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Original scientific paper

Synthesis and structural characterization of organotin(IV) complexes formed with [O,O] donor atoms of carboxylic acids

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Abstract: Organotin(IV) carboxylates of the general formula R_nSnL_{4-n} (where $R = \text{Me}$, $n\text{-Bu}$ or Ph , and $L = \alpha\text{-phenyl-2,3-(methylenedioxy)cinnamate}$ anion or $2\text{-}(2,3\text{-dimethylanylino)nicotinate}$ anion) have been prepared. The mono-, di- and tri-organotin(IV) carboxylates were synthesized by the reaction of organotin(IV) oxides or hydroxides with a stoichiometric amount of the ligand acids at an elevated temperature in dry toluene. The composition of the synthesized organotin(IV) complexes, the bonding behavior of the donor groups and structural assignments were studied by elemental analysis, FT-IR, ^1H -, ^{13}C -NMR and mass spectrometry. The spectral data suggest that the ligand acts in a bidentate manner, coordinating through the oxygen atoms. These spectroscopic techniques revealed a distorted tetrahedral geometry in the solution state for the tri-organotins, while a mean coordination number between five to six for the di-organotin(IV) dicarboxylates. In the solid phase, the tri-organotins were essentially trigonal bipyramidal polymeric while the di-organotins were octahedral. However, mono-organotin tricarboxylates were predicted to exist in the octahedral state both in solution as well as in the solid phase.

Keywords: organotin(IV) complexes; O-donor ligands; IR, NMR and mass spectrometry.

INTRODUCTION

In general, tri-organotin(IV) compounds display a larger array of biological activity than their di-organotin and mono-organotin analogues. This has been attributed to their ability to bind proteins.¹ Furthermore, many organotin(IV) carboxylates were found to possess anticancer activity in a variety of tumor cells and the structure of these organotin(IV) compounds were characterized in the solid phase and in solution.² Di-alkyltin(IV) compounds have a selective effect on lymphocytes^{3,4} and hence can be used in cancer chemotherapy.

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In addition to their medicinal and pesticidal impact,^{5–12} tin compounds have a fascinating solution and solid phase chemistry, which led to countless publications, reviews and books based on structural elucidation in both phases.^{11–13} It is well known that organotin carboxylates have versatile molecular structures, such as monomers, dimers, tetramers, oligomeric ladders and hexameric drums, *etc.*, both in the solid phase and in solution. It has also been demonstrated that the different structural types are formed due to the presence of additional coordinating sites (S, N or O, *etc.*) along with a carboxylic moiety.^{13–15} Herein, organotin(IV) complexes of α -phenyl-2,3-(methylenedioxy)cinnamic acid (HL¹, Fig. 1) and 2-(2,3-dimethylanilino)nicotinic acid (HL², Fig. 1) and their special characterization to ascertain their geometry in the solid and solution phase are reported.

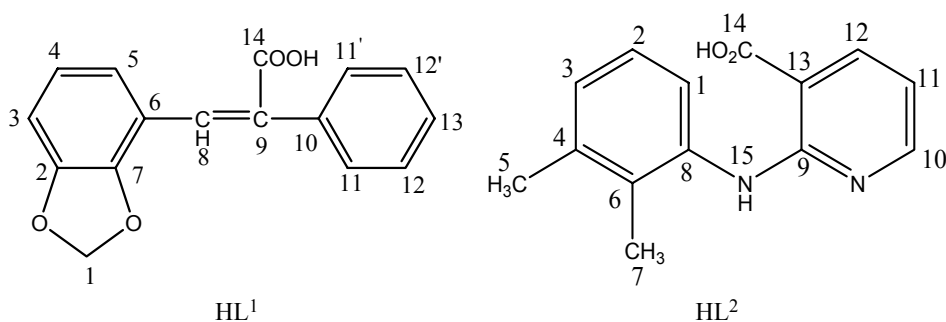


Fig. 1. α -Phenyl-2,3-(methylenedioxy)cinnamic acid (HL¹) and 2-(2,3-dimethylanilino)nicotinic acid (HL²), with the numbering scheme.

