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SYNTHESIS AND SPECTRAL STUDIES OF DI- AND TRIORGANOTIN(IV) COMPLEXES WITH 2-(6-METHOXYNAPHTHYL)PROPIONIC ACID (NAPROXEN)

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ABSTRACT

Complexes of the composition $R_{4-n}SnL_n$ (R = Me, Et, Bu, Ph, Bz, n = 1 and 2, and L = 2-(6-methoxynaphthyl)propionic acid anion have been synthesized by the reaction of tri- and diorganotin halides with the silver salt of 2-(6-methoxynaphthyl)propionic acid in dry chloroform. Conductance data show that the complexes are non-electrolytes. Structural assignments were made on the basis of spectral studies (FTIR, ¹H, ¹³C, ¹¹⁹Sn NMR, mass and UV-Vis spectroscopy).

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INTRODUCTION

Organotin compounds show a large spectrum of biological activity but mainly are used commercially as industrial and agricultural biocides because of their antifungal properties¹. Some organotins are currently being investigated for antitumour activity². Some R³SnL derivatives (L = monodentate or bidentate ligand) are highly toxic³⁻⁸, while diorganotin(IV) derivatives like diethyltin(IV) and dibutyltin(IV) carboxylates are known anti-tumor agents^{9–12}. In various studies it has been suggested that ligand replacement changes the toxicity of the organotin moiety³⁻⁸, because it has been assumed that, eventually, coordinated organic ligands would facilitate the transport of the potentially active R₂Sn²⁺ moiety to the site of action, where it is released by hydrolysis. If the compound is hydrolytically unstable, the R₂Sn²⁺ species is released too early and reacts at unsuitable sites; if it is too stable, it may be released too late or very slowly for the activity to be effective¹³.

In order to explore their biological activity, we have prepared a series of organotin carboxylates of 2-(6-methoxynaphthyl)propionic acid commonly known as Naproxen, one of the most frequently used analgesic, antipyretic and anti-inflammatory drugs^{14–16}. In the accessible literature, no organotin(IV) derivatives have been synthesized so far.

In this paper we report the synthesis and spectral properties of tri- and diorganotin derivatives of Naproxen (Fig. 1)

RESULTS AND DISCUSSION

Complexes of di- and triorganotin chlorides with 2-(6-methoxynaphthyl)propionic acid (Naproxen) have been synthesized by mixing dry chloroform solutions of the respective organotin compound and the silver



Figure 1. Numbering scheme and structure of 2-(6-methoxynaphthyl)propionic acid (naproxen).

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salt of the ligand in 1:1 and 1:2 molar ratios. The preparation of the complexes may be represented by the following general equations.

$$\begin{aligned} R_3 SnCl + AgL &\longrightarrow R_3 SnL + AgCl \\ [R = Bu \ (\textbf{2}), Me \ (\textbf{4}), Ph \ (\textbf{7}), Bz \ (\textbf{9})] \end{aligned}$$

$$R_2SnCl_2 + AgL \longrightarrow R_2SnL_2 + 2AgCl$$

[R = Bu (1), Me (3), Et (5), Ph (6), Bz (8)]

All the newly synthesized complexes are quite stable to air and are creamy white, crystalline solids, which are mostly soluble in common organic solvents. The complexes were sufficiently soluble in absolute ethanol to enable their molar conductivity measurements. The molar conductivity of 10^{-3} M solutions of the complexes is in the range of 2–15 µS/cm², which indicates their non-electrolytic nature¹⁷ (Table I).

Electronic Spectra

The electronic spectra for the ligand and its complexes were recorded in absolute ethanol. The bands are derived from interligand and charge transfer or $(n \rightarrow \pi^*)$ transitions. The UV spectra of the complexes are similar to that of the ligand and show very little or no shifts in the positions of the absorption maxima. The bands near 285 and 270 nm are assigned to interligand $(\pi \rightarrow \pi^*)$ transitions for the aromatic moiety of the ligand¹⁸. Further, a few sharp absorption bands were observed in the region 240–270 nm in the spectra of the complexes which could be assigned as charge transfer $(L \rightarrow M)^{19}$ or $(n \rightarrow \pi^*)$ transition²⁰.

