APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 63–69 (1993)

Organotin(IV) complexes of dibasic tridentate Schiff bases containing ONO donor atoms*

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Organotin(IV) Schiff base complexes of the type (L)SnR$_2$ [where R = CH$_3$, C$_6$H$_5$ or CH$_2$CH$_2$CO$_2$CH$_3$], (LH)Sn(C$_6$H$_5$)$_3$ and (L)SnCl(CH$_2$CH$_2$CO$_2$CH$_3$) [where LH$_2$ = 2-*N*-salicylideneimino-2-methyl-1-propanol, derived from the condensation of salicylaldehyde and 2-amino-2-methyl-1-propanol] have been prepared and characterized on the basis of their elemental analyses, IR, ^{1}H, ^{13}C and ^{119}Sn NMR studies. In these mononuclear complexes the Schiff base acts either as a dianionic tridentate or as a monobasic bidentate moiety by coordinating through an alkoxy group, an azomethine nitrogen and a phenoxide ion to tin. Sulphur dioxide inserts in the tin–methyl/–phenyl bond in the above Schiff base complexes to give tin-*O*-sulphinates of formulae (L)RSn(SO$_2$R) and (LH)(C$_6$H$_5$)$_2$Sn(SO$_2$C$_6$H$_5$).

Keywords: Organotin Schiff base complexes, spectroscopic studies

INTRODUCTION

Yamada and co-workers have synthesized and characterized copper(II)[1] and vanadium(IV)[2] complexes of the Schiff bases derived from salicylaldehyde and ethanol- or propanol-amines and binuclear structures have been assigned to the complexes formed. The lower-than-normal magnetic moment found was due to exchange interactions between the respective metal ions.

Several mononuclear transition-metal complexes of the above Schiff bases have been described in the literature[3–12] in which the ligands act as dibasic tridentate as well as monobasic bidentate moieties. Prashar and Tandon[13] have studied reactions of titanium tetraisopropoxide with the Schiff base derived from salicylaldehyde and 2-hydroxyethylamine. A trigonal bipyramidal structure has been suggested on the basis of spectroscopic data and molecular weight. However, studies of organotin(IV) complexes with the above Schiff base have not been reported.

The Schiff base 2-*N*-salicylideneimino-2-methyl-1-propanol has an interesting ligating ability because of its potential phenolic and alcoholic hydroxyl (OH) groups and azomethine nitrogen, and acts as a dibasic tridentate ligand. In the present communication the synthesis and characterization of five new organotin(IV) complexes of 2-*N*-salicylideneimino-2-methyl-1-propanol are reported.

EXPERIMENTAL

The starting materials were of reagent or analytical grade and were used without further purification. The solvents were dried and distilled before use. Infrared spectra were recorded as KBr pellets, in dichloromethane (CH$_2$Cl$_2$) solution or Nujol mulls, on a Perkin–Elmer Model 1600 FT-IR spectrophotometer. The ^{1}H NMR spectra were recorded at 80 MHz using a Varian FT-80A spectrometer and a Bruker WH-90 spectrometer in deuteriochloroform (CDCl$_3$) solution. The ^{13}C and ^{119}Sn NMR spectra were measured with a Bruker MSL 300 spectrometer at 75.47 and 111.89 MHz respectively. The spectra were recorded in CDCl$_3$ solution at ambient temperature. The ^{13}C chemical shifts are related to the CDCl$_3$ signal (^{13}C CDCl$_3$ = 76.9 ppm) and δ(^{119}Sn) values are related to external neat tetramethylstannane.

Dimethyl-/diphenyl-tin dichloride and triphenyltin hydroxide were from Alfa Inorganics, USA. The ester–tin compounds Cl$_2$Sn(CH$_2$CH$_2$CO$_2$CH$_3$)$_2$ and Cl$_3$Sn(CH$_2$CH$_2$CO$_2$CH$_3$) were prepared according to a method reported in the literature.[14] The Schiff base 2-*N*-salicylideneimino-2-methyl-1-propanol was prepared as follows.