EXPERIMENTAL

Materials and Methods

Analytical grade organotin chlorides, oxides, hydroxide, 2,3-dihydroxybenzaldehyde, 2,3-dimethylaniline, NaOH (> 97%), 2-chloronicotinic acid and benzene were purchased from Aldrich, Fluka and Alfa-Aesar (Johnson Matthey Chemical Company). The organic solvents, such as toluene, chloroform and acetone, were purchased from Merck (Germany) and dried *in situ* using standard procedures.^{16,17}

Melting points were determined with melting point apparatus model MPD Mitamura Riken Kogyo (Japan) and are uncorrected. The infrared spectra were recorded on a Bio-Rad Excalibur FT-IR Model FTS 3000MX as KBr pellets. The ¹H- and ¹³C-NMR spectra in solution (CDCl₃) were recorded at ambient temperature on a Bruker 300 MHz FT NMR spectrometer using deuterated chloroform and benzene as internal references. The elemental analyses were performed using a CHNS-932 elemental analyzer, Leco Corporation (USA). The mass spectrometric analyses were performed on a MAT-312 mass spectrometer.

Synthesis

The acid ligands, α -phenyl-2,3-(methylenedioxy)cinnamic acid (HL¹) and 2-(2,3-dimethylanilino)nicotinic acid (HL²) were prepared according to a standard procedure.¹⁸ The new organotin(IV) compounds were prepared according to the following procedure.

The ligand acid, RCOOH (HL¹, 10 mmol, 2.68 g; HL², 10 mmol, 2.42 g) and the stoichiometric amount of the organotin(IV) compound (Me₂SnO, Bu₂SnO, Ph₃SnOH, BuSn(O)OH,

BuSn(OH)₂Cl were suspended in dry toluene (100 ml) in a two-necked round bottom flask (250 ml), equipped with a Dean–Stark apparatus, magnet bar and water condenser. The contents were refluxed for 6–8 h with continuous removal of the formed water then cooled to room temperature and toluene was removed under reduced pressure. The resulting solid was recrystallized from a chloroform/*n*-hexane mixture (1:4).

RESULTS AND DISCUSSION

The physical properties, yields and elemental analysis of the compounds are given in Table I.

TABLE I. Physical properties of the synthesized organotin(IV) complexes

Comp. No.	Compound	Molecular formula	M_r g mol ⁻¹	M.p. °C	Yield %	Content calcd.(found), %		
						C	H	N
1	Me ₂ SnL ¹ ₂	C ₃₄ H ₂₈ O ₈ Sn	682.69	230–231	68	59.76 (60.20)	4.10 (4.32)	–
2	Bu ₂ SnL ¹ ₂	C ₄₀ H ₄₀ O ₈ Sn	766.69	71–72	78	62.60 (61.96)	5.21 (5.01)	–
3	Ph ₃ SnL ¹	C ₃₄ H ₂₆ O ₄ Sn	616.69	115–116	77	66.15 (65.79)	4.21 (4.32)	–
4	BuSnL ¹ ₃	C ₅₂ H ₄₂ O ₁₂ Sn	976.69	147–148	71	63.88 (64.12)	4.30 (4.41)	–
5	BuSnClL ¹ ₂	C ₃₆ H ₃₁ O ₈ ClSn	745.19	150–151	80	57.97 (58.00)	4.16 (3.97)	–
6	Bu ₂ SnL ² ₂	C ₃₆ H ₄₄ N ₄ O ₄ Sn	714.19	100–101	68	60.48 (60.21)	6.16 (6.16)	7.84 (7.48)
7	Ph ₃ SnL ²	C ₃₂ H ₂₈ N ₂ O ₂ Sn	590.19	158–160	70	65.06 (64.97)	4.74 (4.69)	4.74 (4.71)
8	BuSnL ² ₃	C ₄₆ H ₄₈ N ₆ O ₆ Sn	898.19	155–157	72	61.45 (60.74)	5.34 (5.50)	9.35 (9.21)
9	BuSnClL ² ₂	C ₃₂ H ₃₅ N ₄ O ₄ ClSn	692.69	219–220	74	55.43 (55.43)	5.05 (4.96)	8.09 (7.29)