Infrared Spectra

Infrared spectra of the di- and triorganotin(IV) derivatives of 2-(6-methoxynaphthyl)propionic acid have been recorded in the range of $4000-250 \text{ cm}^{-1}$ as KBr disc and important bands are given in Table II.

The broad band in the range of $3189-3140 \text{ cm}^{-1}$ due to v(OH) present in the acid ligand is absent in the spectra of its silver salt and the corresponding di- and triorganotin(IV) derivatives.

In case of diorganotin carboxylates, the most important bands observed for $v(COO)_{asvm}$ and $v(COO)_{svm}$ occur at 1580–1630 cm⁻¹ and

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Comp. No.	Compounds	Empirical Formula (F. W)	Yield (%)	M. p. (°C)	(%)C Calc. (Found)	(%)H Calc. (Found)	Conductance μS/cm ²
(1)	Bu_2SnL_2	$C_{36}H_{44}O_6Sn$ (692)	95.0	95—98	62.5 (62.85)	6.36 (6.62)	11.2
(2)	Bu ₃ SnL	$C_{26}H_{40}O_3Sn$ (520)	71.3	I	60.12 (59.98)	7.71 (7.72)	10.2
(3)	Me_2SnL_2	$C_{30}H_{32}O_6Sn$ (607)	65.0	165—67	59.29 (59.35)	5.27 (5.16)	12.7
(4)	Me ₃ SnL	$C_{17}H_{22}O_{3}Sn$ (394)	51.0	132—34	51.92 (52.2)	5.59 (5.48)	13.7
(5)	Et_2SnL_2	$C_{32}H_{36}O_{6}Sn$ (363)	36.0	123–25	60.45 (59.89)	5.67 (5.58)	4.7
(9)	Ph_2SnL_2	$\mathrm{C_{40}H_{36}O_6Sn}$ (732)	49.0	95—97	65.69 (65.78)	4.93 (4.72)	13.5
(1)	Ph_3SnL	$C_{32}\dot{H}_{28}\dot{O_{3}}Sn$ (580)	62.0	4648	66.36 (66.32)	4.84 (4.79)	6.7
(8)	Bz_2SnL_2	$C_{42}H_{40}O_6Sn$ (760)	64.0	15557	66.38 (66.72)	5.27 (5.38)	4.7
(6)	Bz ₃ SnL	$C_{35H_{34}O_3Sn}$ (622)	73.0	13840	67.64 (67.25)	5.47 (5.62)	7.7
L	Ligand	$C_{14}H_{13}O_{3}$ (230)	I	150-51	1	I	I

Table I. Physical Data for Organotin(IV) Derivatives of Nanroxen

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		v(C	00)			
No	Compounds	asym	sym	Δv	v(Sn-C)	v(Sn-O)
(1)	Bu_2SnL_2	1628 s	1380 s	248	545 s	474 s
(2)	Bu ₃ SnL	1610 s	1320 s	290	520 m	472 s
(3)	Me_2SnL_2	1602 s	1381 s	221	541 s	479 w
(4)	Me ₃ SnL	1593 s	1344 s	299	553 s	477 m
(5)	Et_2SnL_2	1596 s	1380 s	216	536 s	479 s
(6)	Ph_2SnL_2	1610 s	1413 s	197	510 s	477 s
(7)	Ph ₃ SnL	1628 s	1399 s	229	560 s	452 s
(8)	Bz_2SnL_2	1587 s	1389 s	198	536 m	475 s
(9)	Bz ₃ SnL	1628 s	1399 s	229	536 w	478 s
L	Ligand	1674 s	1453 s	220	_	_
L-Ag	Ligand-Ag	1665 s	1389 s	276	_	_

Table II. Infrared Data^a (cm⁻¹) for Organotin Derivatives of Naproxen

^as, strong; m, medium; w, weak.