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* NCL Communication No. 5406

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0268–2605/93/010063–07 $08.50
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Received 30 April 1992
Accepted 18 August 1992

Preparation of 2-*N*-salicylideneimino-2-methyl-1-propanol (LH_2)

Salicylaldehyde (4.05 g; 0.03 mol) and 2-amino-2-methyl-1-propanol (2.94 g; 0.033 mol) were mixed in ethanol (50 cm^3) and the solution was heated to reflux on a water bath for approx. 4 h. The resulting yellow solution was concentrated to a small volume to give a syrupy liquid which was poured onto crushed ice (made from distilled water) and stirred vigorously for 30 min. The pale yellow solid separated and was filtered and washed with a small portion of ice-cold water and air-dried [yield 4.14 g (65%), m.p. 68 °C]. The Schiff base was freely soluble in benzene, carbon tetrachloride and chloroform, and insoluble in hexane.

Preparation of $(L)Sn(CH_3)_2$

The Schiff base LH_2 (0.19 g; 0.001 mol) was dissolved in benzene (50 cm^3) and to this was added dimethyltin oxide (Me_2SnO) (0.17 g; 0.001 mol). The reaction mixture was heated to reflux and the water formed was removed azeotropically. The benzene solution after filtration and upon concentration gave a yellow low-melting solid which was washed with n-hexane and dried *in vacuo*. The product was recrystallized from a CH_2Cl_2–hexane mixture [yield 0.24 g (71%), m.p. 173–175 °C]. The compound $(LH)Sn(C_6H_5)_3$ was similarly prepared using Ph_3SnOH and the ligand in a 1:1 molar ratio [yield 0.34 g (63%)].

Preparation of $(L)Sn(CH_2CH_2CO_2CH_3)_2$

A solution of Schiff base LH_2 (0.19 g; 0.001 mol) in chloroform (20 cm^3) was added dropwise to a stirred solution of $Cl_2Sn(CH_2CH_2CO_2CH_3)_2$ (0.36 g; 0.001 mol) in $CHCl_3$ (20 cm^3). After the addition was complete, the reaction mixture was refluxed for 10 min and then cooled. Dilute ammonia solution was added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about 2 h, and removal of solvent *in vacuo* gave a yellow solid. The solid was further dissolved in dichloromethane (5 cm^3) and the solution was cooled in an ice–salt mixture. Crystallization of the pure product was effected by layering n-hexane (15 cm^3) over the well cooled solution. The yellow crystalline solid separated was filtered, washed with n-hexane and dried *in vacuo* [yield 0.36 g (69%), m.p. 122–123 °C]. The complexes, $(L)Sn(C_6H_5)_2$ [yield 0.29 g (62%), m.p. 168–170 °C] and $(L)SnCl(CH_2CH_2CO_2CH_3)$ [yield 0.30 g (69%), m.p. 104–105 °C] were prepared similarly.

Preparation of $(L)CH_3Sn(SO_2CH_3)$

The complex $(L)Sn(CH_3)_2$ (0.5 g) was finely ground and kept in a well cooled Schlenk tube fitted with a gas inlet reaching to the bottom. Dry sulphur dioxide gas was condensed into the flask until the volume reached approx. 3 cm^3. The tube was shaken occasionally and kept for 2 h in the refrigerator, after which it was taken out and the liquid sulphur dioxide was allowed to evaporate. Finally the tube was kept *in vacuo* at room temperature for 1 h to produce a yellow crystalline solid, m.p. 175 °C [yield 0.54 g (90%)]. These complexes are insoluble in benzene, chloroform and alcohol.

The complexes $(L)C_6H_5Sn(SO_2C_6H_5)$ and $(LH)(C_6H_5)_2Sn(SO_2C_6H_5)$ were prepared similarly using the above method.

