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New chelated complexes of bis-β-carboalkoxyethyltin(IV) dichloride with *S*-benzyldithiocarbazate Schiff bases*

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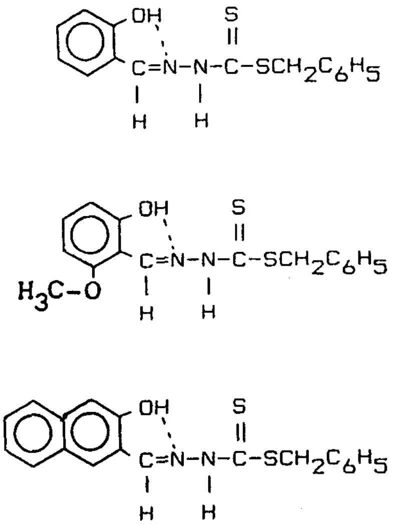
The Schiff bases [H_2SBSaD], [H_2SBVD] and [H_2SBND], derived by the condensation of *S*-benzyldithiocarbazate and salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-1-naphthaldehyde respectively, react with diestertin dichlorides, R_2SnCl_2 [R = —$CH_2CH_2CO_2CH_3$, —$CH_2CH_2CO_2C_2H_5$ or —$CH_2CH_2CO_2C_4H_9$] in 1:1 molar proportion to yield chlorine-substituted complexes of the type R_2Sn(Schiff base), the base being tridentate. The complexes are characterized on the basis of their elemental analyses, IR and ^{1}H NMR spectral studies. The ^{13}C and ^{119}Sn NMR and the tin–carbon coupling constant data reveal the structures of the complexes to be octahedral with *trans* ester grouping, and bidentate ester linkages. The pentacoordinated complex $(CH_3)_2$Sn(SBSaD) was prepared by the reaction of dimethyltin oxide with H_2SBSaD in equimolar proportions.

Keywords: Estertin complexes, *S*-benzyldithiocarbazate, Schiff bases

INTRODUCTION

β-Alkoxycarbonylethyltin(IV) chlorides (estertins), a class of excellent PVC-stabilizer intermediates, have aroused considerable interest because of their simple and relatively inexpensive methods of preparation.[1-4] These estertin stabilizers have excellent heat stability and are claimed to have lower migration tendencies and better light-stabilizing properties than simple alkyltin stabilizers. They are used in various formulations, particularly for rigid extrusions and for food packages.[5]

The chlorine atoms in diestertin dichlorides can be replaced fully or partially using ligands such as oxine,[6] dithiocarbamates[7] and some Schiff bases.[8-11] The tin atom in bis-β-carboalkoxyethyltin dichlorides has been observed to be hexacoordinated and the compound itself is quite stable. We have carried out replacement of both of the chlorine atoms of this compound with tridentate chelating Schiff base ligands. There is no report in the literature about the reaction of ester-tin chlorides with this type of Schiff bases. The Schiff bases used for the study are shown in Scheme 1.



Scheme 1

EXPERIMENTAL

The starting chemicals were of analytical grade and were used without further purification. The solvents were dried and distilled before use. Infrared spectra were recorded in nujol mull and as KBr pellets on a Perkin–Elmer Model 1620

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Table 1 Analytical data for bis(β-carboalkoxyethyl)tin(IV) Schiff base complexes