IR spectroscopy

The infrared spectra of the prepared compounds were recorded in the range 4000–400 cm⁻¹ as KBr discs. The absorption bands were assigned by comparison with earlier reports^{19,20} and important absorption frequencies, such as $\nu(\text{COO})$, $\nu(\text{Sn-O})$, $\nu(\text{Sn-C})$ and $\nu(\text{O-CH}_2)$ are listed in Table II. In the spectra, medium to weak bands in the region 490–434 cm⁻¹ are assigned to Sn–O, whereas those in the region 571–529 cm⁻¹ indicate the presence of Sn–C bonds.²¹ Complexation by deprotonation of the acid ligand was evidenced by the absence of a $\nu(\text{O-H})$ broad band in the range 3434–3424 cm⁻¹, which was supplemented by the pronounced change in $\Delta\nu$, ($\Delta\nu = \nu(\text{COO})_{\text{asy}} - \nu(\text{COO})_{\text{sym}}$), which is important to describe the tin–carboxylate–chelate interaction.²² Hence, the carboxylate group acts as a bidentate ligand in these complexes in the solid state.

TABLE II. Infrared spectral data (cm⁻¹) of organotin (IV) carboxylates

Compd. No.	Compound	$\nu(\text{COO})$		$\Delta\nu$	$\nu(\text{Sn-C})$	$\nu(\text{Sn-O})$	$\nu(\text{OCH}_2)$ (ring)	$\nu(\text{NH})$
		Asym.	Sym.					
HL ¹	Acid ¹	1695	1420	275	–	–	928	–
1	Me ₂ SnL ¹ ₂	1630	1451	179	539	490	926	–
2	Bu ₂ SnL ¹ ₂	1677	1497	180	537	485	930	–
3	Ph ₃ SnL ¹	1605	1449	156	–	446	927	–
4	BuSnL ¹ ₃	1625	1453	172	531	460	929	–
5	BuSnCIL ¹ ₂	1626	1452	174	535	488	931	–
HL ²	Acid ²	1678	1468	210	–	–	–	3316
6	Bu ₂ SnL ² ₂	1649	1465	184	529	434	–	3304
7	Ph ₃ SnL ²	1608	1427	181	–	473	–	3314
8	BuSnL ² ₃	1635	1446	189	579	461	–	3376
9	BuSnCIL ² ₂	1630	1455	175	571	470	–	3318

¹H-NMR spectroscopy

The characteristic resonance peaks in the ¹H-NMR spectra for the complexes are given in Tables III and IV. The expected resonances are assigned on the basis of their peak multiplicity, intensity pattern and/or tin satellites. The signals due to the –OH group in the acid ligands (HL¹, HL²), at 12.00 and 11.46 ppm, respectively, are absent in all the complexes, which suggests the replacement of the carboxylic proton by the organotin(IV) moiety. The methyl protons of the dimethyltin(IV) derivative appear as a sharp singlet around 1.22 ppm, both with well-defined tin satellites; the coupling constants are included in Tables III and IV.^{23–27} Theoretically, the phenyl ring protons must give doublet of doublets or a double doublet of doublets on the *meta* and *para* positions but the presence of more than one ring in these compounds results in a complex multiplet pattern. It was noticed that in most of these complexes, the ¹H- and ¹³C-NMR signals are broad, hence satellites due to ^{*n*}J [¹¹⁹Sn – ¹H] or ^{*n*}J [¹¹⁹Sn – ¹³C] couplings are not clearly visible. This shows that there is a competition in the coordination behavior of the carboxylate oxygens for the tin center.