RESULTS AND DISCUSSION

The complexes described in this paper have been synthesized by refluxing R_2SnCl_2 [where $R = CH_3$, C_6H_5 or $CH_2CH_2CO_2CH_3$], $(C_6H_5)_3SnCl$ or $Cl_3Sn(CH_2CH_2CO_2CH_3)$, with stoichiometric amounts of Schiff base (LH_2) in chloroform medium using aqueous ammonia as HCl acceptor (Eqns [1] and [2])

$$R_2SnCl_2 + LH_2 \xrightarrow[-NH_4Cl]{aq.NH_3} (L)SnR_2 + 2HCl \qquad [1]$$

$$Cl_3Sn(CH_2CH_2CO_2CH_3) + LH_2 \xrightarrow[-NH_4Cl]{aq.NH_3}$$

$$(L)SnClCH_2CH_2CO_2CH_3 + 2HCl \qquad [2]$$

The complexes $(L)Sn(CH_3)_2$ and $(LH)Sn(C_6H_5)_3$ were prepared by an alternative procedure in which Me_2SnO/Ph_3SnOH reacted with the stoichiometric quantity of Schiff base in refluxing benzene followed by azeotropic removal of liberated water.

These complexes are yellow crystalline solids soluble in benzene, chloroform and dichloromethane and insoluble in hexane. The complexes

Table 1. Analytical data for 2-*N*-salicylideneimino-2-methyl-1-propanol tin(IV) Schiff base complexes

	Compound	Colour	m.p. (C)	Elemental analysis: Found (calcd) (%) Sn	C	H	N
	LH_2	Yellow	68	—	68.45	7.97	7.03
	$C_{11}H_{15}NO_2$			—	(68.37)	(7.82)	(7.25)
1	$(L)Sn(CH_3)_2$	Yellow	173–175	34.82	45.66	5.67	4.01
	$C_{13}H_{19}NO_2Sn$			(34.91)	(45.92)	(5.64)	(4.12)
2	$(L)Sn(C_6H_5)_2$	Yellow	168–170	25.38	59.61	4.75	2.91
	$C_{23}H_{23}NO_2Sn$			(25.57)	(59.52)	(5.00)	(3.02)
3	$(LH)Sn(C_6H_5)_3$	Yellow	Low-melting	21.91	64.01	5.25	2.36
	$C_{29}H_{29}NO_2Sn$			(21.89)	(64.23)	(5.39)	(2.58)
4	$(L)SnCl(CH_2CH_2CO_2CH_3)$	Yellow	104–105	27.33	41.70	4.51	3.15
	$C_{15}H_{20}ClNO_4Sn$			(27.45)	(41.66)	(4.66)	(3.24)
5	$(L)Sn(CH_2CH_2CO_2CH_3)_2$	Yellow	122–123	24.33	46.95	5.46	2.77
	$C_{19}H_{27}NO_6Sn$			(24.52)	(47.14)	(5.62)	(2.89)

isolated are presented in Table 1 together with their analytical data.

The IR spectrum of the Schiff base in Nujol shows two medium-intensity bands at 3255 and 3167 cm^{-1} attributed to ν(OH) of alcoholic and hydrogen-bonded phenolic hydroxyl groups respectively. In the region below 1700 cm^{-1}, the strong bands at 1631 and 1611 cm^{-1} are due to ν(C=N) and ν(C=C) respectively.[15] The strong band at 1582 cm^{-1} is assigned to coupled vibration of ν(C=N + C=C) groups.[16] The characteristic band at 1280 cm^{-1} is due to a coupled vibration of phenolic groups [ν(CO) + δ(OH)].[17] The region below 1200 cm^{-1} shows a large number of bands mostly due to ν(CH) deformations and ring breathing. The bands at 795 and 764 cm^{-1} are due to *o*-substituted benzene rings.

