

Organotin(IV) Complexes of Aniline Derivatives Part-II*- Synthesis and Spectroscopic Characterization of Organotin(IV) Derivatives of 2-[(4-Bromoanilino)carboxyl]benzoic Acid

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A series of organotin(IV) complexes with the general formula R_2SnL_2 and R_3SnL , where $R = CH_3$, C_2H_5 , $n-C_4H_9$, C_6H_5 , $C_6H_5CH_2$ and $L = 2-[(4-bromoanilino)carboxyl]benzoate$, were synthesized and characterized by infrared, mass and multinuclear NMR (1H , ^{13}C , ^{119}Sn) spectroscopies. The coordination around tin in solid as well as in solution has been proposed on the basis of spectroscopic results.

Introduction

In the past three decades the chemistry of tin compounds has gained considerable importance, both in basic research and in industrial applications. There are many interesting aspects of inorganic and organic tin chemistry discussed in various reviews². Organotin compounds have gained an edge over other organometallics due to their bioavailability in the ecosystem and entrance into the food chain, the fact they are less harmful to the environment and their pharmaceutical applications, including antitumour and anticancer uses. For these reasons, tin and its derivatives are in commercial use more than any other element³.

In the present work, organotin derivatives of the type R_2SnL_2 ($R = Me$ (1), Et (2), Bu (3), Ph (4), Bz (5)) and R_3SnL ($R = Me$ (6), Bu (7), Ph (8), Bz (9)) whereas $L = 2-[(4-bromoanilino)carboxyl]benzoic$ acid, have been synthesized and characterized by infrared, mass and multinuclear NMR (1H , ^{13}C , ^{119}Sn) spectroscopies.

Experimental

Organotin compounds are moisture and air sensitive, so the reactions were carried out under inert atmosphere. All the di- and triorganotin compounds except benzyl were procured from Aldrich Chemicals or

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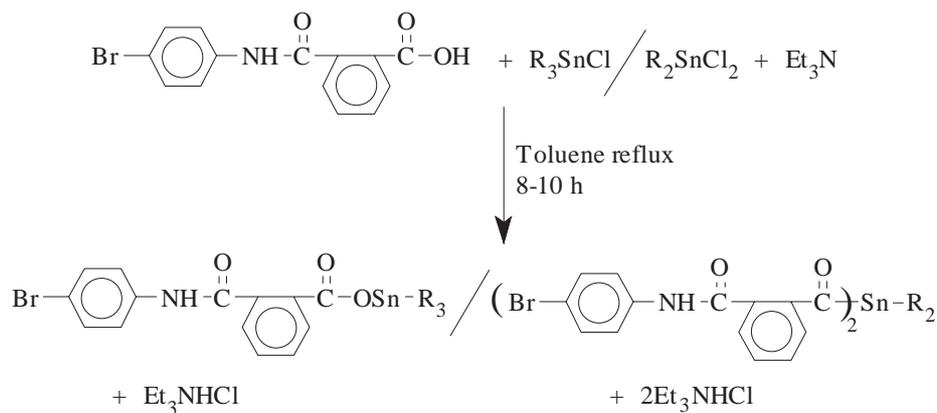
Fluka, while di- and tribenzyltin compounds were prepared by the reported methods⁴. All the solvents were dried before use by the methods in the literature⁵.

Melting points were determined in capillary tubes using a MP-D Mitamura Riken Kogyo (Japan) electrothermal melting point apparatus and are uncorrected. Infrared absorption spectra were recorded as KBr (4000-600 cm^{-1}) or CsI (600-250 cm^{-1}) pellets on a Perkin Elmer Spectrum 1000 FT-IR spectrometer. ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AM 250 spectrometer (Germany), using CDCl_3 as an internal reference [$\delta^1\text{H}(\text{CDCl}_3) = 7.25$ and $\delta^{13}\text{C}(\text{CDCl}_3) = 77.0$]. ^{119}Sn NMR spectra were obtained with Me_4Sn as external reference [$\Xi(\text{Sn}) = 37.290665$]. Mass spectral data were measured on a MAT 8500 Finnigan 70 eV mass spectrometer (Germany).