TABLE III. ¹H-NMR data of the organotin(IV) derivatives of α -phenyl-2,3-(methylenedioxy)cinnamic acid^a

¹ H No.	HL ¹ Acid	Me ₂ SnL ¹ ₂	<i>n</i> -Bu ₂ SnL ¹ ₂	Ph ₃ SnL ¹	<i>n</i> -BuSnL ¹ ₃	<i>n</i> -BuCILSnL ¹ ₂
1	5.95 (s)	5.89 (s)	5.89 (s)	5.89 (s)	5.85 (s)	5.88 (s)
3	6.21 (<i>d</i> , 8.4)	6.27 (<i>d</i> , 8.1)	6.25 (<i>d</i> , 8.1)	6.25 (<i>d</i> , 8.1)	6.21 (<i>d</i> , 8.1)	6.23–6.15 (<i>m</i>)
4	6.49 (<i>t</i> , 7.8)	6.52 (<i>t</i> , 7.8)	6.52 (<i>t</i> , 7.8)	6.51 (<i>t</i> , 8.1)	6.52 (<i>t</i> , 7.8)	6.51 (<i>t</i> , 7.8)
5	6.70 (<i>d</i> , 7.5)	6.70 (<i>d</i> , 7.5)	6.51 (<i>d</i> , 7.5)	6.67 (<i>d</i> , 7.8)	6.65 (<i>d</i> , 7.2)	6.69 (<i>d</i> , 7.8)
8	8.05 (<i>m</i>)	8.09 (<i>m</i>)	8.06 (<i>m</i>)	8.06 (<i>m</i>)	8.06 (<i>m</i>)	8.06 (<i>m</i>)
11,11'	7.29–7.26 (<i>m</i>)	7.42–7.31 (<i>m</i>)	7.40–7.35 (<i>m</i>)	7.40–7.34 (<i>m</i>)	7.37–7.38 (<i>m</i>)	7.36–7.28 (<i>m</i>)
12,12',13	7.39–7.37 (<i>m</i>)	7.30–7.18 (<i>m</i>)	7.30–7.27 (<i>m</i>)	7.29–7.28 (<i>m</i>)	7.21–7.11 (<i>m</i>)	7.36–7.28 (<i>m</i>)
14	12.00 (s)	–	–	–	–	–
α	–	1.22 ² J[78]	1.65–1.70 (<i>m</i>)	–	1.90–1.96 (<i>m</i>)	1.90–1.96 (<i>m</i>)
β	–	–	–	7.6 (<i>m</i>)	–	–

TABLE III. Continued

¹ H No.	HL ¹ Acid	Me ₂ SnL ¹ ₂	<i>n</i> -Bu ₂ SnL ¹ ₂	Ph ₃ SnL ¹	<i>n</i> -BuSnL ¹ ₃	<i>n</i> -BuClSnL ¹ ₂
γ	–	–	1.35–1.42 (<i>m</i>)	7.45 (<i>m</i>)	1.46–1.39 (<i>m</i>)	1.17–1.15 (<i>m</i>)
δ	–	–	0.89 (<i>t</i> , 7.0)	7.80 (<i>m</i>)	0.86 (<i>t</i> , 7.2)	0.88 (<i>t</i> , 7.0)

^aMultiplicity is given as *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet. ³*J* [¹H, ¹H] in Hz are given, along with the multiplicity in parenthesis. Protons α–δ belong to the R groups. ²*J* [¹¹⁹Sn – ¹H] are not visible, except for dimethyl derivative, due to the broadness of the peaks

TABLE IV. ¹H-NMR data of the organotin(IV) derivatives of 2-(2,3-dimethylanilino)nicotinic acid^a

