SYNTHESIS AND INFRARED AND ^{1}H, ^{13}C, ^{119}Sn NMR SPECTRA OF SOME TRIS- AND BIS(1-BUTYL)TIN(IV) NAPHTHOATES AND HYDROXYNAPHTHOATES

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

The synthesis and structure of tris(1-butyl)tin(IV) and bis(1-butyl)tin(IV) 1-naphthoates, 2-naphthoates, 1-hydroxy-2-naphthoates, 2-hydroxy-1-naphthoates, 3-hydroxy-2-naphthoates as well as the groups of the corresponding tetrakis(1-butyl)dinaphthoato- and tetrakis(1-butyl)bis(hydroxynaphthoato)distannoxanes have been studied in solutions of both coordinating and noncoordinating solvents by means of infrared and multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR spectroscopies. In the solutions of noncoordinating solvents, all the tris(1-butyl)tin(IV) compounds are present as isolated monomeric molecules with pseudotetrahedral environment of the central tin atom, or as strongly deformed *cis*-trigonally bipyramidal chelate complexes with anisobidentate carboxylic group. The bis(1-butyl)tin(IV) compounds form molecular pseudooctahedral complexes with chelate anisobidentate carboxylic groups of naphthoate or hydroxynaphthoate ligands. The (1-butyl)chlorotin(IV) compounds are molecular complexes containing a chelate-bound carboxylic group, their tin atom having a pentacoordinated environment of the bond partners. The tetrakis(1-butyl)dinaphthoato- and tetrakis(1-butyl)bis(hydroxynaphthoato)distannoxanes form dimeric molecular complexes with two pentacoordinated tin atoms and two hexacoordinated ones. In solutions of a coordinating solvent (hexadeuteriodimethyl sulfoxide), the tris(1-butyl)tin(IV) compounds form *trans*-trigonally bipyramidal complexes with one molecule of the solvent, whereas the bis(1-butyl)tin(IV) and bis(1-butyl)chlorotin(IV) compounds form trapezoidally bipyramidal complexes with two molecules of the solvent. The dimeric tetrakis(1-butyl)bis(hydroxynaphthoato)distannoxanes are monomerized by coordinating solvent, each monomeric unit adding two solvent molecules per one tin atom. The environment of the tin atom is then pseudooctahedral. The hydroxyl groups of naphthoate systems do not take part in any bonds to the tin atom in any of the compounds studied.

Key words: Tris(1-butyl)tin(IV) naphthoates and hydroxynaphthoates; Bis(1-butyl)tin(IV) dinaphthoates and bis(hydroxynaphthoates); Structure; ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy; Infrared spectroscopy.

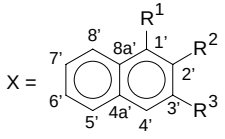
The organotin(IV) compounds are well-known by their applications in chemical industry, agriculture and other fields of human activities[1]. Recently they also have been extensively studied as potential antitumor drugs[2]. Along with the studies of synthesis, and perhaps due to the potential applications, also the amount of data on structure of this very interesting class of organometallics is increasing. However, most of them concern their structure in crystalline state and were obtained by analysis of diffraction data[3–5]. Substantially less pieces of information are available about structure of these compounds dissolved in various types of solvents.

The aim of the present paper is to study the structure of particles of (so far only exceptionally studied[6–9]) tris(1-butyl)tin(IV), bis(1-butyl)tin(IV) and bis(1-butyl)chlorotin(IV) 1-naphthoates, 2-naphthoates, 1-hydroxy-2-naphthoates, 2-hydroxy-1-naphthoates and 3-hydroxy-2-naphthoates as well as the groups of the corresponding tetrakis(1-butyl)dinaphthoatodistannoxanes and tetrakis(1-butyl)bis(hydroxynaphthoato)distannoxanes (Scheme 1) in solutions of various types of solvents by means of infrared and multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR spectroscopies. For the purposes of identification of these compounds as well as for some considerations of their structure, Tables II–IV and VI give besides the spectral parameters of the (1-butyl)tin(IV) compounds studied also those of purely organic esters and sodium salts of the corresponding naphthoic and hydroxynaphthoic acids (Scheme 1).