General Procedure for Synthesis

A solution of phthalic anhydride (10 g, 0.0675 mol) in HOAc (300 ml) was added to a solution of *p*-bromoaniline (11.60 g, 0.0675 mol) in HOAc (150 ml) and the mixture was stirred at room temperature overnight. The light grey precipitates were filtered, washed with cold distilled H_2O (200 ml) and air dried. 2-[(4-Bromoanilino)carboxyl]benzoic acid (1 g, 0.00313 mol) was suspended in dry toluene (100 ml) and treated with Et_3N (0.115 ml, 0.00313 mol). The mixture was refluxed for 2-3 h. To a solution of triethylammonium 2-[(4-Bromoanilino)carboxyl]benzoate, diorganotin dichloride (0.00156 mol) or triorganotin chloride (0.00313 mol) was added as solid with constant stirring and was refluxed for 8-10 h. The Et_3NHCl which formed was filtered off and the solvent was removed through rotary apparatus. The mass left behind was recrystallized from chloroform and *n*-hexane (1:1).

General Equation:



Results and Discussion

All the compounds are quite stable with good yield (70-80%) and are soluble in most organic solvents. The physical data for the investigated compounds are reported in Table 1.

Table 1. Physical Data for R₂SnL₂ and R₃SnL.

Comp.	General Formula	Empirical Formula F. Wt.	M.p. °C % yield	% C Calc.(Exp.)	% H Calc.(Exp.)
(1)	Me ₂ SnL ₂	C ₃₀ H ₂₄ N ₂ O ₆ Br ₂ Sn 787	– 82	54.74 (54.6)	3.05 (3.2)
(2)	Et ₂ SnL ₂	C ₃₂ H ₂₈ N ₂ O ₆ Br ₂ Sn 815	192 77	47.12 (47.32)	3.44 (3.38)
(3)	Bu ₂ SnL ₂	C ₃₆ H ₃₆ N ₂ O ₆ Br ₂ Sn 871	165-7 80	49.6 (49.55)	4.13 (4.21)
(4)	Ph ₂ SnL ₂	C ₄₀ H ₂₈ N ₂ O ₆ Br ₂ Sn 911	– 45	52.69 (52.81)	3.07 (2.99)
(5)	Bz ₂ SnL ₂	C ₄₂ H ₃₂ N ₂ O ₆ Br ₂ Sn 939	174-6 65	53.67 (53.43)	3.41 (3.5)
(6)	Me ₃ SnL	C ₁₇ H ₁₈ NO ₃ BrSn 483	185 75	42.24 (42.32)	3.73 (3.8)
(7)	Bu ₃ SnL	C ₂₆ H ₃₆ NO ₃ BrSn 609	– 89	51.23 (51.09)	5.91 (6.01)
(8)	Ph ₃ SnL	C ₃₂ H ₂₄ NO ₃ BrSn 669	143-5 58	57.4 (57.36)	3.59 (3.66)
(9)	Bz ₃ SnL	C ₃₅ H ₃₀ NO ₃ BrSn 711	120-2 70	59.07 (58.95)	4.22 (4.36)

Infrared spectra were recorded in the range of 4000-250 cm⁻¹ and important bands for structural assignments are given in Table 2. The characteristic vibrational frequencies have been identified by comparing the spectra of the complexes with their precursors. The complexation of the tin(IV) with the ligand is confirmed by the presence of Sn–O and Sn–C bands in the range of 420-490 cm⁻¹ 500-539 cm⁻¹, respectively^{6,7}.

Table 2. IR Spectral Data (cm⁻¹) for R₂SnL₂ and R₃SnL.

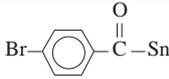
Comp.	ν NH	ν (COO) _{asym}	ν (COO) _{sym}	$\Delta\nu$	ν C = O	ν Sn–C	ν Sn–O
L	3342	1635	1364	271	1714	–	–
(1) Me ₂	3324	1590	1402	188	1720	515	460
(2) Et ₂	3335	1580	1390	190	1711	510	435
(3) Bu ₂	3320	1590	1398	192	1717	500	420
(4) Ph ₂	3310	1575	1391	184	1714	505	428
(5) Bz ₂	3350	1580	1391	189	1740	533	480
(6) Me ₃	3358	1590	1385	205	1710	520	490
(7) Bu ₃	3365	1579	1379	200	1735	529	469
(8) Ph ₃	3339	1585	1383	202	1749	539	475
(9) Bz ₃	3314	1570	1369	201	1729	525	445