¹ H No.	(HL ²) Acid	<i>n</i> -Bu ₂ SnL ² ₂	Ph ₃ SnL ²	<i>n</i> -BuSnL ² ₃	<i>n</i> -BuClSnL ² ₂
1	7.03 (<i>d</i> , 7.5)	7.02 (<i>d</i> , 6.6)	7.00 (<i>d</i> , 7.5)	6.60 (<i>d</i> , 6.9)	6.67 (<i>d</i> , 7.1)
2	6.72 (<i>d</i> , 5.4)	6.95 (<i>d</i> , 5.5)	6.68 (<i>d</i> , 4.8)	6.62 (<i>d</i> , 6.6)	7.56 (<i>d</i> , 4.7)
3	7.50 (<i>d</i> , 7.8)	7.38 (<i>d</i> , 7.3)	7.16 (<i>d</i> , 7.2)	6.78 (<i>d</i> , 7.9)	7.04 (<i>d</i> , 7.1)
5	2.21 (<i>s</i>)	2.21 (<i>s</i>)	2.36 (<i>s</i>)	2.35 (<i>s</i>)	2.35 (<i>s</i>)
7	2.36 (<i>s</i>)	2.31 (<i>s</i>)	2.18 (<i>s</i>)	2.35 (<i>s</i>)	2.33 (<i>s</i>)
10	8.8 (<i>d</i> , 2.1)	8.40 (<i>d</i> , 3.3)	8.31 (<i>d</i> , 3.0)	8.12 (<i>d</i> , 2.1)	8.78 (<i>d</i>)
11	7.12–7.20 (<i>m</i>)	7.00–7.07 (<i>m</i>)	7.74–7.93 (<i>m</i>)	7.10–7.38 (<i>m</i>)	7.04–7.27 (<i>m</i>)
12	7.57–7.60 (<i>m</i>)	7.72–7.75 (<i>m</i>)	7.58–7.60 (<i>m</i>)	7.73–7.77 (<i>m</i>)	7.04–7.27 (<i>m</i>)
14	11.46 (<i>s</i>)	–	–	–	–
15	5.4 (<i>s</i>)	5.4 (<i>s</i>)	5.4 (<i>s</i>)	5.4 (<i>s</i>)	5.4 (<i>s</i>)
α	–	1.70–1.74 (<i>m</i>)	–	1.90–1.96 (<i>m</i>)	1.90–1.94 (<i>m</i>)
β	–	–	7.50 (<i>m</i>)	–	–
γ	–	1.38–1.45 (<i>m</i>)	7.44 (<i>m</i>)	1.17 (<i>m</i>)	1.15 (<i>m</i>)
δ	–	0.90 (<i>t</i> , 7.0)	7.78 (<i>m</i>)	0.88 (<i>t</i> , 7.0)	0.90 (<i>t</i> , 7.0)

^aMultiplicity is given as *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet. ³*J* [¹H, ¹H] in Hz are given, along with the multiplicity in parenthesis. Protons α–δ belong to the R groups.

¹³C-NMR spectroscopy

The characteristic resonance peaks in the ¹³C-NMR spectra of the complexes as well as those of the ligand acids (HL¹, HL²) are given in Tables V and VI. The ¹³C-NMR spectral data for the R– groups attached to the tin atom, where R = Me, *n*-Bu, and Ph, were assigned by the incremental method and comparison with analogous compounds, on the basis of ^{*n*}*J* [¹¹⁹Sn – ¹³C] coupling constants.^{28–31} The carboxylate carbon shifts to a lower field region in all the complexes, indicating participation of the carboxyl group in the coordination to tin(IV).³⁰ For tri-organotin compounds, the magnitudes of the ¹*J* [¹¹⁹Sn – ¹³C] coupling suggest the typical tetrahedral geometry around the tin atom in solution, di-organotin- and mono-organotin derivatives are expected to be octahedral in solution as well as in the solid state.^{1,29,30}

Mass Spectrometry

The fragment ions with their *m/z* (%) values for the compounds are given in Tables VII and VIII. Molecular ion peaks were observed only for complexes **3**, **6** and **7**, while for the other complexes, these were either absent or of very low intensity. In tri-organotin derivatives, the primary decomposition is due to the

loss of the R group, while di-organotin derivatives prefer the elimination of one ligand. Secondary decomposition is a consequence of the loss of either the R group or CO₂ molecules. However, the latter is the more frequent and probable pathway. In case of di-organotin derivatives, primary decomposition is mostly due to the loss of one ligand. However, if primary decomposition is due to the loss of the R group then there is successive elimination of two CO₂ molecules.^{30,31} Complexes with the general formula RSnClL₂ and RSnL₃ behave in a similar manner to di-organotin carboxylates after the release of the chloride ion and L group, respectively. Peaks for [R₃Sn]⁺ and [RSn]⁺ have either very low intensities or are absent, thus indicating that fragmentation through these species is not favorable.