	Compound	Sn	C	H	N
		Elemental analysis (%): Found (Calcd)			
1	$(CH_2CH_2CO_2CH_3)_2Sn(SBSaD)$	19.88	46.29	4.45	4.66
	$C_{23}H_{26}O_5N_2S_2Sn$	(20.01)	(46.56)	(4.42)	(4.72)
2	$(CH_2CH_2CO_2C_2H_5)_2Sn(SBSaD)$	19.25	48.47	4.52	4.41
	$C_{25}H_{30}O_5N_2S_2Sn$	(19.10)	(48.32)	(4.87)	(4.51)
3	$(CH_2CH_2CO_2C_4H_9)_2Sn(SBSaD)$	17.37	51.18	5.73	4.19
	$C_{29}H_{38}O_5N_2S_2Sn$	(17.52)	(51.41)	(5.65)	(4.34)
4	$(CH_2CH_2CO_2CH_3)_2Sn(SBVD)$	19.21	46.36	4.19	4.23
	$C_{24}H_{28}O_6N_2S_2Sn$	(19.05)	(46.24)	(4.53)	(4.49)
5	$(CH_2CH_2CO_2C_2H_5)_2Sn(SBVD)$	18.13	47.62	4.61	4.41
	$C_{26}H_{32}O_6N_2S_2Sn$	(18.22)	(47.94)	(4.95)	(4.30)
6	$(CH_2CH_2CO_2C_4H_9)_2Sn(SBVD)$	16.52	50.63	5.35	3.72
	$C_{30}H_{40}O_6N_2S_2Sn$	(16.78)	(50.93)	(5.70)	(3.96)
7	$(CH_2CH_2CO_2CH_3)_2Sn(SBND)$	18.57	50.23	4.57	4.22
	$C_{27}H_{28}O_5N_2S_2Sn$	(18.45)	(50.41)	(4.39)	(4.35)
8	$(CH_2CH_2CO_2C_2H_5)_2Sn(SBND)$	17.32	51.91	4.59	4.28
	$C_{29}H_{32}O_5N_2S_2Sn$	(17.68)	(51.88)	(4.80)	(4.17)
9	$(CH_2CH_2CO_2C_4H_9)_2Sn(SBND)$	16.18	54.37	5.41	3.72
	$C_{33}H_{40}O_5N_2S_2Sn$	(16.32)	(54.48)	(5.54)	(3.85)

FT-IR spectrophotometer. The proton NMR spectra were recorded at 80 MHz using a Varian FT-80 A spectrometer and Bruker WH-90 spectrometer in $CDCl_3$ 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 in $CDCl_3$ solution or the solid state at ambient temperature. The ^{13}C chemical shifts are related to the TMS signal and $\delta(^{119}Sn)$ values are related to external neat tetramethylstannane. The electronic spectra were run on a Pye–Unicam SP8-100 UV/Vis spectrophotometer.

The ligands H_2SBSaD,[12] H_2SBVD[13] and H_2SBND[12] and the ester-tin compounds $(CH_2CH_2CO_2CH_3)_2SnCl_2$,[3] $(CH_2CH_2CO_2C_2H_5)_2SnCl_2$,[3] $(CH_2CH_2CO_2C_4H_9)_2SnCl_2$[3] and $(SBSaD)Sn(CH_3)_2$[13] were prepared according to methods reported in the literature.

Preparation of $(SBSaD)Sn(CH_2CH_2CO_2CH_3)_2$ (I)

In a typical experiment, a mixture of $(CH_2CH_2CO_2CH_3)_2SnCl_2$ (0.36 g; 1 mmol) and H_2SBSaD (0.30 g; 1 mmol) in chloroform (50 cm^3) was refluxed on a water bath for 10 min. A few drops of ammonia solution were added dropwise to neutralize the liberated acid and the ammonium chloride formed was removed by filtration. The filtrate was further refluxed for about two

Table 2 IR data (cm^{-1}) for bis(β-carboalkoxyethyl)tin(IV) Schiff base complexes

Compd	(C═O)	(C—O)(est.)	(C═N)(C═C)	(C—O)(L)	(C═S)	(N—N)
1	1732, 1707	1263, 1219	1582, 1536	1311	1026	959
2	1730, 1705	1260, 1205	1585, 1538	1310	1024	960, 925
3	1731, 1711	1264, 1216	1586, 1540	1302	1028	966, 937, 917
4	1727, 1712	1246, 1213	1582, 1549	1316	1026	962
5	1727, 1701	1247, 1211	1584, 1548	1342	1015	960, 917
6	1726, 1672	1250, 1215	1586, 1547	1313	1028	966, 915
7	1730, 1713	1253, 1191	1598, 1536	1301	1024	985, 962, 943
8	1725, 1704	1256, 1204	1598, 1536	1300	1024	987, 960, 942
9	1728, 1676	1260, 1193	1598, 1538	1301	1029	989, 963, 944