The IR spectra of $(L)Sn(CH_3)_2$, $(L)Sn(C_6H_5)_2$, $(L)SnCl(CH_2CH_2CO_2CH_3)$ and $(L)Sn(CH_2CH_2CO_2CH_3)_2$ complexes do not show any band attributable to ν(OH), indicating deprotonation of alcoholic and phenolic protons by tin. The complex $(LH)Sn(C_6H_5)_3$ shows alcoholic ν(OH) at 3356 cm^{-1}. The 1631 cm^{-1} band due to ν(C=N) in the ligand has been shifted to lower-frequency regions in the complexes, indicating participation of the azomethine nitrogen lone-pair coordination to tin.[5] The phenolic ν(C—O) has been shifted to *ca* 1320 cm^{-1}, suggesting increased C—O bond order as a result of complex formation.[17] The complex, $(L)Sn(CH_3)_2$, shows medium-intensity bands at 523 cm^{-1} and 476 cm^{-1} which are attributable to ν(Sn—C), which suggests a *cis* position of the methyl groups.[18] An additional band at 452 cm^{-1} is assigned to ν(Sn—O). In the starting material [ester-tin chlorides, $Cl_2Sn(CH_2CH_2CO_2CH_3)_2$ and $Cl_3Sn(CH_2CH_2CO_2CH_3)$], the intramolecularly

Table 2. IR data (cm^{-1}) for 2-*N*-salicylideneimino-2-methyl-1-propanol tin (IV) Schiff base complexes

Compd	OH	(C=N) + (C=C)	(C—O)(L)	(C=O)(est.)	(C—O)(est.)
LH_2	3255, 3167	1631, 1582	1280	—	—
I[a]	— —	— —	—	1654	1231
II[b]	— —	— —	—	1672	1225
1	— —	1617, 1536	1323	—	—
2	— —	1619, 1543	1317	—	—
3	3356, —	1617, 1540	1318	—	—
4	— —	1622, 1544	1303	1666	1260, 1210
5	— —	1625, 1533	1334	1732, 1682	1265, 1216

[a] I, $Cl_3Sn(CH_2CH_2CO_2CH_3)$. [b] II, $Cl_2Sn(CH_2CH_2CO_2CH_3)_2$.

Table 3. ^1H NMR data (δ, ppm) for 2-*N*-salicylideneimino-2-methyl-1-propanol tin(IV) Schiff base complexes

									Aromatic protons			
Compd	CH_3	CH_2—O	CH	OH	α-CH_2	β-CH_2	OCH_3 (est.)	$Sn(CH_3)_2$	H_3	H_4	H_5	H_6
LH_2	1.28	3.55	8.31	13.66	—	—	—	—	6.75	7.23	6.88	7.30
I	—	—	—	—	2.2	2.93	3.97	—	—	—	—	—
II	—	—	—	—	1.89	2.90	3.76	—	—	—	—	—
1[a]	1.36	3.76	8.27	—	—	—	—	0.63	6.60	7.15	6.69	7.33
2	1.33	3.90	8.30	—	—	—	—	—	—6.55—		—8.02—	
3	1.35	3.46	8.29	7.20	—	—	—	—	—6.48—		—7.74—	
4	1.32	3.75	8.33	—	1.60	2.84	3.75	—	6.65	7.72	6.75	7.35
5	1.30	3.74	8.28	—	1.50	2.66	3.68	—	6.50	7.12	6.61	7.20

[a] Complex **1**: $^2J(^{117}Sn-^1H) = 72$ Hz; $^2J(^{119}Sn-^1H) = 76$ Hz; $^3J(^{117}Sn-^1H)(CH_2) = 34$ Hz; $^3J(^{119}Sn-^1H)(CH) = 46$ Hz.

coordinated ester $\nu(C{=}O)$ appears at 1672 and 1654 cm^{-1} respectively. The complex $(L)SnCl(CH_2CH_2CO_2CH_3)$ obtained by the reaction of the Schiff base and trichloro-ester-tin shows $\nu(C{=}O)$ at 1666 cm^{-1}, which confirms coordination of ester groups to tin, whereas in the case of $(L)Sn(CH_2CH_2CO_2CH_3)_2$ two bands are observed due to $\nu(C{=}O)$ at 1732 and 1682 cm^{-1}, which suggests a free and coordinated nature of ester groupings (Table 2).