1 : $(1\text{-}C_4H_9)_3SnX$
2 : $(1\text{-}C_4H_9)_2SnX_2$
3 : $[(1\text{-}C_4H_9)_2SnX]_2O$
4 : $(1\text{-}C_4H_9)_2Sn(Cl)X$
5 : Na^+X^-
6 : C_2H_5X

1-C_4H_9 = $CH_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2$-

X =



	R^1	R^2	R^3
a	COO	H	H
b	H	COO	H
c	OH	COO	H
d	COO	OH	H
e	H	COO	OH

SCHEME 1

EXPERIMENTAL

Tris(1-butyl)tin(IV) naphthoates and hydroxynaphthoates **1a**–**1e** were prepared by reaction of hexakis(1-butyl)distannoxane with the respective naphthoic or hydroxynaphthoic acid (molar ratio 1 : 1) in benzene[10]. The water formed in the reaction was removed by azeotropic distillation. Similar reaction was also used for synthesis of bis(1-butyl)tin(IV) dinaphthoates or bis(hydroxynaphthoates) **2a**–**2e** by the reaction of bis(1-butyl)stannyl oxide with the respective acids at the molar ratio of 1 : 2, and for synthesis of tetrakis(1-butyl)dinaphthoato- and tetrakis(1-butyl)bis(hydroxynaphthoato)distannoxanes **3a**–**3e** using the molar ratio 1 : 1 of the reacting components[10]. Compounds **1a**, **2a**–**2e** and **3a**–**3e** were then recrystallized from benzene, compound **1b** was purified by vacuum distillation. Compounds **1c**–**1e** were used without further purification. The bis(1-butyl)chlorotin(IV) naphthoates and hydroxynaphthoates were prepared by reaction of bis(1-butyl)stannyl chloride with silver, lead(II) or alkali salts of the respective acids at the molar ratio of 1 : 1 in dichloromethane medium[10]. The metal chlorides

formed in the reaction were filtered off and the solvent was evaporated. The evaporation residue was a yellow-brown viscous liquid giving always a mixture (see below) on attempts at crystallization: it contained besides the expected product also bis(1-butyl)stannyl dichloride and the respective bis(1-butyl)tin(IV) dinaphthoate or bis(hydroxynaphthoate). All the compounds isolated in pure state were identified by elemental analysis (Table I) and by analysis of their ^{1}H, ^{13}C and ^{119}Sn NMR (Tables II–VII) and infrared spectra (Table VIII) and characterized by some physical parameters (Table I). The molecular weights of compounds were determined by means of cryoscopy (benzene, camphor).

The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were measured with a Bruker AMX 360 apparatus in a 5 mm tuneable probe and with help of an X32 computer (UXNMR software – version 940501.3). The compounds synthesized were measured in 5–30% solutions or saturated solutions in deuteriochloroform or hexadeuteriodimethyl sulfoxide at 300 K. The chemical shifts $\delta(^{13}C)$ were referred to the respective solvent signal and recalculated to δ scale [$\delta(^{13}C)$ = 77.00 ($CDCl_3$), 39.60 ($(CD_3)_2SO$)]. The $\delta(^{1}H)$ and $\delta(^{119}Sn)$ chemical shifts were referenced to the internal hexamethyldisiloxane (δ = 0.05) or external tetramethylstannane (δ = 0.00). Unambiguous assignment of the ^{1}H and ^{13}C NMR signals was carried out by a combination of one-dimensional (selective INEPT and differential NOE) and two-dimensional (H,H-COSY and H,C-COSY) NMR techniques.

The infrared spectra of the substances prepared were measured in chloroform solutions and in paraffin suspensions using a Perkin–Elmer 684 apparatus linked with a DS 3600 data station.

RESULTS AND DISCUSSION

Preparation of Compounds

The simplest way of preparation of organotin(IV) carboxylates is either the esterification of the acids with organotin(IV) oxides or hydroxides, or reaction of salts of the carboxylic acids with organotin(IV) halogenides[10]. Whereas the esterification of carboxylic acids or reaction of their salts with triorganotin(IV) compounds only produces single products – triorganotin(IV) carboxylates, the composition of products of both types of reactions of the carboxylic acids or their salts with diorganotin(IV) oxides, hydroxides or halogenides depends on the molar ratio of reacting components. Both reactions can give products with the ratio of carboxylate : organotin(IV) fragment equal to 1 : 1 or 1 : 2. The products of both reactions with the molar ratio of components equal to 1 : 2 are identical – diorganotin(IV) dicarboxylates. The esterification reactions of carboxylic acid with diorganotin(IV) oxides or hydroxides at the molar ratio of 1 : 1 give the respective tetraorganodicarboxylatodistannoxanes, whereas the reaction of diorganotin(IV) dihalogenides with salts of the carboxylic acids at the molar ratio of 1 : 1 can provide diorgano(halogeno)tin(IV) carboxylates.