1320–1420 cm⁻¹, respectively (Table II). The Δv value [$\Delta v = v(COO)_{asym} - v(COO)_{sym}$] has been utilized to identify the mode of carboxylate interaction. According to the earlier reports, if this value is comparable to that of the silver salt of the acid ligand, then the carboxylate ion behaves as a bidentate chelate group. It is, therefore, suggested that the carboxylate group in these compounds is acting as a bidentate ligand^{21–23} (Fig. 4). The bands in the range of 510–545 cm⁻¹ and 450–480 cm⁻¹ indicate the Sn-C and Sn-O bonds, respectively.

Multinuclear NMR Spectra

The ¹H NMR spectral data in CDCl_3 solution of the acid and complexes are listed in Tables III and IV. The absence of the COOH proton resonance in the compounds shows that organotin carboxylates have been formed. A complex multiplet due to the aromatic protons of the phenyl group (both in the ligand and phenyltin) is observed in the range of 7.13–7.73 ppm. The resonance assigned to butyltin protons fall in the region of 0.72–1.60 ppm.

The methyl protons of the di- and trimethyltin derivatives appear as sharp singlets with coupling satellites from tin. The coupling constant ${}^{2}J({}^{119}Sn{}^{-1}H)$ provides valuable information about hybridization^{24,25}. For four-coordinated methyltin(IV) compounds, ${}^{2}J({}^{119}Sn{}^{-1}H)$ values have been

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		Table III. ¹ H NMI	R Data ^{a,b,c} of Diorg	anotin Derivatives c	of Naproxen	
Comp.	L	(1)	(3)	(5)	(9)	(8)
'N No.	Naproxen	Bu_2SnL_2	Me_2SnL_2	Et_2SnL_2	$\mathrm{Ph}_2\mathrm{SnL}_2$	Bz_2SnL_2
7	3.92 (m)	3.95 (m)	3.92 (m)	3.98 (m)	3.97 (m)	3.70 (m)
Э	1.62 (d, 7.2)	1.62 (d, 7.2)	1.62 (d, 7.1)	1.62 (d, 7.1)	1.31 (d, 7.2)	1.44 (d, 6.9)
4	3.94 (s)	3.94 (s)	3.92 (s)	3.98 (s)	3.95 (s)	3.90 (s)
1′	7.17 (d, 2.5)	7.18 (d, 2.5)	7.2 (d, 2.5)	7.19 (d, 2.5)	7.15 (d, 2.3)	7.14 (d, 2.5)
3,	7.50 (dd, 8.4, 1.5)	7.47 (dd, 8.4, 1.5)	7.46 (dd, 8.4, 1.6)	7.49 (dd, 8.4, 1.7)	7.43 (dd, 8.4, 1.6)	7.41 (dd, 6.7, 1.4)
4	7.70 (d, 8.2)	7.73 (d, 8.2)	7.75 (d, 8.7)	7.74 (d, 8.2)	7.71 (d, 8.3)	7.71 (d, 8.6)
5'	7.15 (m)	7.13 (m)	7.15 (m)	7.15 (m)	7.14 (m)	7.15 (m)
7'	7.73 (d, 8.2)	7.73 (d, 8.2)	7.75 (d, 8.7)	7.74 (d, 8.2)	7.71 (d, 8.3)	7.71 (d, 8.6)
8′	7.73 (d, 8.2)	7.73 (d, 8.2)	7.75 (d, 8.7)	7.74 (d, 8.2)	7.71 (d, 8.3)	7.71 (d, 8.6)
ъ	I	0.95 (m)	1.0 (s)	1.45-1.55 (m)	I	2.95 (t, 4.9, 8.0)
β	Ι	1.20–1.50 (m)	I	1.21 (t, 7.9)	6.5–7.12 (m)	6.94-6.98 (m, Bz)
λ	I	1.20–1.50 (m)	Ι			-7.20-7.30 (m, Bz)
§	I	0.72 (m)	I	I	I	

^aChemical shift (δ) in ppm. ²J(¹¹⁹Sn-¹H) in Hz. Multiplicity is given by s, singlet; d, doublet; t, triplet and m, multiplet. ^bNumbering is according to Fig. 1.