The ^1H NMR spectrum of the Schiff base in $CDCl_3$ shows signals at δ 1.28, 3.58, and 8.31 ppm due to CH_3—, CH_2—O— and azomethine protons respectively. A broad signal extending from δ 12.26 to 15.01 ppm, centred at δ 13.60 ppm, is due to hydrogen-bonded phenolic and alcoholic OH protons. No separate signal was observed for an alcoholic OH proton in the expected region

Table 4. ^{13}C and ^{119}Sn NMR data (δ ppm) for 2-*N*-salicylideneimino-2-methyl-1-propanol tin(IV) complexes

Compd	$(CH_3)_2$	$\overset{\backslash\,/}{\underset{/\,\backslash}{C}}$	CH_2—O	CH	α-CH_2	β-CH_2	C═O (est.)	^{119}Sn (δ ppm)
LH_2	23.74	60.86	70.90	162.25	—	—	—	—
1[a]	25.66	62.21	73.85	168.86	—	—	—	−150.10
2	25.85	62.69	73.75	169.45	—	—	—	−322.72
3	23.43	60.95	69.98	162.82	—	—	—	−323.44
4[b]	23.90	61.33	71.50	163.00	18.33	29.16	168.35	−200.00
5[c]	25.86	63.12	74.02	163.83	17.50	28.87	176.88	−224.30

[a] Complex **1**: $Sn(CH_3)_2 = 0.11$ ppm; $^1J(^{119}Sn,^{13}C) = 638.15$ Hz.

[b] Complex **4**: Ester $OCH_3 = 53.98$ ppm; $^1J(^{119}Sn,^{13}C)(\alpha\text{-}CH_2) = 769.04$ Hz; $^2J(^{119}Sn,^{13}C)(\beta\text{-}CH_2) = 49.90$ Hz.

[c] Complex **5**: Ester $OCH_3 = 52.10$ ppm; $^1J(^{119}Sn,^{13}C)(\alpha\text{-}CH_2) = 768.36$ Hz; $^2J(^{119}Sn,^{13}C)(\beta\text{-}CH_2) = 53.25$ Hz.

Chemical shift of aromatic carbons (ppm)

Compd	C_1	C_2	C_3	C_4	C_5	C_6
LH_2	118.73	163.07	117.81	131.87	118.11	132.70
1	117.59	169.34	116.67	135.07	122.72	136.28
2[d]	117.72	170.11	116.63	129.56	122.99	135.36
3[e]	119.12	171.07	116.59	132.35	122.37	132.54
4	118.04	167.87	117.26	135.19	122.85	135.82
5	118.31	170.90	116.10	132.89	123.30	136.70

[d] Complex **2**: $Sn(C_6H_5)_2 = 127.92$–130.06 ppm and 136.79–137.49 ppm.

[e] Complex **3**: $Sn(C_6H_5)_3 = 128.13$–129.01 ppm, 129.63–130.04 ppm and 136.80–137.25 ppm.

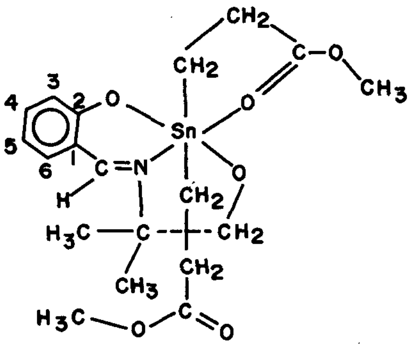

Figure 1. Structure of complex (L)Sn$(CH_3)_2$.

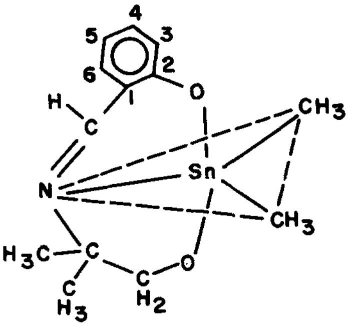

Figure 2. Structure of complex 5.