As it was mentioned in Experimental most of the esterification reactions were successful in providing very pure compounds **1**–**3** (except for **1a**). The reaction of bis(1-butyl)stannyl dichloride with sodium, potassium, silver or lead(II) salts of both naphthoic and all three hydroxynaphthoic acids studied was only partially successful. After the reaction mixture was rid of coproducts (insoluble metal halogenides) it always contained besides the chief reaction product – the respective bis(1-butyl)chlo-

TABLE I
Analytical and physical data of organotin(IV) naphthoates and hydroxynaphthoates

Compound	M.p., °C	Formula	M.w.[a]	Calculated/Found		
				% H	% C	% Sn
1a	26–28[b]	$C_{23}H_{34}O_2Sn$	461.2 (425)	7.42 7.38	59.89 59.12	25.73 25.52
1b	118–120[c]	$C_{23}H_{34}O_2Sn$	461.2 (455)	7.42 8.07	59.89 58.99	25.73 25.18
1c	[d]	$C_{23}H_{34}O_3Sn$		7.18 6.89	57.89 57.11	24.87 26.07
1d	[d]	$C_{23}H_{34}O_3Sn$		7.18 6.97	57.89 57.89	24.87 24.86
1e	[d]	$C_{23}H_{34}O_3Sn$		7.18 6.83	57.89 56.16	24.87 24.78
2a	45–48	$C_{30}H_{32}O_4Sn$	575.0 (570)	5.61 5.91	62.64 62.11	20.63 19.99
2b	88–90	$C_{30}H_{32}O_4Sn$	575.0 (575)	5.61 5.68	62.64 63.01	20.63 20.73
2c	115–116	$C_{30}H_{32}O_6Sn$	602.3 (570)	5.31 5.54	59.34 59.24	19.54 18.94
2d	105–109	$C_{30}H_{32}O_6Sn$	[f]	5.31 5.73	59.34 58.59	19.54 20.95
2e	107–109	$C_{30}H_{32}O_6Sn$	602.3 (605)	5.31 5.51	59.34 59.39	19.54 20.38
3a	99–102	$C_{38}H_{50}O_5Sn_2$	824.2 (1 625) (1 320[c])	6.11 6.16	55.38 55.78	28.81 28.64
3b	146–148	$C_{38}H_{50}O_5Sn_2$	824.2 (1 725) (1 370[c])	6.11 6.06	55.38 54.81	28.81 29.22
3c	215–217	$C_{38}H_{50}O_7Sn_2$	[f]	5.89 5.81	53.31 54.35	27.73 28.31
3d	30–35 (dec.)	$C_{38}H_{50}O_7Sn_2$	[f]	5.89 5.85	53.31 53.68	27.73 27.24
3e	139–141	$C_{38}H_{50}O_7Sn_2$	856.2 (1 700)	5.89 5.91	53.31 53.52	27.73 27.24

[a] The values in brackets were obtained by cryoscopic measurements in benzene if not otherwise

rotin(IV) naphthoate or hydroxynaphthoate – also bis(1-butyl)stannyl dichloride and the respective bis(1-butyl)tin(IV) dinaphthoate or bis(hydroxynaphthoate) in the amounts of 10–20% (as compared with the chief product). We cannot give any unambiguous interpretation of formation of the said by-products. The fact that the content of

TABLE II
$\delta(^1H)$ Values of 1-butyl substituents of compounds **1**–**4** in $CDCl_3$ and $(CD_3)_2SO$ at 300 K