TABLE V. ¹³C-NMR data of the organotin(IV) derivatives of α -phenyl-2,3-(methylenedioxy)cinnamic acid^a

¹³ C No.	(HL ¹) Acid	Me ₂ SnL ¹ ₂	<i>n</i> -Bu ₂ SnL ¹ ₂	Ph ₃ SnL ¹	<i>n</i> -BuSnL ¹ ₃	<i>n</i> -BuClSnL ¹ ₂
1	101.22	101.11	101.08	101.01	101.01	101.18
2	147.43	147.35	147.35	147.28	147.22	147.37
3	109.28	108.98	108.87	108.62	108.79	113.51
4	121.74	121.88	121.89	121.94	121.78	121.75
5	121.08	121.05	121.00	120.73	120.85	121.05
6	116.90	117.25	117.38	117.68	117.41	116.93
7	147.38	147.06	147.02	146.79	147.32	137.47
8	135.23	136.86	136.11	135.72	136.12	136.27
9	132.24	137.18	137.19	137.50	137.87	137.77
10	134.59	132.89	133.84	133.86	129.06	134.99
11,11'	128.14	127.96	126.79	126.53	126.52	126.52
12,12'	131.19	129.70	128.70	128.88	128.69	128.49
13	129.74	128.46	128.07	128.45	128.19	128.12
14	172.92	177.15	176.98	176.47	177.81	177.21
α	–	4.92	22.68 [654]	129.30 [611]	22.73	24.17
β	–	–	22.72	137.0	31.96	24.17
γ	–	–	13.65	128.88	26.00	25.79
δ	–	–	13.65	128.19	13.70	13.63

^a¹J [¹¹⁹Sn – ¹³C] is only visible for the di-*n*-butyl and triphenyl derivative and are given in square brackets, while it could not be measured for the others due to broadness of the peaks. Carbons α – δ belong to the R groups

TABLE VI. ¹³C-NMR data of the organotin(IV) derivatives of 2-(2,3-dimethylanilino)nicotinic acid^a

¹³ C No.	(HL ²) Acid	Bu ₂ SnL ² ₂	Ph ₃ SnL ²	<i>n</i> -BuSnL ² ₃	<i>n</i> -BuClSnL ² ₂
1	112.59	114.04	112.11	112.38	112.61
2	126.71	125.59	126.03	126.77	126.50
3	122.12	122.13	121.98	121.87	122.08
4	137.70	136.74	137.91	137.58	137.08
5	20.70	19.61	20.86	20.78	20.78
6	125.87	125.45	125.59	125.32	125.95
7	13.90	13.06	13.85	13.41	13.64

TABLE VI. Continued

¹³ C No.	(HL ²) Acid	Bu ₂ SnL ² ₂	Ph ₃ SnL ²	<i>n</i> -BuSnL ² ₃	<i>n</i> -BuClSnL ² ₂
8	142.16	142.27	141.94	141.82	141.50
9	161.32	167.64	161.90	161.60	161.03
10	156.80	152.83	153.45	157.44	155.97
11	120.80	119.63	119.45	120.36	120.89
12	137.86	137.28	137.33	137.58	137.19
13	108.87	108.99	107.45	109.38	108.61
14	171.27	173.45	173.59	173.65	173.85
α	–	19.93 [650]	129.02 [615]	20.70	13.92
β	–	20.21	137.33	27.75	22.72
γ	–	26.01	128.60	26.67	26.35
δ	–	13.36	129.02	13.92	14.16

^a₁J [¹¹⁹Sn – ¹³C] is only visible for the di-*n*-butyl and triphenyl derivative and are given in square brackets, while it could not be measured for the others due to broadness of the peaks. Carbons α – δ belong to the R groups

TABLE VII. Mass spectral data (*m/z* (%)) of the organotin(IV) complexes of α -phenyl-2,3-(methylenedioxy)cinnamic acid at 70 eV