Table 3 ^{1}H NMR data for bis(β-carboalkoxyethyl)tin(IV) Schiff base complexes

	Chemical shifts, δ, in $CDCl_3$ (ppm)							
Compd	α-CH_2	β-CH_2	OCH_2/OCH_3 (ester)	CH_3 (ester)	SCH_2	OCH_3	CH	Aromatic protons
1	1.64	2.69	3.58	—	4.33	—	8.60	6.60–7.36
2	1.63	2.64	4.12	1.20	4.34	—	8.61	6.58–7.41
3	1.77	2.70	4.02	0.87	4.35	—	8.59	6.50–7.36
4	1.76	2.76	3.64	—	4.40	3.82	8.64	6.53–7.42
5	1.70	2.71	4.10	1.25	4.35	3.80	8.60	6.55–7.50
6	1.73	2.70	3.77	0.90	4.33	3.80	8.70	6.53–7.46
7	1.69	2.72	3.60	—	4.38	—	9.42	6.80–7.92
8	1.63	2.66	4.00	1.15	4.33	—	9.38	6.55–8.00
9	1.80	2.77	4.03	0.88	4.40	—	9.60	6.78–8.00

hours, and evaporated to dryness at reduced pressure. The resulting solid was dissolved in methylene chloride (5 cm^3), cooled and n-hexane was then added. Any solid which separated was filtered off and the filtrate was concentrated *in vacuo* to yield the complex.

Ester-tin complexes of all other Schiff bases were prepared by the above procedure (Table 1).

Preparation of $(CH_3)_2Sn(SBSaD)$

Freshly prepared and dried dimethyltin oxide (0.27 g; 1 mmol) was mixed with the ligand, H_2SBSaD (0.30 g; 1 mmol), in benzene (50 cm^3) and refluxed for 8 h. The water formed in the reaction was collected azeotropically. After the reaction, the benzene solution was concentrated