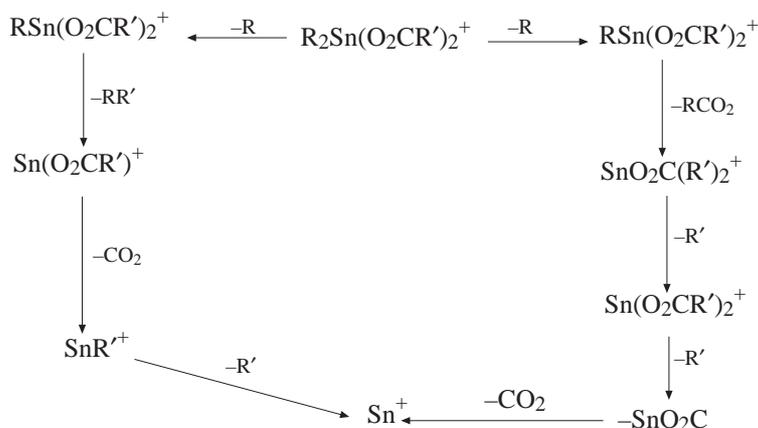
Based on the difference, $\Delta\nu$, between $\nu(\text{COO})_{\text{sym}}$ and $\nu(\text{COO})_{\text{asym}}$ and the corresponding band position, it is proposed that the carboxylate group acts as a bidentate in all these complexes⁸. According to Lebl et al.,⁹ the values of $\Delta\nu$ [$\Delta\nu = \nu_{\text{asym.}}(\text{COO}) - \nu_{\text{sym.}}(\text{COO})$] can be divided into three groups; (a) In compounds where $\Delta\nu(\text{COO}) > 350$, hence these compounds contain, with high probability, the monodentate carboxylate group. However, other very weak intra- and intermolecular interactions cannot be excluded. (b) When $\Delta\nu(\text{COO}) < 200$, the carboxylate groups of these compounds can be considered to be practically bidentate. (c) Compounds where $\Delta\nu(\text{COO}) < 350$ and > 200 are considered as an intermediate state

between monodentate and bidentate, which is called anisobidentate. It has also been suggested that the $\Delta\nu(\text{COO})$ value in chelating mode is less than $\Delta\nu(\text{COO})$ in bridging¹⁰. Some characteristic vibrational frequencies of different groups fall within the range $\nu(\text{C}=\text{O})$ 1710-1749 cm^{-1} and $\nu(\text{N}-\text{H})$ 3310-3365 cm^{-1} .

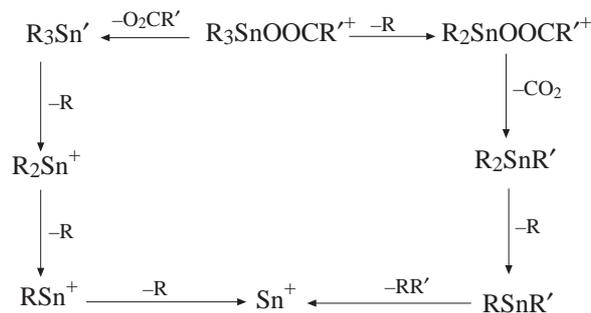
The 70 eV mass spectra for the investigated compounds are recorded for all di- and triorganotin(IV) derivatives, and their general fragmentation patterns are given in Schemes 1 and 2. The molecular ion peaks of very low intensity are observed in almost all complexes¹¹. In di- and triorganotin(IV) derivatives a rather similar pattern of fragmentation is observed. In both cases primary fragmentation is due to the successive loss of R groups followed by the elimination of CO_2 from the ligand and then the remaining part of the ligand which leaves Sn^+ or SnH^+ as an end product. The second route of fragmentation is the loss of CO_2 in the first step followed by R groups and then the elimination of the remaining part of the ligand with Sn^+ or SnH^+ as a residue. Some common and other peaks (with m/z and % abundance) which were observed in di- and triorganotin(IV) derivatives are reported in Table 3.

Table 3. Mass Spectral Data for R_2SnL_2 and R_3SnL .

