In a typical reaction 0.015 mol of Bu_2SnCl_2 in 150 ml CH_2Cl_2 was stirred in the dark with $AgOCOCH_3$ (0.039 mol) for 24 hours and then was filtered, the filtrate was evaporated and dried in vacuum (Bonire et al., 1998).

$$R_2SnCl_2 + 2AgOCOR' \longrightarrow R_2Sn(OCOR')_2 + 2AgCl \qquad (2\text{-}12)$$
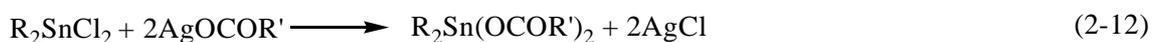
In another example, thiosalicylic acid is converted to its salt by using NaOEt and then reacts with R_2SnCl_2 (Handong et al., 2005).

$$nR_2SnCl_2 + n \underset{SH}{\overset{COOH}{C_6H_4}} \xrightarrow{NaOEt} [R_2Sn(OCO)_2C_6H_4S]_n \qquad (2\text{-}13)$$
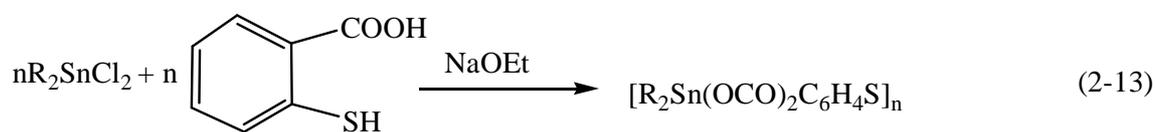
R = Me, nBu, Ph, 3Cl-PhCH$_2$

By using triethylamine as a base, organotin carboxylate can be prepared from organotin halides.

$$R_2SnCl_2 + 2LHNEt_3 \longrightarrow R_2SnL_2 + 2Et_3NHCl \qquad (2\text{-}17)$$
$$R_3SnCl + LHNEt_3 \longrightarrow R_3SnL + Et_3NHCl \qquad (2\text{-}18)$$

HL = 4-(2,5Dioxo-2,5-dihydro -1H-pyrrol-1-yl)benzoic acid

2.3 Spectroscopic investigation of organotin compounds:

After the organotin compounds (OTCs) are prepared, they are usually characterized by using IR, NMR (^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR) and Mossbauer spectroscopies.

2.3.1 ^{119}Sn NMR spectroscopy:

There are ten naturally occurring isotopes of tin, of these only ^{115}Sn, ^{117}Sn and ^{119}Sn have nuclear spin quantum number of +1/2. ^{115}Sn has abundance of only 0.35%, ^{117}Sn abundance is 7.61% and ^{119}Sn has abundance of 8.58% and is usually selected for spectroscopic investigation because of larger abundance. The sensitivity of ^{119}Sn is 4×10^{-3} times of ^{1}H and 25 times of ^{13}C and is highest in multinuclear species.

^{119}Sn NMR, chemical shift of OTCs covers a range of 600 ppm and are referenced by tetra methyltin (Omae, 1989). There is no solvent effect unless the solvent coordinated to the Sn atom. A large shift difference is observed with very slightly differing in electron density around Sn atom. As shown in Table 2 .1, the Sn bonds to electron withdrawing agent causes deshielded of tin and the δ [119]Sn moves to lower field. From the series, Me_3SnX to $MeSnX_3$ (X = Cl, Br, I), the δ [119]Sn values moves up field with the increase in the number of inorganic group (X).

Table 2.1: [119]Sn chemical shift (δ) of Me_nSnX_{4-n} (ppm) (OMAE, 1989)

Compound	X = Cl	X = Br	X = I
Me_3SnX	+ 164.4	+ 128	+ 38.6
Me_2SnX_2	+ 140	+ 70	- 159
$MeSnX_3$	+ 21	-165	-
SnX_4	- 150	- 638	-170.1

This may be due to the back-donation of the halogen p- ion pair electron into an empty 5d orbital on Sn having π symmetry, resulting in a (p-d) overlap between these two orbitals and shielding Sn and moving to high field shift. Effect of alkyl group R on ^{119}Sn NMR chemical shift is shown in Table 2.2 (Wilkinson, 1995).