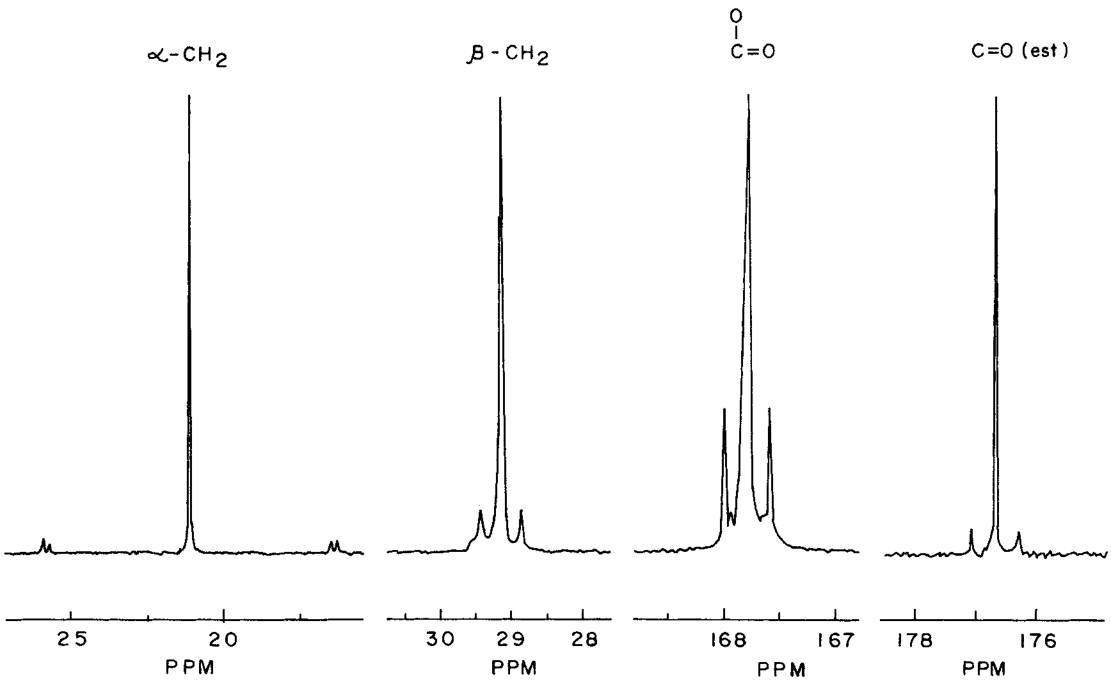

Figure 1 ^{13}C NMR spectra of $(CH_2CH_2CO_2CH_3)_2Sn(SBSaD)$ complex (**1**).

Table 4 ^{13}C NMR data (δ, ppm) for bis(β-carboalkoxyethyl)tin(IV) Schiff base complexes

Compd	α-CH_2	β′-CH_2	SCH_2—	OCH_3(est.)	═CH	C—O	C═S	C═O (est.)
H_2SBSaD^a	—	—	40.54	—	148.21	172.42	198.88	—
H_2SBVD^a	—	—	41.32	56.05	149.05	169.78	197.09	—
H_2SBND^a	—	—	46.19	—	128.59	173.95	210.73	—
$(CH_2CH_2CO_2CH_3)_2SnCl_2$	24.15	28.39	—	53.68	—	—	—	181.13
$(CH_3)_2Sn(SBSaD)$	—	—	36.00	—	165.84	167.50	173.17	—
1	21.07	29.12	36.09	52.07	165.05	167.78	172.73	176.65
4	21.03	28.98	36.13	52.04	165.04	158.50	172.58	176.74
7	20.32	29.13	36.28	52.11	160.00	170.33	170.06	176.65

[a] Recorded in solid state. **4–8** in $CDCl_3$ solution.

[b] CH_3 in $(CH_3)_2Sn(SBSaD) = 6.27$ ppm.

[c] OCH_3 in $(CH_2CH_2CO_2CH_3)_2Sn(SBVD) = 55.97$ ppm.

to a small volume and cooled overnight at 10 °C to produce a yellow crystalline solid, which was separated, washed with n-hexane and dried *in vacuo* [yield 0.40 g (71 %)].

RESULTS AND DISCUSSION

A few bis-β-carboalkoxyethyltin Schiff base complexes have been prepared by refluxing $(CH_2CH_2CO_2R)_2SnCl_2$ with the stoichiometric amounts of bifunctional Schiff bases in chloroform medium using aqueous ammonia as hydrochloric acid acceptor.

The Schiff base complexes are oils at room temperature, melting at ~−20 °C. They were characterized by elemental analysis and spectroscopic data. The complex $(CH_3)_2Sn(SBSaD)$ was prepared by azeotropic dehydration of a mixture of dimethyltin oxide and H_2SBSaD in benzene.

The infrared spectra of bis-β-carboalkoxyethyltin dichlorides exhibit intramolecularly coordinated carbonyl bands in the region 1660–1680 cm^{-1}. In the spectra of diestertin Schiff base complexes (Table 2), two strong bands are observed at ~1700 and 1730 cm^{-1} due to ν(C═O), which suggests coordinated and free ester groupings in the complexes. The ν(C—OR) frequency, found at ~1220 cm^{-1} in the estertin,[2] is observed as a split band in the complexes, one at ~1260 cm^{-1} and other at ~1205 cm^{-1}. The low-frequency shift could be due to the non-involvement of one of the ester groups in coordination to tin to give a —C═O→Sn band.

The IR spectra of the Schiff base ligands in nujol mull show ν(NH) at ~3085 cm^{-1}. Intramolecularly hydrogen-bonded ν(OH) is discernible at ~3400 cm^{-1} in dilute chloroform solutions. The ν(C═N) frequency is observed at ~1600 cm^{-1} and ν(C═S) at ~1030 cm^{-1}. The shift of ν(C═N) band to ~1585 cm^{-1} in the complexes suggests coordination of the lone pair on nitrogen to tin. The phenolic ν(C—O) of the ligands observed at ~1240 cm^{-1} has been shifted to higher wave numbers ~1310 cm^{-1} due to increased C—O bond order as a result of proton replacement with tin.[14] The absence of NH and lowering of C═S bands suggest thioenolization followed by complex formation. The ν(Sn—C) is observed at ~560 cm^{-1} in all the complexes. Hence the Schiff bases act as dianionic tridentate ligands.