Fragment ion	Me ₂ SnL ¹ ₂	<i>n</i> -Bu ₂ SnL ¹ ₂	Ph ₃ SnL ¹	<i>n</i> -BuSnL ¹ ₃	<i>n</i> -BuSnClL ¹ ₂
[R ₂ SnOO] ⁺	182(6)	209(8)	306(7)	–	–
[R ₃ Sn] ⁺	–	–	351(10)	–	–
[RSn] ⁺	135(15)	177(10)	197(12)	177(7)	177(9)
[C ₆ H ₄] ⁺	76(11)	76(9)	76(16)	76(11)	76(16)
[Sn] ⁺	120(6)	120(5)	120(8)	120(5)	120(4)
[OCOL ¹] ⁺	268(24)	268(67)	268(19)	268(94)	268(84)
[C ₁₅ H ₁₁ O ₂] ⁺	223(12)	223(26)	223(5)	223(32)	223(44)
[SnO ₂ CH ₂] ⁺	165(100)	165(100)	–	165(100)	165(100)
[C ₄ H ₉] ⁺	–	–	57(100)	–	–

Table VIII. Mass spectral data (*m/z* (%)) of organotin(IV) complexes of 2-(2,3-dimethylamino) nicotinic acid at 70 eV

Fragment ion	<i>n</i> -Bu ₂ SnL ² ₂	Ph ₃ SnL ²	<i>n</i> -BuSnL ² ₃	<i>n</i> -BuSnClL ² ₂
[R ₂ SnOO] ⁺	–	306(5)	–	–
[R ₃ Sn] ⁺	–	351(60)	–	–
[RSn] ⁺	177(3)	195(37)	177(11)	177(3)
[C ₆ H ₄] ⁺	76(48)	76(456)	76(63)	76(22)
[Sn] ⁺	120(22)	120(6)	120(32)	120(53)
[OCOL ²] ⁺	242(67)	242(6)	242(66)	242(33)
[C ₁₃ H ₁₁ N ₂ O ₂] ⁺	227(100)	–	–	–
[C ₆ H ₄ O ₂ N] ⁺	–	–	–	122(100)
[C ₁₃ H ₁₃ N ₂] ⁺	197(68)	197(100)	197(100)	197(54)

CONCLUSIONS

Organotin(IV) derivatives were synthesized in quantitative yield by refluxing the synthesized carboxylic acids and respective organotin(IV) compounds in dry toluene. Elemental analyses showed good agreement between the calculated

and observed % of C, H and N. It is proposed from the FT-IR spectral data that the organotin(IV) moieties react with the [O,O] atoms of the ligand, which behaves as bidentate. NMR data showed that the bidentate nature of carboxylate group is probably lost in solution and that the tri-organotin(IV) derivatives contained four-coordinated tin with a tetrahedral arrangement, while the mono- and di-organotin(IV) derivatives exhibit penta- or hexa-coordinated geometry due to fluxional behavior.

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ИЗВОД

СИНТЕЗА И СТРУКТУРНА КАРАКТЕРИЗАЦИЈА ОРГАНОКАЛАЈ(IV) КОМПЛЕКСА СА [O,O] ДОНОРИМА КАРБОКСИЛНИХ КИСЕЛИНА

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У раду су добијени оргонокалај(IV)-карбоксилати опште формуле R_nSnL_{4-n} (где је R = Me, *n*-Bu и Ph група, а L = α -фенил-2,3-(метилендиокси)-цинаматни анијон и 2-(2,3-диметиланилино)-никотинатни анијон). Моно-, ди- и три- оргонокалај(IV) карбоксилати синтетисани су реакцијом оргонокалајних оксида или хидроксида са стехиометријском количином киселине на повишеној температури у сувом толуену. Састав изолованих оргонокалај(IV)-комплекса, понашање везујућих донорских група и структурно означавање испитивани су елементалном анализом, FT-IR, ¹H-, ¹³C-NMR и масеном спектрометријом. Спектрални подаци указују на то да је лиганд бидентантно везан, координирајући се преко кисеоникових атома. Ове спектроскопске технике потврдиле су дисторговану тетраедарску геометрију у раствору за триоргонокалај, а координациони број између пет и шест за диоргонокалај(IV)-дикарбоксилате. У чврстом стању, три-оргонокалајна једињења су претежно тригонално-бипирамидални полимери, а ди-оргонокалајна октаедарска. Међутим, за монооргонокалајне трикарбоксилате предложено је да су октаедарски, и у раствору и у чврстој фази.

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