Table 2.2: [119]Sn Chemical shift (ppm) of different alkyltin chlorides (Wilkinson, 1995)

R	$RSnCl_3$	R_2SnCl_2	R_3SnCl
Me	+20	+141	+164
Et	+6.5	+126	+155
Bu	+6.0	+122	+141
Bu^t	-	+52	+50
Ph	-63	-32	-48

An increase in the coordination number of the Sn causes shielding and shifting to high field. Four coordination compounds have chemical shifts (δ) ranging from +200 to -60 ppm, five coordination compounds from -90 to -190 ppm and six coordinated compounds from -210 to -400 ppm. Coordination of donor solvent to Sn causes [119]Sn chemical shift moves to high field, for example as the mole ratio of a mixture of Me_3SnCl and pyridine in carbon tetrachloride is altered from 1:0 to 1:12 the [119]Sn chemical shift moves from +159 ppm to -9 ppm.

Table 2.3: Effect of coordination number on ^{119}Sn chemical shift (ppm) [Otera, 1981]

Four coordinate compounds		Five coordinate compounds		Six coordinate compounds	
Ph₃SnOOBu	-95	**Ph₃Sn(oxin)**	192	**Me₂Sn(acac)₂**	-365
Ph₃SnSMe	-47	**Ph₃Sn(edtc)**	-191	**Me₂Sn(oxin)₂**	-237
Me₃SnSMe	+85.1	**Me₃Sn(mdtc)**	+25	**Ph₂Sn(acac)₂**	-514
Me₃Sn(OBt)₂	-1.8	**Me₂Sn(SAB)**	-150	**Me₂Sn(mdtc)₂**	-338
Me₂Sn(SMe)₂	+144	**Me₂SnCl(oxin)**	-92		
		Ph₂Sn(SAB)	-329		
		Me₂SnCl(mdtc)	-204		

acac = acetylacetonate, oxin = oxinate, mdtc and, edtc = *N, N´*–dimethyl and *N, N´* diethyldithiocarbamate, SAB = *N* –(2–hydroxyphenyl)salicylaldimine.

2.3.2 Infrared Spectroscopy of OTCs:

The stretching frequencies of functional groups bonded , such as Sn-C, Sn-O, Sn-Halogen and Sn-N are important.

Sn-C Streching frequencies:

The di and tri-alkyltin compounds generally show two bands asymmetric Sn-C vibration essentially in the range 500-600 cm^{-1} and the second band at approximately 470-530 cm^{-1} due to symmetric Sn-C vibration band. Monoalkyltin compounds exhibit a single Sn-C stretching band. The two bands for butyltin trichloride belong to two conformational isomer of this compound. Information on the factors which affect the position of Sn-C band is not known but it has been observed in methyltin halides that electronegativity of halogen and greater the number of halogen causes greater effective nuclear charge on tin and hence the

higher of Sn-C frequencies. Infrared of some Sn-C stretching vibration of OTCs is shown in Table 2.-4. It can be seen from the table that the position of $\bar{v}$ Sn-C bands are not particularly sensitive to change in the coordination number of tin (Poller, 1970).

Tin –halogen stretching frequencies:

Some recent tin-halogen stretching frequencies assignment for the alkyl and phenyl-tin halides is shown in Table 2.5 , $\bar{v}$ Sn-Cl are in the range 385 - 318 cm^{-1} , $\bar{v}$ for Sn-Br 264-222 cm^{-1} and $\bar{v}$ for Sn-I are 207-170 cm^{-1}.

The tin-halogen stretching frequencies are very sensitive to changes in the coordination of the tin atom. Conversion of a 4 coordinate dichloride to a 6-coordinate adduct with a Lewis base causes a reduction in the frequency of the $\bar{v}$ Sn-Cl bonds by some 100 cm^{-1}. Similar results for the reduction of frequencies are observed for other halides.