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Compound	(2)	(4)	(L)	(6)
¹ H No.	Bu ₃ SnL	Me ₃ SnL	Ph_3SnL	Bz_3SnL
2	3.92 (m)	3.92 (m)	4.06 (m)	3.78 (m)
3	1.60 (d, 7.2)	1.58 (d, 7.1)	1.66 (d, 7.1)	1.45 (d, 6.9)
4	3.94 (s)	3.94 (s)	3.96 (s)	3.93 (s)
1'	7.17 (d, 2.6)	7.17 (d, 2.6)	7.17 (d, 2.5)	7.17 (d, 2.7)
3/	7.50 (dd, 8.3, 1.8)	7.49 (dd, 8.4, 1.9)	7.47 (dd, 8.4, 1.8)	7.40 (dd, 6.6, 1.4)
4'	7.73 (d, 8.3)	7.74 (d, 8.4)	7.72 (d, 8.7)	7.75 (m, 8.6)
5'	7.13 (m)	7.14 (m)	7.14 (m)	7.16 (m)
7'	7.73 (d, 8.3)	7.74 (d, 8.4)	7.72 (d, 8.7)	7.75 (d, 8.6)
8′	7.73 (d, 8.3)	7.74 (d, 8.4)	7.72 (d, 8.7)	7.75 (d, 8.6)
ø	(m) 00.0	0.54 ² $J[57.13]$	I	3.1 (s)
β	1.10–1.55 (m)	I	7.43–7.49 (m)	7.17–7.20 (m)
λ	1.10–1.55 (m)	Ι	7.69–7.74 (m)	7.21–7.24 (m)
8	0.88 (t, 7.2)	I	I	I

^bNumbering is according to Fig. 1. ^cSee footnotes of Table III for α , β , γ , δ , ϵ .

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reported, which increase as the coordination number of tin increases from four to five to six or seven depending upon the stereochemistry^{26–28}. For trimethyltin derivative ²J[¹¹⁹Sn-¹H] = 57.13 Hz falls in the range of tetrahedral environment²⁹, which is further supported by the C-Sn-C bond angle (111.0°) calculated using Lockhart's equation²⁹. In case of *n*-butyl, phenyl and benzyl derivatives the ⁿJ[¹¹⁹Sn-¹H] couplings are not visible due to a complex multiplet pattern.

¹³C NMR spectral data in CDCl₃ solutions of the acid ligand and of the compounds are given in the Tables V and VI. The number of signals found corresponds to the presence of expected magnetically nonequivalent carbon atoms. The position of the aromatic carbon signals remains unchanged in the complexes as compared to that of the ligand acid. The position of the carboxylate carbon in all of the complexes shifts to lower field as compared to the free acid indicating the participation of carboxylate group in coordination to tin(IV)³⁰. In the butyl complexes there are four types of magnetically non-equivalent carbons. The identification of alkyl/phenyl carbons in all the complexes along with ¹J values confirms the complexation.

Compound ¹³ C No.	L Naproxen	(1) Bu ₂ SnL ₂	(3) Me ₂ SnL ₂	(5) Et ₂ SnL ₂	(6) Ph ₂ SnL ₂	(8) Bz ₂ SnL ₂
1	181.0	n.o	185.20	185.49	183.46	184.71
2	45.5	45.8	45.58	45.72	48.41	38.36
3	18.6	19.17	19.26	19.31	18.67	18.91
4	55.80	55.80	55.77	55.76	55.72	55.69
1'	127.60	127.50	127.66	127.55	127.57	127.45
2'	119.5	119.29	119.43	119.36	118.99	119.31
3',8'	129.3	129.22	129.34	129.33	129.29	128.53
4′	106.0	105.93	105.98	105.97	105.95	105.99
4''	135.4	134.13	134.14	134.13	135.93	134.15
5',7'	126.5	126.64	126.50	126.59	126.68	126.59
6'	158.1	156.99	158.06	158.01	157.83	158.03
8''	134.2	136.18	135.93	136.13	135.93	135.97
α	_	24.15	14.53	18.09	143.75	32.27
β	_	26.89	_	9.25	137.69	124.37
γ	_	26.34	_	_	133.96	128.87
δ		13.81	_	_	129.76	126.33
3	_	_	_	_	_	125.79

Table V. ¹³C NMR Data^{a,b,c} of Diorganotin Derivatives of Naproxen

^aChemical shifts (δ) in ppm.