Fragment Ion	(1) Me ₂	(2) Et ₂	(3) Bu ₂	(4) Ph ₂	(5) Bz ₂	(6) Me ₃	(7) Bu ₃	(8) Ph ₃	(9) Bz ₃
$\text{R}_3\text{SnOOCR}'$	-	-	-	-	-	484 (15)	610 (10)	670 (22)	712 (11)
$\text{R}_2\text{Sn}(\text{OOCR}')_2$	789 (16)	815 (11)	873 (13)	907 (22)	937 (18)	-	-	-	-
$\text{RSn}(\text{OOCR}')_2$	773 (30)	787 (25)	815 (32)	835 (41)	849 (36)	-	-	-	-
$\text{Sn}(\text{OOCR}')_2$	758 (15)	758 (15)	758 (30)	758 (19)	758 (13)	-	-	-	-
$\text{R}_2\text{SnR}'$	425 (n.o.)	453 (10)	509 (21)	549 (n.o.)	577 (8)	425 (11)	509 (15)	549 (9)	577 (18)
RSnR'	410 (6)	424 (13)	452 (7)	472 (21)	486 (n.o.)	410 (n.o.)	452 (15)	472 (12)	486 (6)
$\text{R}_2\text{SnOOCR}'$	469 (9)	497 (16)	553 (19)	593 (n.o.)	621 (11)	469 (n.o.)	553 (9)	593 (11)	621 (17)
$\text{RSnOOCR}'$	454 (21)	468 (2)	496 (10)	516 (26)	530 (17)	454 (n.o.)	496 (18)	516 (25)	530 (n.o.)
SnR'	395 (7)	395 (9)	395 (12)	395 (22)	395 (14)	395 (17)	395 (27)	395 (20)	395 (9)
OCOR'	318 (32)	318 (37)	318 (22)	318 (40)	318 (36)	318 (42)	318 (38)	318 (11)	318 (29)
R_3Sn^+	-	-	-	-	-	164 (4)	290 (11)	347 (n.o.)	392 (1)
R_2Sn^+	194 (n.o.)	178 (23)	233 (12)	271 (1)	301 (1)	149 (n.o.)	233 (18)	277 (2)	301 (97)
RSn^+	135 (12)	149 (n.o.)	177 (21)	197 (32)	211 (5)	135 (26)	177 (26)	197 (12)	211 (n.o.)
Br^+	80 (15)	80 (4)	80 (13)	80 (n.o.)	80 (2)	80 (n.o.)	80 (50)	80 (26)	80 (11)
	76 (45)	76 (57)	76 (15)	76 (18)	76 (10)	76 (38)	76 (44)	76 (12)	76 (24)
Sn^+	120 (12)	120 (10)	120 (11)	120 (2)	120 (4)	120 (n.o.)	120 (15)	120 (80)	120 (26)
C_4H_9^+	57 (n.o.)	57 (3)	57 (100)	57 (7)	57 (11)	57 (n.o.)	57 (100)	57 (3)	57 (8)
	91 (2)	91 (5)	91 (18)	91 (n.o.)	91 (100)	91 (n.o.)	91 (13)	91 (4)	91 (2)
	301 (100)	301 (100)	301 (2)	303 (100)	301 (12)	301 (100)	301 (95)	301 (18)	301 (100)
Ph_2H^+	154 (5)	154 (6)	154 (8)	154 (4)	154 (3)	154 (2)	154 (19)	154 (100)	154 (3)

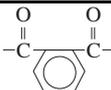


Scheme 1. Fragmentation Pattern for Diorganotin Carboxylates.

**Scheme 2.** Fragmentation Pattern for Triorganotin Carboxylates.

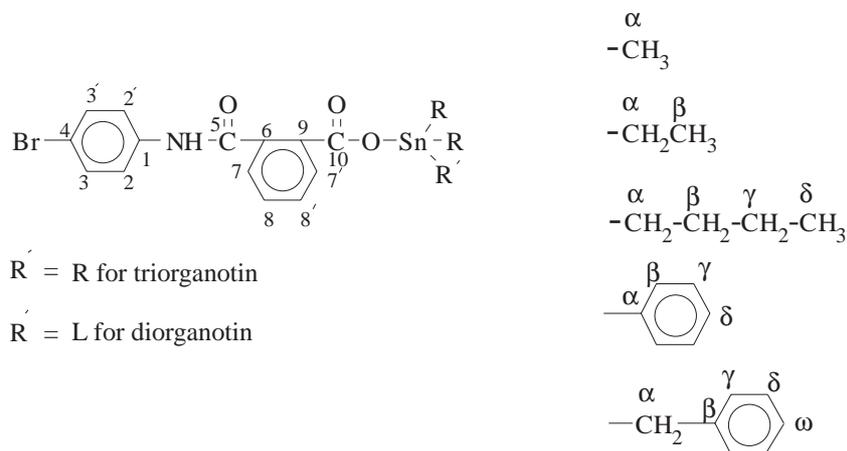
1H NMR for the investigated compounds are reported in Table 4. Different protons were assigned on the basis of their multiplicity and intensity patterns. Aromatic protons of the bromophenyl group and the benzoate group were assigned with difficulty due to the narrow range on the NMR scale. Alkyl groups bonded to tin were assigned in their characteristic range. The $^2J(^{119}Sn, ^1H)$ for di- and trimethyltin(IV) derivatives have approximately the same value, confirming the tetrahedral environment in solution, i.e., carboxylate groups act as monodentate in solution.