(*ca* 47 ppm) when recorded in $CDCl_3$ as solvent. The integrated peak area for the broad hydrogen-bonded OH signal and azomethine proton is in the ratio of 12:7, which again indicates that the broad signal is due to two hydroxyl protons. Further D_2O exchange studies show complete disappearance of this broad signal, which confirms the above assignment.

In order to study the nature of the hydrogen bonding of the alcoholic OH proton, the ligand spectrum was recorded in DMSO-d_6. The spectrum showed a signal at δ 4.95 ppm attributable to alcoholic OH and another broad signal at δ 14.40 ppm due to hydrogen-bonded phenolic OH; both disappeared on D_2O exchange. These studies show that in a non-coordinating solvent such as $CDCl_3$ the alcoholic and phenolic OH protons are hydrogen-bonded and appear in the downfield region, whereas in a hydrogen-bond weakening solvent such as DMSO the alcoholic OH protons appear separately, indicating that the alcoholic OH proton is weakly hydrogen-bonded, may be intermolecularly, and these bonds break up in a coordinating solvent such as DMSO.

The ^1H NMR spectra of the complexes (L)SnR_2 and (L)SnCl($CH_2CH_2CO_2CH_3$) do not show any signal due to hydroxyl protons, suggesting proton replacement by tin. No significant shift has been observed for the azomethine δ(CH) proton after nitrogen coordination to tin. The methylene protons in the complexes **1**, **2**, **4** and **5** are deshielded as a result of deprotonation of bonding of alcoholic OH. In the spectrum of complex **3** a signal at 7.2 ppm has been observed due to an alcoholic proton which disappeared on D_2O exchange. The methylene protons show a marginal shift of 0.09 ppm in the higher magnetic field, which again supports the free nature of alcoholic OH. In the complex the ligand acts as a monobasic bidentate moiety by the coordination of phenoxide ion and azomethine nitrogen. The methyl protons in all complexes show marginal downfield shifts as expected and the aromatic protons resonate in the expected region of 6.44–8.02 ppm (Table 3).

In the complex (L)Sn$(CH_3)_2$, the resonances due to the Sn—CH_3 protons are observed as a sharp singlet at 0.63 ppm having two satellite signals on either side of this signal as doublets due to coupling of methyl protons with ^{117}Sn and ^{119}Sn nuclei. The coupling constants observed were ^2J (^{117}Sn, ^1H) = 72 Hz and ^2J(^{119}Sn, ^1H) = 76 Hz. This increase in coupling constants compared with those in Me_2SnCl_2 [^2J(^{117}Sn, ^1H) = 66 Hz; ^2J(^{119}Sn, ^1H) = 70 Hz] is suggested to be due to the increase in the coordination number of tin as a result of complex formation.[19] Further, satellite signals are also observed for azomethine and

Table 5. Sulphur dioxide insertion compounds of 2-*N*-salicylideneimino-2-methyl-1-propanol tin (IV) complexes

Compound	Colour	M.p. (°C)	IR frequencies (cm^{-1})	
			ν_{as} (S—O)	ν_s (S—O)
(L)CH_3Sn(SO_2CH_3)	Yellow	175	1047	897
(L)C_6H_5Sn($SO_2C_6H_5$)	Yellow	130	1070	873
(LH)$(C_6H_5)_2$Sn($SO_2C_6H_5$)	Yellow	70	1034	890

methylene protons with coupling constants of $^3J(^{119}Sn, ^1H) = 46$ Hz and $^3J(^{119}Sn, ^1H) = 34$ Hz respectively, which again confirms the mode of bonding to tin.

The spectrum of complex **5** shows two triplets centred at 1.50 and 2.66 ppm and a singlet at 3.68 ppm due to α-CH_2. β-CH_2 and OCH_3 of the ester residue respectively. The shift to higher magnetic field compared with those of the complex $Cl_2Sn(CH_2CH_2CO_2CH_3)$ is attributed to replacement of electronegative chlorine atoms by the donor atoms ONO of the chelating Schiff base.[20] A similar upfield shift is observed in complex **4** for α-CH_2, β-CH_2 and OCH_3 as compared with $Cl_3Sn(CH_2CH_2CO_2CH_3)$.