^bNumbering is according to Fig. 1.

^cSee footnotes of Table III for α , β , γ , δ , ϵ .

Compound ¹³ C No.	(2) Bu ₃ SnL	(4) Me ₃ SnL	(7) Ph ₃ SnL	(9) Bz ₃ SnL
1	180.37	180.55	181.48	n.o
2	46.67	46.51	46.04	42.52
3	19.67	19.91	19.86	18.90
4	55.72	55.74	55.71	55.56
1′	127.03	127.34	127.04	127.42
2'	119.03	119.14	119.16	119.45
3', 8'	129.37	129.38	129.30	129.04
4'	105.93	105.96	106.00	106.00
4''	133.89	133.89	133.99	129.74
5',7'	126.16	126.17	126.23	126.57
6'	157.76	157.83	157.93	158.00
8''	137.77	137.66	133.58	132.56
α	27.39	-1.94 [390]	137.23	32.78
β	27.91	_	138.73	129.29
γ	28.17	_	130.52	128.77
δ	14.05	_	128.79	126.32
3	_	_	_	125.65

Table VI. ¹³C NMR Data^{a,b,c} of Triorganotin(IV) Derivatives of Naproxen

^aChemical shifts (δ) in ppm. ¹J(¹¹⁹Sn-¹³C) in Hz in parentheses.

^bNumbering is according to Fig. 1.

^cSee footnotes of Table III for α , β , γ , δ , ϵ .

Compound No.	Compounds	¹¹⁹ Sn NMR
(1)	Bu_2SnL_2	-146.15
(2)	Bu ₃ SnL	111.137
(3)	Me_2SnL_2	n. p. ^a
(4)	Me ₃ SnL	135.449
(5)	Et_2SnL_2	-152.03
(6)	Ph_2SnL_2	-223.120
(7)	Ph_3SnL	-108.90
(8)	Bz_2SnL_2	-246.34
(9)	Bz ₃ SnL	33.929

Table VII. ¹¹⁹Sn NMR Data for Organotin(IV) Derivatives of Naproxen

^an. p. (not performed).

The chemical shifts δ^{119} Sn (Table VIII) for triorganotin carboxylates are comparable with shift earlier reports describing tetrahedral geometry^{31,32}. In diorganotin(IV) derivatives δ^{119} Sn chemical shifts reveal a coordination number greater than 5 for tin as reported earlier³⁰.

Mass Spectrometry

The mass fragmentation patterns of the diorganotin and triorganotin carboxylates are given in Figs. 2 and 3, respectively. A molecular ion peak of reasonable intensity was observed in almost all of the compounds except the phenyl derivatives. In the triorganotin derivatives primary fragmentation is due to the loss of an R group, while the secondary fragmentation occurs by the elimination of either R or $CO_2^{21,33}$. In case of the diorganotin derivatives, the primary fragmentation is mostly by the loss of one ligand and CO_2 is eliminated in a second step. If the primary fragmentation is due to the loss of an R group, then there is a successive elimination of two CO_2 molecules. There is another route for the fragmentation of diorganotin in which primary fragmentation occurs by the loss of a ligand molecule followed by the loss of two R groups. The base peak of the ligand molecule $[C_{13}H_{13}O]^+$ is observed in

Fragmentation (1) Int.(%) (3) Int.(%) (5) Int.(%) (6) Int.(%) (8) Int.(%) $[R_2SnC_{28}H_{26}O_6]^+$ n.o n.o $[R_2SnC_{14}H_{13}O_3]^+$ $[RSnC_{14}H_{13}O_3]^+$ [SnC14H13O3] $[SnC_{13}H_{13}O]^{-1}$ [C₁₃H₁₃O] $[C_{14}H_{13}O_3]^+$ [R]⁺ $[R_2SnC_{13}H_{13}O]^+$ [RSnC13H13O] n.o n.o $[Sn^+/SnH]^+$ n.o $[RSnC_{28}H_{26}O_6]$ $[R_2SnC_{27}H_{26}O_4]^+$ $[SnC_{28}H_{26}O_6]$ $[SnC_{27}H_{26}O_4]^{-1}$

Table VIII. Mass Fragmentation Pattern for Diorganotin(IV) Derivatives of Naproxen



R = n-Bu, Me, Et, Ph and Bz R'CO₂ = Naproxen (ligand)





R = n-Bu, Me, Ph and Bz R'CO₂ = Naproxen (ligand)

Figure 3. Fragmentation pattern of R₃SnL.