Sn-N sreching frequencies:

The $\bar{v}$ Sn-N absorption bands occur over a wide range of frequencies and appears to be very sensitive to changes in the molecular environment of the Sn-N group. Organotin oxinate bands are in the region of 406-387 cm^{-1} that has been assigned to Sn-N mode, Sn-N frequency in Me_2SnX_2 .2pyridine is about 200 cm^{-1}. The $\bar{v}$ Sn-N in N-trimethylstannyl aniline occurs at 843 cm^{-1} for a compound that shows the N atom incorporated into the aromatic ring, the stretching vibration for Sn - N coordinated compounds occurs at a lower frequency. The Sn-N stretching frequencies for some OTCs is shown in Table 2.6.

Sn-O stretching frequencies:

An empirical calculation indicated that Sn-O stretching frequencies should occur in the range of 575-550 cm^{-1}. Although frequency of trimetyltin hydroxide solution is in this

range, but solid state spectrum show that different frequencies was observed. The Sn-O

frequencies for some OTCs are shown in Table 2.7.

Table 2.4: Infrared stretching frequencies of Sn–C for some (aliphatic) OTCs (Poller, 1970)

Compound	State	$\nu\ cm^{-1}$	
Compounds with 4 Sn-C bonds			
Me_4Sn	Liquid	528s	
Et_4Sn	Liquid	508s	
Pr_4Sn	Liquid	590s	500s
Bu_4Sn	Soln. in CS$_2$	592s	503s
$Me_3SnC{\equiv}CH$	Liquid	538vs	517w
Compounds with 3 Sn-C bonds			
Me_3SnCl	Soln. in Cyclohexane	542s	513w
Me_3SnBr	Soln. in Cyclohexane	539s	511m
Me_3SnI	Soln. in Cyclohexane	536m	508w
Me_3SnOH		540s	
Me_3SnOH	Solid	571m	504m
$Me_3SnOCOH$	Soln in CCl$_4$	555s	
$Me_3SnOCOH$	Solid	550m	513w
$Me_3SnMn(CO)_5$	Soln. in CHCl$_3$	517s	500s
$Me_3SnCF_2CF_2Mn(CO)_5$	Solid	539s	518m
Et_3SnC1	Solid Soln. in cyclohexane	518vs	489s

Table 2.4 Continued:

Compound	State	ν cm⁻¹		
Et₂SnCl₂	Soln. in CS₂	531		497
Et₂SnBr₂	Soln. in Benzene	528m		493m
Et₂SnI₂				
	Soln. in Benzene	520m		490m
Et₂SnO				
(Et₂SnS)₃	Solid	532s		493m
Pr₂SnCl₂	Solid	524m-s		493s
	Soln. in CS₂	598		512
Pr₂SnI₂				
	Soln. in CS₂	589		501
Bu₂SnCl₂				
	Soln. in CS₂	602		517
Bu₂SnBr₂				
	Soln. in Benzene	600m		511m
Bu₂SnI₂				
	Soln. in Benzene	592m		508s
(C₈H₁₇)₂SnCl₂				
	Soln. in CS₂	606		518
R₂Sn(OR')₂				
Me₂SnCl₂.2pyridine	Solid	~600	563m	521-504
Me₂SnCl₂.bipy	Solid		572m	
Me₂SnCl₂.2Me₂So	Solid			
[Me₂SnCl₄]²⁻	Solid	575m	580m	507vw
Me₂SnCl₂.phenᶜ	Solid		578m	
Me₂SnBr₂.2pyridine	Solid		563m	
Me₂SnBr₂.2bipy	Solid		571w	
Me₂SnBr₂.phen	Solid			
[Me₂SnBr₃]⁻	Solid	572m		551w
Me₂SnI₂.2pyridine	Solid	566		522
Me₂SnI₂.bipy	Solid	550m	569m	514vw
Me₂SnI₂.phen	Solid			
[Me₂Sn(OH)₄]²⁻	Solid	560m	523ᵇ	554sh
	Soln. in Water			
Et₂SnCl₂.2pyridine	Solid	580w		531m
Et₂SnCl₂.bipy	Solid	529m		481w
Et₂SnCl₂.phen	Solid	525m	493s	470w
Et₂SnCl₂.dipyamᵈ	Solid		485s	
Et₂SnCl₂.tripyamᵉ	Solid		523m	
Et₂SnBr₂.bipy	Solid		520w	
Et₂SnBr₂.phen	Solid		488s	
Et₂SnBr₂.dipyam	Solid			