Compound	$\delta(^1H)$, ppm; $CDCl_3$, $((CD_3)_2SO)$			
	1	2	3	4
1a	1.37 (1.28)	1.68 (1.74)	1.37 (1.39)	0.90 (0.91)
1b	1.42 (1.33)	1.73 (1.79)	1.42 (1.43)	0.97 (0.94)
1c	1.61 (1.31)	1.61 (1.75)	1.31 (1.41)	0.85 (0.92)
1d	1.71 (1.38)	1.41 (1.80)	1.36 (1.45)	0.91 (0.95)
1e	1.66 (1.32)	1.66 (1.75)	1.38 (1.42)	0.91 (0.93)
2a	2.09 (1.32)	2.01 (1.73)	1.61 (1.73)	1.04 (0.77)
2b	1.90 (1.33)	1.82 (1.79)	1.42 (1.43)	0.87 (0.94)
2c	1.88 (1.40)	1.76 (1.53)	1.41 (1.23)	0.81 (0.72)
2d	1.86 (1.67)	1.74 (1.67)	1.35 (1.29)	0.81 (0.76)
2e	1.91 (1.67)	1.78 (1.67)	1.42 (1.31)	0.89 (0.79)
3a	1.73 ([a])	1.83 ([a])	1.38 ([a]) 1.22 ([a])	0.86 ([a]) 0.70 ([a])
3b	1.76 ([a])	1.86 ([a])	1.44 ([a]) 1.31 ([a])	0.88 ([a]) 0.75 ([a])
3c	1.80 (1.41)	1.36 (1.53)	1.42 (1.23)	0.87 (0.72) 0.75
3d	1.75 (1.34)	1.34 (1.51)	1.42 (1.21)	0.88 (0.72) 0.79
3e	1.86 (1.60)	1.81 (1.46)	1.42 (1.30) 1.41	0.86 (0.80) 0.78
4a	1.81 (1.60)	1.81 (1.66)	1.39 (1.32)	0.89 (0.84)
4b	1.81 (1.60)	1.41 (1.60)	1.81 (1.29)	0.89 (0.81)
4c	1.85	1.75	1.41	0.89
4d	1.78	1.78	1.41	0.89
4e	1.78	1.78	1.39	0.89

[a] Low solubility.

the reaction by-products does not correspond to the mutually equivalent ratios of amounts can be explained by simultaneous incomplete conversion of the components to the first degree (bis(1-butyl)chlorotin(IV) naphthoate or hydroxynaphthoate) as well as to the second degree (bis(1-butyl)tin(IV) dinaphthoate or bis(hydroxynaphthoate)). The finding that the content of both by-products increased on attempts at concentrating the solutions for crystallization or on prolonged standing of reaction mixture rather indicates a disproportionation of transient bis(1-butyl)chlorotin(IV) carboxylates to give equivalent mixtures of bis(1-butyl)stannyl dichloride and bis(1-butyl)tin(IV) dinaph-

TABLE III
$\delta(^1H)$ Values of naphthoate and hydroxynaphthoate substituents of compounds **1**–**4** in $CDCl_3$ at 300 K

Compound	$\delta(^1H)$, ppm								
	1′	2′	3′	4′	5′	6′	7′	8′	OH
1a	–	8.24	7.41	7.86	7.76	7.41	7.53	9.05	–
1b	8.71	–	8.19	7.84	7.81	7.47	7.49	7.94	–
1c	–	–	7.81	7.18	7.65	7.43	7.38	8.35	12.73
1d	–	–	7.15	7.81	7.68	7.31	7.51	9.11	13.19
1e	7.25	–	–	8.51	7.77	7.23	7.39	7.63	11.35
2a	–	8.64	7.61	8.10	7.95	7.62	7.77	9.35	–
2b	8.8	–	8.21	7.86	7.81	7.48	7.50	7.93	–
2c	–	–	7.96	7.31	7.74	7.55	7.48	8.42	11.82
2d	–	–	7.12	7.81	7.65	7.31	7.57	9.22	12.23
2e	7.32	–	–	8.72	7.84	7.31	7.47	7.67	10.74
3a	–	8.06	7.48	7.93	7.83	7.48	7.53	8.90	–
3b	8.67	–	8.18	7.95	7.92	7.57	7.57	8.07	–
3c	–	–	7.83	7.41	7.78	7.56	7.62	8.47	12.45
3d	–	–	7.18	7.87	7.74	7.32	7.62	9.01	12.21
3e	7.37	–	–	8.48	7.91	7.36	7.51	7.74	11.15
4a	–	8.43	7.44	7.97	7.81	7.46	7.59	9.11	–
4b	8.72	–	8.11	7.87	7.85	7.58	7.51	7.93	–
4c	–	–	7.94	7.31	7.75	7.56	7.48	8.42	11.78
4d	–	–	7.16	7.87	7.71	7.34	7.61	9.22	12.23
4e	7.29	–	–	8.67	7.79	7.27	7.45	7.64	10.27