Table 5 ^{119}Sn NMR data and coupling constants for bis(β-carboethoxyethyl)tin(IV) Schiff base complexes

Compd	^{119}Sn(δ, ppm)	$^1J(^{119}Sn,^{13}C)$ (Hz)	$^1J(^{117}Sn,^{13}C)$ (Hz)	$^2J(^{119}Sn,^{13}C)$ (Hz)	$^2J(^{117}Sn,^{13}C)$ (Hz)	$^3J(^{119}Sn,^{13}C)$ (Hz)	θ, C–Sn–C (deg)
$(CH_2CH_2CO_2CH_3)_2SnCl_2$	−66.40	—	—	—	—	—	—
$(CH_3)_2Sn(SBSaD)$	−110.94	596.39	571.09	—	30.31	—	129.07
1	−181.74	723.82	692.80	42.14	30.58	59.46	140.25
4	−182.70	731.53	699.50	41.77	28.29	52.95	140.92
7	−183.00	720.73	689.03	42.00	27.88	51.11	139.98

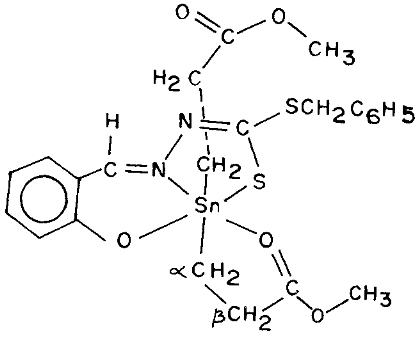

Figure 2 Structure of $(CH_2CH_2CO_2CH_3)_2Sn(SBSaD)$ complex (**1**).

^1H NMR spectra of bis-β-carboalkoxyethytin dichlorides show two triplets centred at ~1.89 and ~2.90 ppm due to α-CH_2 and β-CH_2 respectively. These resonances are shifted to higher field and are seen at ~1.7 and ~2.7 ppm in the complexes (Table 3). The shielding may be attributed to the replacement of electronegative chlorine atoms by the donor atoms oxygen, nitrogen and sulphur of the ligand. Similar shielding has been observed in the case of estertin oxinate complexes as reported by Deb and Ghosh.[6] Marginal shielding is observed for the OCH_3/OCH_2 protons of the ester groupings. Furthermore, the presence of only one singlet due to —OCH_3 protons suggests magnetic equivalence of both the ester groupings in which one coordinates to metal at one time while the other remains free, presumably involving a rapid exchange of the carbonyl groups. The complex $(CH_3)_2Sn(SBSaD)$ shows a singlet at 0.93 ppm due to methyl resonances with two satellite signals having the coupling constants $^2J(^{119}Sn, {}^1H)$ 69 and $^2J(^{117}Sn, {}^1H)$ 72 Hz.

The Schiff bases display signals at ~4.55, ~8.50, ~10.50 and ~12.00 ppm assignable to SCH_2—, =CH (aldehydic), NH and OH protons respectively. In the complexes both NH and OH proton resonances are absent. The aldehydic proton becomes deshielded in the complexes as expected, whereas benzyl SCH_2— signal shifts to higher magnetic field.