Compound	State	ν cm^{-1}		
Et$_3$SnBr	Soln. in Cyclohexane	510m		484w
Et$_3$SnI	Soln. in Cyclohexane	506m		482w
Et$_3$SnOH	Solid	510vs		485m(sh)
(Et$_3$Sn)$_2$O	Liquid	509vs		485s(sh)
(Et$_3$Sn)$_2$S	Liquid	505vs	520	483s
Et$_3$SnOCOH	Solid		525	
Et$_3$SnOCOH	Soln. in Heptanes			
Et$_3$SnOCOR	Solid	521-517vs		490-487m
Et$_3$SnSnEt$_3$	Liquid	496vs		475vs
(Et$_3$Sn)$_2$SO$_4$	Solid	524s		490vw
(Et$_3$Sn)$_2$CO$_3$	Solid	518vs		491m
Bu$_3$SnCl	Liquid	601s		513m
Bu$_3$SnBr	Soln. in Cyclohexane	599s		503m
Bu$_3$SnI	Soln. in Cyclohexane	598s		501s
(Bu$_3$Sn)$_2$O	Soln.	648, 895		509
Me$_3$SnOR	Soln.	648±3,		510
Me$_3$SnCl.pyridine	Solid	601±6		512vw
Me$_3$SnCl.bipy[a]	Solid	541s		544w
Me$_3$SnBr.pyridine	Solid	554w		509vw
Me$_3$SnBr.bipy	Solid	542s		543w
Me$_3$SnI.pyridine	Solid	551w		504vw
Me$_3$SnI.bipy	Solid	541s 567w		538w
Compounds with 2 Sn-C bonds				
Me$_2$SnCl$_2$	Soln. in CS$_2$	560		524
Me$_2$SnBr$_2$	Soln. in Benzene	554m		518w
Me$_2$SnI$_2$	Soln. in Cyclohexane	542m		511w
Me$_2$SnCO$_3$	Solid	576		523w
Me$_2$SnSO$_4$	Solid		600s	
[Me$_2$Sn]$^{2\ominus}$	Soln. in water		529[b]	

Table 2.4 continued

Compound	State	ν cm^{-1}	
Et$_2$SnI$_2$.bipy	Solid	514m	
Et$_2$SnI$_2$.phen	Solid	513w	594vw
Bu$_2$SnCl$_2$.Phen	Solid	624 vw	587w, br
Bu$_2$SnBr$_2$.bipy	Solid	~620sh	588w
Bu$_2$SnBr$_2$.bipy	Solid	15vw	584w
Bu$_2$SnI$_2$.bipy	Solid	613w	582w
Bu$_2$SnI$_2$.phen	Solid	610w	
Compounds with 1 Sn – C bond			
MeSnCl$_3$	Soln	551-546w-m	
MeSnBr$_3$	Soln		
MeSnI$_3$	Soln. in Cyclohexane	538m 527w	
EtSnCl$_3$	Soln. in Benzene	522w	
EtSnBr$_3$	Soln. in Benzene	511m	
BuSnCl$_3$	Liquid	596	518
BuSnBr$_3$	Soln. in Benzene	596w	513w
MeSnCl$_3$.bipy	Solid	536w	
MeSnCl$_3$.phen	Solid	529w	
MeSnBr$_3$.bipy	Solid	519m	
MeSnBr$_3$.phen	Solid	515m,508w	
MeSnI$_3$.bipy	Solid	497m	
MeSnI$_3$.phen	Solid	500w,495w	
EtSnCl$_3$.bipy	Solid	504w	
EtSnCl$_3$.phen	Solid	507w	
EtSnBr$_3$.bipy	Solid	484w	
EtSnBr$_3$.phen	Solid	496w,479w	
BuSnCl$_3$.bipy	Solid	592w	
BuSnCl$_3$.phen	Solid	608w	
BuSnBr$_3$.bipy	Solid	595w	
BuSnBr$_3$.phen	Solid	595w	