thoate or bis(hydroxynaphthoate). In our opinion both these effects operate in the systems studied by us (the parameters in ^{1}H, ^{13}C and ^{119}Sn NMR spectra of compounds **4a** and **4b** in Tables II–VII come from spectra of reaction mixtures containing the lowest possible amounts of the by-products, the signals of lower intensity being neglected if they were safely assigned to the by-products).

Identification of Compounds

Besides the results of chemical analysis, which confirmed the composition of the compounds studied, the analysis of their ^{1}H, ^{13}C and ^{119}Sn NMR spectra supports the identification. All compounds **1** and **2** always show only one signal in their ^{119}Sn NMR spectra (Table VII) and one set of signals in their ^{1}H and ^{13}C NMR spectra both in deuteriochloroform (Tables II, III, V) and in hexadeuteriodimethyl sulfoxide solutions (Tables II, IV, VI). The numbers of signals in both ^{1}H and ^{13}C NMR spectra of these

TABLE IV
$\delta(^{1}H)$ Values of naphthoate and hydroxynaphthoate substituents of compounds **1**–**4** in $(CD_3)_2SO$ at 300 K

Compound	$\delta(^{1}H)$, ppm								
	1′	2′	3′	4′	5′	6′	7′	8′	OH
1a	–	8.05	7.51	7.90	7.88	7.51	7.51	9.01	–
1b	8.66	–	8.19	7.90	7.87	7.50	7.49	7.99	–
1c	–	–	7.93	7.26	7.75	7.52	7.48	8.37	14.32
1d	–	–	7.19	7.86	7.74	7.31	7.51	9.42	14.64
1e	7.27	–	–	8.54	7.85	7.45	7.45	7.72	12.71
2a	–	8.27	7.53	8.05	7.93	7.51	7.60	9.12	–
2b	8.68	–	8.09	7.96	7.96	7.57	7.57	8.09	–
2c	–	–	7.83	7.33	7.83	7.59	7.52	8.31	13.21
2d	–	–	7.17	7.94	7.79	7.29	7.41	9.16	13.37
2e	7.27	–	–	8.56	7.87	7.27	7.44	7.71	[a]
3c	–	–	7.85	7.03	7.71	7.47	7.38	8.41	[a]
3d	–	–	7.03	7.85	7.71	7.38	7.47	8.41	[a]
3e	7.15	–	–	8.40	7.82	7.25	7.15	7.55	[a]
4a	–	8.17	7.56	8.12	8.01	7.58	7.62	8.98	–
4b	8.64	–	8.09	7.97	7.95	7.59	7.59	8.04	–

[a] Unresolved.

TABLE V
$\delta(^{13}C)$ Values of naphthoate and hydroxynaphthoate substituents of compounds **1–6** in $CDCl_3$ at 300 K