The ^{13}C NMR spectral data of tin(IV) complexes and the ligand are presented in Table 4. In the complexes **1** and **2**, a large deshielding (6–7 ppm) has been observed for both the phenolic and azomethine carbons. The alkoxy (CH_2—O—) carbon also shows a similar downfield shift by 3–4 ppm. These data indicate the participation of these groups in bond formation. In complex **3** the phenolic and azomethine carbons show the expected downfield shift; however the alkoxy carbon does not show any change in its resonance. These observations support the bonding of phenolic and azomethine groups to the metal with non-involvement of the alkoxy group. The complex **4** shows a marginal downfield shift of 0.75 ppm for the azomethine carbon, whereas the phenolic CO and alkoxy CH_2—O have been shifted downfield by 3.8 and 0.6 ppm respectively. Large downfield shifts have been observed for these carbons in complex **5**, as in the case of diorganotin(IV) complexes **1** and **2**. The ester carbonyl carbon in complexes **4** and **5** resonates at higher magnetic field than the ester–tin chlorides,[21] as a singlet at 167.87 and 170.9 ppm respectively.

Furthermore, for the determination of the structure of the complexes, their tin–carbon coupling constants $^1J(Sn, ^{13}C)$ and ^{119}Sn NMR have been studied.

The tin–carbon coupling constant $^1J(^{119}Sn, ^{13}C)$ for the dimethyltin complex $(L)Sn(CH_3)_2$ is 638.15 Hz. The C–Sn–C bond angle θ, calculated from the above coupling constants using the expression[22]

$$|^1J(^{119}Sn, ^{13}C)| = 11.4\theta - 875$$

is 132°. This value is consistent with trigonal bipyramidal geometry with equatorial disposition of methyl groups in the complex $(L)Sn(CH_3)_2$, as shown in Fig. 1.

The (^{119}Sn) chemical shift value observed for $(L)Sn(CH_3)_2$ is at δ −150.1 ppm, which is consistent with the $\delta(^{119}Sn)$ value reported for the well characterized pentacoordinated complex $Me_2Sn(SAB)$.[23] In the complex $(L)Sn(C_6H_5)_2$, the $\delta(^{119}Sn)$ value is at −322.72 ppm. A similar upfield shift of $\delta(^{119}Sn)$ by 150–170 ppm is reported when methyl groups in Me_2Sn(chelate) are replaced by phenyl groups.[24] The tin atom in the ester–tin complexes **4** and **5** resonates at −200.00 ppm and −224.30 ppm respectively compared with $\delta(^{119}Sn)$ in the pentacoordinated complex **1**. The increased shielding is attributed to the coordination of the ester carbonyl to tin, thereby increasing the coordination number of tin to six.

The complexes **4** and **5** are assigned a distorted octahedral geometry as shown in Fig. 2 for the complex **5**.

Reactivity of organotin complexes towards SO_2

The complexes $(L)Sn(CH_3)_2$, $(L)Sn(C_6H_5)_2$ and $(LH)Sn(C_6H_5)_2$ insert one molecule of sulphur dioxide into the tin–carbon (Sn–C) bond giving complexes of the type $(L)CH_3Sn(SO_2CH_3)$, $(L)C_6H_5Sn(SO_2C_6H_5)$ and $(LH)(C_6H_5)_2Sn(SO_2C_6H_5)$ (Table 5). These complexes are stable at room temperature. On treatment with dilute HCl, SO_2 is evolved and this has been utilized for the estimation of SO_2 in these complexes.

The IR spectra of the insertion products show characteristic bands at ~1040 cm^{-1} and 885 cm^{-1} due to ν_{as}(S—O) and ν_s(S—O) respectively, which is consistent with an *O*-sulphinate structure for the complex.[25]

Acknowledgements We thank Dr P R Rajamohanan and Dr S Ganapathy of the NMR Group for recording ^{13}C and ^{119}Sn NMR spectra.

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