Bipy = 2,2'bipyridil , phen = 1,10 – phenantrolin , dipyam = 2,2'– dipyridylamine , tripyam = 2,2',2''tripyridylamine

37

Table 2.5: Tin- halogen stretching frequencies (cm^{-1}) for some OTCs (Poller, 1970)

Compound		ν cm^{-1}	
Bu$_3$SnF[b]	—	—	330
Ph$_3$SnF[b]	—	—	350
Ph$_3$SnF[b]	—	—	372
(C$_6$F$_5$)$_3$SnF[b]	—	—	330
R$_3$SnCl	—	—	336-318
Ph$_3$SnCl	—	—	346-332
R$_3$SnBr	—	—	234-222
Ph$_3$SnBr	—	—	256
R$_3$SnI	—	—	189-182
Ph$_3$SnI	—	—	170[c]
Pr$_2$SnF$_2$		330	—
R$_2$SnCl$_2$	361-356	356-340	—
Ph$_2$SnCl$_2$	364	356-350	—
R$_2$SnBr$_2$	260-248	241-238	—
R$_2$SnI$_2$	204-169	186-176	—
RSnCl$_3$	384-376	368-358	—
BuSnCl$_3$		355[c]	—
PhSnCl $_3$		385-364	—
RSnBr$_3$	264-256	253-225	—
MeSnI$_3$	207	174	—

Table 2.6: Sn-N stretching frequency (cm^{-1}) for some OTCs

Compound		ν cm^{-1}
Ph$_3$SnCl.phepy[b]	1 or 2 bands	226
R$_2$SnCl$_2$.bipy[c]	1 or 2 bands	244-215
R$_2$SnCl$_2$.phen[d]		247-220
Et$_2$SnCl$_2$.Dipyam[e]		284, 275sh
Et$_2$SnCl$_2$.tripyam[f]		247br
Bu$_2$SnCl$_2$.4,4'-bipy[g]		247-231br
Bu$_2$SnCl$_2$.2phepy	1 or 2 bands	225-200br
R$_2$SnCl$_2$.2Me$_2$SO		244-187
[Me$_2$SnCl$_3$]$^{\ominus}$		333, 322, 235
[Me$_2$SnCl$_4$]$^{2\ominus}$		227
Ph$_2$SnCl$_2$.2pyridine		248
Ph$_2$SnCl$_2$.bipy		252, 246
Ph$_2$SnCl$_2$.dipyam		265, 254sh
Ph$_2$SnCl$_2$.trypyam		262, 248
Ph$_2$SnCl$_2$.4,4'-bipy	1 or 2 bands	240-228br
R$_2$SnBr$_2$.bipy	1 or 2 bands	169-140
R$_2$SnBr$_2$.phen	2 bands	169-149
R$_2$SnI$_3$.bipy	2 bands	156-139
R$_2$SnI$_3$.phen	2 bands	147-126
RSnCl$_3$.bipy	1 or 2 bands	294-267
RSnCl$_3$.phen		299-270
PhSnCl$_3$.4,4'-bipy	2 or 3 bands	330-318, 286-281
RSnBr$_3$.bipy	2 or 3 bands	201-170
RSnBr$_3$.phen		200-177
MeSnI$_3$.bipy		176, 159, 147
MeSnI$_3$.phen		184, 158, 140

Table 2.7 : Sn-O stretching frequencies for some OTCs (Poller, 1970)