Compound	$\delta(^{13}C)$, ppm										
	1′	2′	3′	4′	5′	6′	7′	8′	4a′	8a′	COO
1a	129.03	131.58	124.38	133.77	128.18	125.61	127.97	126.43	132.31	130.42	173.05
2a	126.64	131.65	124.43	133.76	128.42	125.95	127.64	126.21	133.71	131.82	177.43
3a	128.24	128.95	124.55	133.88	128.39	125.88	127.01	126.24	131.96	131.27	174.63
4a	125.09	132.31	124.28	134.26	128.41	125.97	127.96	125.82	133.61	131.45	177.09
5a	129.55	127.81	124.89	128.56	124.14	125.68	126.22	125.28	137.73	133.55	178.13
6a	127.14	129.84	124.21	132.95	128.28	125.88	127.41	125.99	133.58	131.12	167.26
1b	131.03	129.14	126.11	127.41	127.41	125.98	127.41	128.94	134.99	132.44	171.46
2b	132.04	127.05	125.86	127.93	127.61	126.46	128.14	129.21	135.52	132.86	175.96
3b	130.94	130.69	126.14	127.88	127.75	126.43	128.25	129.22	135.26	132.71	172.82
4b	132.38	125.96	125.71	128.08	127.66	128.46	126.64	129.29	135.71	132.31	176.19
5b	128.81	131.94	125.26	127.22	127.02	127.02	126.01	128.47	133.84	133.18	174.93
6b	130.24	127.15	124.61	124.41	127.07	124.41	125.87	128.65	134.81	131.85	165.81
1c	160.51	107.45	126.11	117.75	127.31	128.59	125.17	123.73	137.04	124.86	175.13
2c	160.97	105.72	125.81	118.67	127.48	129.37	125.65	128.89	137.62	124.74	178.29
3c	160.98	107.35	125.62	118.28	127.49	129.11	125.51	123.91	137.25	125.11	176.15
4c	160.97	105.49	125.76	118.65	127.47	129.42	125.65	123.86	137.62	124.67	178.28
5c	158.23	110.92	126.48	117.88	127.36	128.31	125.46	122.52	136.16	124.16	176.18
6c	160.61	105.28	123.93	118.25	127.16	129.01	125.37	123.58	136.91	124.45	171.08
1d	105.67	164.13	119.24	135.76	128.65	123.02	127.82	125.67	128.48	133.08	176.21
2d	104.11	164.61	119.24	137.18	128.79	123.66	128.68	125.53	128.57	132.98	178.94
3d	106.89	164.39	119.38	136.25	128.77	123.38	128.32	125.59	128.32	133.17	178.61
4d	103.62	164.71	118.96	137.45	128.63	123.63	128.44	125.27	128.42	131.71	178.95
5d	111.23	159.23	118.39	133.54	128.49	123.11	127.51	124.97	128.42	132.57	176.04
6d	104.62	164.36	119.27	136.89	129.08	123.63	128.44	125.27	128.61	131.71	172.88
1e	110.83	116.35	156.77	133.14	128.99	123.29	128.34	125.05	126.05	137.65	173.98
2e	111.42	114.39	156.21	134.11	128.99	123.67	128.04	126.08	127.02	128.17	177.47
3e	111.59	116.79	156.78	132.81	128.97	123.87	128.97	126.23	127.07	137.95	175.27
4e	111.33	113.74	155.89	134.26	129.15	123.81	129.07	126.07	126.97	138.17	177.33
5e	109.71	119.67	155.29	131.64	128.82	123.46	127.99	125.67	126.97	136.27	174.89
6e	111.25	113.74	156.02	138.03	128.91	123.52	128.76	125.89	126.64	137.54	169.87

TABLE VI
$\delta(^{13}C)$ Values of naphthoate and hydroxynaphthoate substituents of compounds **1**–**6** in $(CD_3)_2SO$ at 300 K