High-resolution ^{13}C NMR spectra of the estertin complexes (Fig. 1, Table 4) show sharp signals due to α-CH_2, β-CH_2 and —C=O (ester) resonances along with well separated ^{119}Sn satellite signals. An upfield shift has been observed for the α-CH_2 and alkoxy carbon resonances in the complexes compared with those of $(CH_2CH_2CO_2CH_3)_2SnCl_2$, which suggests breaking or weakening of intramolecular ester coordination to tin. The ester carbonyl carbon suffers a high-field shift of 5 ppm, indicating increased electron density, and the appearance of a single signal at ~176 ppm also may suggest fast exchange of metal-bonded and non-bonded carbonyl groups leading to magnetic equivalence of the ester groupings.[15]

Because of the limited solubility, ^{13}C NMR spectra of the free Schiff bases are taken in the solid state. The spectra show resonances due to C=S, =CH(aldehydic), phenolic C—O and SCH_2— at ~198, ~148, ~159 and ~40.5 ppm respectively. In the complexes, large shielding has been observed for the thioketo carbon, which indicates thiolate ion formation. The azomethine and phenolic carbons are deshielded due to coordination of these groups to tin.

Tin–carbon coupling has been observed for α—CH_2, β—CH_2, ester C=O and phenolic C—O groups [Fig. 1]. The coupling constants $^1J(^{119}Sn,{}^{13}C)$ (Table 5) are in the range 720–730 Hz. This coupling constant, ^1J, is directly linked to the values of C–Sn–C bond angle (θ) according to Eqn [1].[14]

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

Table 6 UV spectral data for Schiff base ligands and their bis(β-carboalkoxyethyl)tin(IV) complexes

Schiff base/compound	λ_{max} (nm) (ε_{max})
H_2SBSaD	280(18600), 306(19200), 318(36000), 348(28600)
1	298(8000), 342(7600), 416(6600)
H_2SBVD	237(15780), 338(31100)
4	245(11020), 348(10060), 431(5580)
5	245(11820), 307(8430), 345(11410), 431(6080)
6	243(11400), 344(12660), 424(5120)
H_2SBND	268(14400), 336(14600), 382(22000), 400(19800)
7	334(10440), 348(1992), 444(16271)

The values of θ calculated for the above complexes are between 140 and 141 °. The corresponding values calculated for the complex $(CH_3)_2Sn(SBSaD)$ having a coupling constant of $^1J(^{119}Sn,^{13}C)$ 596 Hz is 129 °. The well-characterized octahedral complex $Me_2Sn(koj)$[16] (koj = kojate ion = 5-oxy-2-(hydroxymethyl)-4H pyran-4-one) with *trans* methyl groups has a θ values of 142°. The $^2J(^{119}Sn,^{13}C)$ for β-CH_2 grouping is ~42 Hz. The tin satellite signals observed for phenolic C—O and ester carbonyl carbons may be attributed to tin–carbon coupling through the oxygen atom and the values are ~30 and ~53 Hz respectively.

It is to be noted that tin chemical shift $\delta(^{119}Sn)$ values reflect the nature of donor atoms to which tin is bonded. The $\delta(^{119}Sn)$ observed for $(CH_2CH_2CO_2CH_3)_2SnCl_2$ is at −66.4 ppm (Table 5). The tin atom in the complex $(CH_3)_2Sn(SBSaD)$ resonates at −111 ppm which suggests the metal atom to be in a pentacoordinated environment as reported in the literature.[17] The increased shielding is attributed to the presence of nitrogen, oxygen and sulphur donors in place of electron-withdrawing chlorine atoms. The ^{119}Sn chemical shift values of diestertin Schiff base complexes fall in the range 182–183 ppm. The cause of increased shielding has been related to a higher coordination number at tin. All these spectral data are consistent with a distorted octahedral geometry for the complexes with *trans* ester groupings. The structure of the complex $(CH_2CH_2CO_2CH_3)_2Sn(SBSaD)$ is shown in Fig. 2.

Electronic spectra

The electronic spectra of the Schiff bases and their estertin complexes have been studied in chloroform solution (Table 6). The spectra of the Schiff bases show high-intensity bands between 300 and 380 nm. In the higher-wavelength region the ligands H_2SBSaD, H_2SBVD and H_2SBND show absorption maxima at 348, 338 and 400 nm respectively. In the complexes these bands undergo a blue shift with reduced intensities as a result of chelate formation. An additional band with medium intensity has been observed between 416 and 444 nm in the complexes which may be attributed to the ligand-to-metal charge transfer band and this is a clear indication of stable complex formation.

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