Compound	state	Absorption bands and assignments (cm^{-1})
Me_3SnOH	Solid	917m (Sn-OH)
Et_3SnOH	Solid	885s (Sn-OH)
Ph_3SnOH	Solid	897s, 912s (Sn-OH)
Me_3SnOH	Solution	576m ν (Sn-O),531s b (Sn-O)
$Ph_3SnOSnPh_3$	Solid or solution	777-770s vas (SnOSn)
$R_3SnOSnR_3$	Liquid	784-769 vas (SnOSn)
Bu_3SnOr	Solution	1100-946w-m vas (SnOC), 525-514w
$Ph_3SnOP(O)Ph_2$	Solid	vs (SnOC)
R_2SnO	Solid	394m ν (Sn-O)
Ph_2SnO	Solid	576-561s ν (Sn-O)
$[Me_2Sn(OH)_4]^{2\ominus}$	Solution	575-571s ν (Sn-O)
$R_2Sn(OR')_2$	Solution	555br[a] ν (Sn-O)
$R_2Sn(OH)NO_3$	Solid	~600w[b] vas(OSnO), 487-466w vs (OSnO)
$RR'Sn(acac)_2$[c]	Solid	2 bands in the range 594-398s ν (Sn-O)
$(Me_3SiO)_nSnMe_{4-n}$ (n = 1-4)	Liquid	461-404 ν (Sn-O)
Me_nSnOx_{4-n}[d] (n=2,3)	Solid or liquid	1070-938 vs (SiOSn)
$Me_2SnX_2.2Ph_3PO$	Solid	528-517 ν (Sn-O)
$Me_2SnX_2.2Ph_3AsO$	Solid	320-300 ν (Sn-O)
$Me_2SnCl_2.2PyO$[e]	Solid	380-370 ν (Sn-O) 325s, br ν (Sn-O)

[a] Raman spectrum [b] overlap with CSnC , [c] acetylacetonate [d] 8-hydroxyquinoline [e] pyridine–N-oxide

2.3.3 ^{119}Sn Mossbauer spectroscopy:

Mossbauer spectroscopy is a powerful tool for investigating the stereochemistry and bonding in OTCs. The two most important parameter in mossbauer spectroscopy are isomer shift and quadruple splitting.

The isomer shift values are dependent on the s- electron density at ^{119}Sn nucleus and for all tin compounds fall in the range of ± 5 mms^{-1} with a positive corresponding to an increase in electronegativity of the halogen attached to tin causes reduction of s-electron density and smaller isomer shift. The isomer shift increase with the electron donating power of alkyl group. Phenyl group with stronger electron–withdrawing nature attached to tin lowers the isomer shift (Omae, 1989). ^{119}Sn isomer shift of some OTCs are summarized in Table 2. 8.

Table 2.8: Isomer shift of ^{119}Sn Mossbauer of some OTCs (mms^{-1}) (OMAE, 1989)

R_nSnX_{4-n}	X	Methyl	Ethyl	n-Propyl	n-Butyl	Phenyl
R$_3$Sn X	F	1.24	1.41	1.44	1.42	1.23
	Cl	1.47	1.49	1.62	1.53	1.34
	Br	1.41	1.52	1.50	1.61	1.33
	I	1.48	1.56	1.52	1.47	1.26
R$_2$SnX$_2$	F	1.31	1.42	1.45	1.42	1.28
	Cl	1.55	1.64	1.70	1.62	1.38
	Br	1.59	1.74	-	1.68	1.43
	I	-	1.72	-	1.80	1.51

A change in coordination number or stereochemistry at the tin atom will also affect the isomer shift parameter. In general an increase in the coordination number of tin atom is associated with a decrease in isomer shift since the increased use of the metal's 5d orbital

for bonding result in a reduction in the 5 s electron density at the tin nucleolus. For example chemical shift for Ph_2SnI_2 and Ph_2SnI_2.bipy are $\delta = 1.51$ mms^{-1} and $\delta = 1.41$ mms^{-1} respectively. Stereochemistry of tin compounds also affect on chemical shift. In table 2. 9 shows the isomer shifts of *cis and trans* isomers of R_2SnX_4.