Figure 4. Proposed structures (a), (b), (c) for triorganotin (IV) carboxylates and (d), (e) for diorganotin (IV) carboxylates.

Table IX. Mass Fragmentation Pattern for Triorganotin(IV) Derivatives of Naproxen^a

Fragmentation	(2)	Int.(%)	(4)	Int.(%)	(7)	Int.(%)	(9)	Int.(%)
$[C_{14}H_{13}O_{3}SnR_{3}]^{+}$	520	20	394	5	580	n.o	622	10
$[C_{14}H_{13}O_3SnR_2]^+$	463	85	379	5	503	2	531	65
$[C_{14}H_{13}OSnR_2]^+$	419	5	335	4	459	_	487	1
$[C_{13}H_{13}OSn]^+$	305	8	305	2	305	16	305	8
$[R_3 Sn]^+$	291	16	165	8	351	85	393	2
$[R_2 Sn]^+$	234	18	150	8	274	10	302	5
$[R Sn]^+$	177	16	135	5	197	20	211	8
$[C_{13}H_{13}O]^+$	185	100	185	100	185	100	185	100
$[SnH^+/Sn]^+$	120	2	120	2	120	18	120	1
$[C_{14}H_{13}O_{3}]^{+}$	229	10	229	2	229	28	229	10
[R] ⁺	57	8	15	1	77	18	91	20
$[C_{13}H_{13}OSnR_3]^+$	476	2	350	5	536	12	578	48

an.o = not observed.

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almost all compounds. The peaks for $[R_3Sn]^+$ and $[R_2Sn]^+$ have either very low intensities or are absent, which indicates that fragmentation through these species is not favourable^{21,34}.

EXPERIMENTAL

All the di- and triorganotin halides except benzyl derivatives, were procured from Aldrich or Fluka while the di- and tribenzyltin chlorides were prepared by the reported method³⁵. All the solvents were dried before use³⁶.

General Procedure for the Synthesis

To a suspension of the silver salt of 2-(6-methoxynaphthyl)propionic acid (2.303 g, 0.01 mol) in dry chloroform (25 mL) in a 250 mL two-necked round bottom flask equipped with a water condenser and magnetic stirring bar, triorganotin chloride (0.01 mol) or diorganotin dichloride (0.005 mol) in dry chloroform (25 mL) was added dropwise with constant stirring. The reaction mixture was refluxed for 7–8 h, in an inert atmosphere and then was allowed to stand overnight at room temperature. The silver chloride formed was filtered off and the solvent was removed under reduced pressure. The solid mass left was recrystallized in dichloromethan/n-hexane (1:1).

Instrumentation

Melting points were determined in a capillary tube using a MPD Mitamura Riken Kogyo (Japan) electrothermal melting point apparatus. Infrared absorption spectra were recorded as KBr pellets on a Perkin Elmer FT-IR (model Spectrum 1000) spectrometer. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on a Bruker AM 250 spectrometer (Germany) using CDCl₃ as an internal reference [δ ¹H(CDCl³) = 7.23 ppm: δ ¹³C (CDCl₃) = 77.0 ppm]. ¹¹⁹Sn NMR spectra were obtained on a Bruker 250ARX spectrometer (Germany) with Me₄Sn [(Sn) = 37.296665 ppm] as an external reference. Mass spectral data were measured on a MAT 8500 Finnigan mass spectrometer (Germany). UV absorption spectra were recorded on a Perkin Elmer UV-Vis Lambda 2S instrument, while conductance measurements were made on a Model DDS-11A (China) conductometer.

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