Compound	$\delta(^{13}C)$, ppm										
	1′	2′	3′	4′	5′	6′	7′	8′	4a′	8a′	COO
1a	128.71	128.26	125.51	130.42	128.11	124.78	127.17	126.61	133.49	130.96	171.49
2a	129.42	130.04	126.02	132.41	128.49	124.93	127.17	126.14	133.58	131.01	175.19
4a	127.91	132.21	124.95	134.26	128.51	126.06	127.22	125.95	133.51	130.84	173.49
5a	129.55	127.80	124.89	128.56	124.14	125.68	126.22	125.28	137.33	133.55	178.13
6a	127.14	129.84	124.20	132.95	128.28	125.68	127.41	125.59	133.58	131.12	167.26
1b	129.79	128.25	126.42	127.23	127.49	126.98	126.03	128.81	134.53	132.61	169.77
2b	134.53	129.14	126.13	128.91	127.61	126.52	126.89	132.61	134.88	132.31	172.96
4b	130.57	129.41	125.78	127.99	127.67	127.99	126.66	129.22	134.85	132.31	172.53
5b	128.80	131.94	125.26	127.22	127.02	127.02	126.00	128.47	133.84	133.18	174.93
6b	130.24	127.15	124.60	124.40	127.07	124.40	125.87	128.63	134.80	131.85	165.81
1c	159.92	110.01	126.57	116.94	127.43	128.04	124.94	123.31	136.48	124.94	174.34
2c	159.75	108.09	124.36	117.91	128.36	128.89	124.36	123.18	136.62	127.59	174.24
3c	162.32	112.53	125.62	114.56	128.97	129.41	124.43	124.03	136.39	128.97	169.11
5c	158.23	110.92	126.48	117.88	127.36	128.31	125.46	122.52	136.16	124.15	176.18
6c	160.61	105.28	123.93	118.25	127.16	129.01	125.37	123.58	136.91	124.45	171.08
1d	107.48	163.18	119.12	133.16	127.89	122.22	126.82	125.57	128.19	134.06	174.96
2d	108.73	162.66	118.68	134.92	128.57	122.94	128.07	125.33	127.58	132.88	175.28
3d	112.54	162.44	114.64	136.45	129.01	124.13	127.52	124.52	127.01	129.46	169.36
5d	111.23	159.23	118.39	133.54	128.49	123.11	127.51	124.97	128.42	132.57	176.04
6d	104.62	164.36	119.21	136.89	129.08	123.63	128.44	125.27	128.61	131.71	172.82
1e	109.97	119.15	157.41	131.94	128.82	123.01	127.83	125.81	126.68	136.91	172.67
2e	110.83	117.91	157.01	132.61	129.06	123.31	128.35	125.84	126.68	137.11	172.97
3e	110.53	118.24	157.06	133.36	128.86	122.25	127.57	125.29	126.25	137.04	173.6
5e	109.71	119.67	155.29	131.64	128.82	123.46	127.99	125.67	126.97	136.27	174.89
6e	111.25	113.74	156.02	132.03	128.91	123.52	128.76	125.89	126.64	137.54	169.87

TABLE VII
^{119}Sn and ^{13}C NMR spectral data ($\delta(^{13}C)$; $^{n}J(^{119}Sn,^{13}C)$) of compounds **1–4** at 300 K

Compound	Solvent	$\delta(^{119}Sn)$	$\delta(^{13}C)^{a}$, ppm/($^{n}J(^{119}Sn,^{13}C)$, Hz)			
			C-1	C-2	C-3	C-4
1a	$CDCl_3$	110.7	16.56 (358.8)	27.81 (21.0)	26.91 (63.26)	13.51 *b*
	$(CD_3)_2SO$	–150.1	18.77 (476.4)	27.97 (27.5)	26.74 (75.21)	13.71 *b*
1b	$CDCl_3$	112.8	16.41 (358.1)	27.67 (20.6)	26.81 (63.9)	13.43 *b*
	$(CD_3)_2SO$	–8.1	18.77 (470.4)	28.04 (27.4)	26.81 (73.6)	13.77 *b*
1c	$CDCl_3$	130.5	16.88 (352.4)	27.73 (20.8)	26.95 (63.7)	13.57 *b*
	$(CD_3)_2SO$	–15.7	19.22 (480.0)	27.99 (27.8)	26.75 (76.1)	13.71 *b*
1d	$CDCl_3$	128.6	17.15 (353.1)	27.84 (21.2)	26.98 (64.8)	13.61 *b*
	$(CD_3)_2SO$	–15.2	19.09 (485.5)	27.18 (25.8)	26.49 (95.3)	13.38 *b*
1e	$CDCl_3$	133.3	16.97 (352.9)	27.69 (21.1)	26.91 (64.9)	13.53 *b*
	$(CD_3)_2SO$	–19.5	19.13 (483.4)	27.86 (28.6)	26.59 (75.3)	13.67 *b*
2a	$CDCl_3$	–151.5	25.47 (594.1)	26.73 (34.7)	26.21 (96.6)	13.45 *b*
	$(CD_3)_2SO$	–318.3	30.51 (889.7)	27.21 (37.6)	25.74 (133.7)	13.59 *b*
2b	$CDCl_3$	–150.4	25.53 (587.5)	26.24 (31.5)	26.24 (93.6)	13.43 *b*
	$(CD_3)_2SO$	–314.2	30.35 (881.5)	32.57 (37.7)	27.03 (135.9)	13.61 *b*
2c	$CDCl_3$	–123.8	26.31 (566.0)	26.58 (34.6)	26.26 (96.6)	13.44 *b*
	$(CD_3)_2SO$	–272.6	31.22 *b*	26.91 (40.9)	27.73 (135.7)	13.57 *b*
2d	$CDCl_3$	–131.9	26.35 (573.9)	26.57 (35.0)	26.22 (96.2)	13.39 *b*
	$(CD_3)_2SO$	–220.2	30.35 *b*	27.01 (30.1)	25.72 (140.3)	13.56 *b*
2e	$CDCl_3$	–122.1	26.45 (553.6)	26.48 *b*	26.11 (96.2)	13.25 *b*
	$(CD_3)_2SO$	–263.5	30.31 *b*	27.01 (38.6)	25.78 (137.6)	13.63 *b*