Table 2.9: Comparison isomer shift of *cis and trans* complexes R_2SnX_4 (Wilkinson, 1995)

Cis R_2SnX_4	δ (mms^{-1})	Trans R_2SnX_4	δ (mms^{-1})
Me$_2$Sn(Ox)$_2$	0.88	**Me$_2$Sn(acac)$_2$**	1.18
Ph$_2$Sn(NCS)$_2$.bipy	0.82	**Ph$_2$SnCl$_2$.bipy**	1.22
Ph$_2$Sn(NCS)$_2$.PhenPh$_2$Sn	0.81	**Ph$_2$SnCl$_2$.Phen**	1.21
(OCOC$_5$H$_4$N$_2$)$_2$	0.83	**Ph$_2$Sn(OCOC$_5$H$_4$N$_3$)$_2$**	1.29

The *cis* complexes have lower isomer shift than the *trans* complexes and this is probably due to higher percentage of s charracter of the Sn-C in the *trans* isomers. The δ isomer shift values for most organotin compounds fall within the approximate range -0.5 to 2.7 mms^{-1}. For R_4Sn (R = Me, Et, n-Pr, Ph, Ph-Cl, CH_3COO^-) only a single line is observed. However any deviation of the ^{119}Sn nuclear Charge from cubic results in a two line. The quadruple splitting of some tetrahedral OTCs are compared in Table 2.10.

The quadrupole-splitting is a separation between two peaks; hence the quadrupole splitting parameter is useful for determination stereochemistry of OTCs. The quadrupole splitting of ^{119} Sn is shown in Figure 2.2.
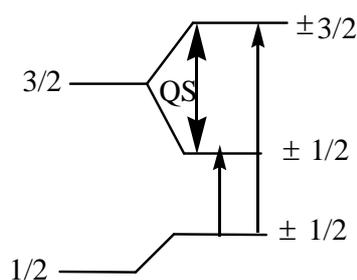
Isomer shift   quadruple splitting

Figure2.2 Quadruple splitting of ^{119}Sn

Table 2.10: Quadruple splitting of some OTCs (Wilkinson, 1995)

R$_3$SnX	ΔE_Q mms^{-1}	R$_2$SnX$_2$	ΔE_Q (mms^{-1})
Ph$_3$ SnSSn Ph$_3$	1.46	**(Ph$_2$SnS)$_3$**	1.60
Ph$_3$SnSC$_6$H$_4$Bu	1.41	**Me$_2$Sn(OSiPh$_3$)$_2$**	2.45
{Me$_3$Si)$_2$CH$_3$}SnCl	2.18	**(Me$_2$SnS)$_3$**	1.51
Ph$_2$Sn(CH$_2$)$_4$SnPh$_2$	2.37	**Ph$_2$SnSCH$_2$CH$_2$S**	1.69

Quadruple parameter is a valuable data that aids in the assignment of structure between *cis* and *trans* isomer in octahedral (diorganotin compounds). The values for the *trans* isomer is double that of the *cis* isomer.

Normally this parameter increase smoothly with increasing C-Sn bond angle, for octahedral diorganotin complexes from 2.00 mms^{-1} for the *cis* derivatives to 4.00 for *trans* isomers (Wilkinson, 1995; Blunden et al., 1987) . The quadruple splitting of some OTCs with different geometries are shown in Table 2.11. The effect of coordination number and geometry on the quadruple splitting is shown in Table 2.12.

Table 2.11: Comparison quadruple splitting of cis and trans R_2SnX_4 (Wilkinson, 1995)

cisR_2SnX_4	ΔE_Q (mms^{-1})	Trans R_2SnX_4	ΔE_Q (mms^{-1})
Me$_2$Sn(ox)$_2$	2.02	**Me$_2$Sn(acac)$_2$**	4.02
Ph$_2$Sn(SCSNEt$_2$)$_2$	1.72	**Ph$_2$SnCl$_2$. 2DMSO**	3.86
Me$_2$Sn(ONHCOMe)$_2$	1.99	**Me$_2$SnCl$_2$.py**	4.00

Table 2.12: Quadrupole splitting (mms^{-1}) of some OTCs with different geometries