Table 4. 1H NMR Data for R_2SnL_2 and R_3SnL .

Comp.	Br-C ₆ H ₄	-NH		R
L	7.57-7.63 m	6.85 s	7.86-8.20 m	-
(1) Me ₂	7.44-7.46 m	6.84 s	7.81-8.08 m	1.2 s (80)
(2) Et ₂	7.21-7.49 m	6.84 s	7.77-7.96 m	1.2 t, 2.1 q
(3) Bu ₂	7.25-7.35 m	6.23 s	7.85-8.51 m	0.88-0.96 t (7.3), 1.36-1.44 m, 1.74-1.89 m
(4) Ph ₂	7.45-7.50 m	6.82 s	7.77-7.92 m	7.32-7.35 m
(5) Bz ₂	7.59-7.62 m	6.84 s	7.77-7.94 m	1.23 s, 7.31-7.35 m
(6) Me ₃	7.35-7.45 m	6.83 s	7.52-8.05 m	0.51 s (58)
(7) Bu ₃	7.33-7.36 m	6.82 s	7.49-7.87 m	0.88-0.94 t (6.9), 1.09-1.2 m, 1.35-1.45 m
(8) Ph ₃	7.63-7.67 m	6.81 s	7.85-8.20 m	7.61-7.64 m
(9) Bz ₃	7.45-7.70 m	6.82 s	7.91-7.96 m	2.1 s, 7.75-7.78 m

^{13}C NMR data are listed in Table 5. The involvement of the carboxylate group in bonding to Sn is confirmed by the resonance ascribed to C(10), which exhibits a shift after coordination. The remaining carbons do not shift significantly after complexation.

The ^{119}Sn chemical shift of organotin compounds covers a range of δ 600. As the electron releasing power of the alkyl group bonded to tin increases, the tin atom becomes progressively more shielded and the δ (^{119}Sn) value moves to a higher field¹². It was reported earlier that the value of δ (^{119}Sn) is directly linked to the coordination number of the central tin atom¹³. According to the data reported in Table 5, all organotin(IV) compounds show a tetrahedral environment around the tin atom in solution.

Table 5. ^{13}C and ^{119}Sn NMR Data for R_2SnL_2 and R_3SnL .

Carbon No.	L	(1) Me ₂	(2) Et ₂	(3) Bu ₂	(4) Ph ₂	(5) Bz ₂	(6) Me ₃	(7) Bu ₃	(8) Ph ₃	(9) Bz ₃
1	134.4	134.3	134.1	134.6	134.8	134.5	134.8	134.9	134.8	134.5
2,2'	132.2	132.1	132.2	132.1	132.5	132.2	132.5	132.1	132.5	132.1
3,3'	134.0	134.9	134.5	134.5	136.3	134.0	134.7	136.6	136.4	136.0
4	127.8	128.5	127.9	127.9	128.1	127.9	128.9	128.5	128.2	128.1
5	166.8	167.2	166.9	166.8	166.1	166.8	169.3	167.2	167.0	166.8
6	131.9	132.5	131.5	131.4	131.8	131.5	131.7	131.8	131.8	131.4
7,7'	116.6	114.2	115.9	114.3	116.9	116.3	115.2	116.3	117.0	114.6
8,8'	121.7	122.1	121.8	121.7	122.0	121.7	122.09	121.1	122.1	121.7
9	130.6	131.8	130.7	130.6	130.9	130.6	130.2	130.8	130.7	130.6
10	180.4	174.9	173.0	171.6	172.6	172.0	172.2	172.5	171.6	174.0
α	—	30.01	29.6	29.5	132.2	29.6	-1.3	30.01	137.5	29.6
β	—	—	13.2	26.4	130.7	132.7	—	27.0	136.4 [48.8]	134.3
γ	—	—	—	26.3	129.4	129.9	—	26.5	130.6 [13.8]	128.3
δ	—	—	—	13.4	124.1	128.5	—	13.6	129.4 [63]	126.8
ω	—	—	—	—	—	126.9	—	—	—	123.7
$\delta^{119}\text{Sn}$	—	-154.0	-155.6	-138.2	-46.0	—	195.0	106.2	—	-45.4

Conclusion

It was concluded that in solid state the carboxylate group acts as a bidentate, having five or six coordinations around tin, while in solution the bidentate carboxylate group is cleaved and the resulting monomer contains four coordinated tins with a distorted tetrahedral arrangement. All the complexes show primary fragmentation due to the successive loss of the alkyl group followed by elimination of CO_2 and the remaining part of the ligand, which leaves Sn^+ as the end product.

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