TABLE VII
(*Continued*)

Compound	Solvent	$\delta(^{119}Sn)$	$\delta(^{13}C)^a$, ppm/($^nJ(^{119}Sn,^{13}C)$, Hz)			
			C-1	C-2	C-3	C-4
3a	$CDCl_3$	–206.9	29.59 (728.9)	27.71 [b]	26.84 [b]	13.57 [b]
		–207.8	28.36 (694.0)	27.48 [b]	26.84 [b]	13.57 [b]
3b	$CDCl_3$	–210.1	30.18 (739.4)	27.93 [b]	26.83 [b]	13.67 [b]
		–212.9	28.49 (721.3)	27.59 [b]	26.83 [b]	13.51 [b]
3c	$CDCl_3$	–189.7	30.87 [b]	27.81 (37.4)	26.72 (65.5)	13.53 [b]
		–200.8	28.89 [b]	27.36 (40.2)	26.72 (65.5)	13.53 [b]
	$(CD_3)_2SO$	–257.7	26.98 (747.0)	26.64 (41.6)	25.68 (113.7)	13.51 [b]
3d	$CDCl_3$	–202.3	[c] [b]	[c] [b]	[c] [b]	13.47 [b]
		–213.4	27.39 [b]	26.81 [b]	26.72 [b]	13.47 [b]
	$(CD_3)_2SO$	–273.7	27.05 (785.8)	26.71 (44.6)	25.74 (114.9)	13.54 [b]
3e	$CDCl_3$	–188.9	30.34 [b]	27.85 [b]	26.71 [b]	13.51 [b]
		–194.1	29.17 [b]	27.36 [b]	26.71 [b]	13.41 [b]
	$(CD_3)_2SO$	–270.3	[b] [b]	26.76 (47.9)	25.78 (119.8)	13.64 [b]
4a	$CDCl_3$	–33.4	26.74 (506.9)	26.55 (33.9)	26.05 (92.54)	13.29 [b]
	$(CD_3)_2SO$	–329.2	34.17 (603.1)	27.40 (42.6)	25.66 (142.6)	13.71 [b]
4b	$CDCl_3$	–29.2	26.18 [b]	26.62 (33.4)	26.18 (88.4)	13.38 [b]
	$(CD_3)_2SO$	–206.1	33.54 (826.7)	27.35 (39.6)	25.71 (139.2)	13.69 [b]
4c	$CDCl_3$	–5.1	26.57 (522.4)	26.57 (34.5)	26.24 (92.4)	13.51 [b]
4d	$CDCl_3$	–14.2	26.53 (491.2)	26.53 (34.7)	26.13 (90.4)	13.34 [b]
4e	$CDCl_3$	0.3	26.49 (471.1)	26.49 (33.5)	26.06 (88.9)	13.24 [b]

[a] Carbon atoms of 1-butyl groups. [b] Not found. [c] $\delta(^{13}C)$ = 26.2–27.7 ppm.

TABLE VIII
Values of ν_a(COO), ν_s(COO), and $\Delta\nu$(COO) (cm^{-1}) in infrared spectra of compounds **1–6**

Compound	$CHCl_3$			Paraffin suspension		
	ν_a(COO)	ν_s(COO)	$\Delta\nu$(COO)	ν_a(COO)	ν_s(COO)	$\Delta\nu$(COO)
1a	1 635	1 308	327	1 642	1 303	339
2a	1 567	1 327	240	1 569	1 324	245
3a	1 560	1 354 1 326	206 234	1 550	1 310	240
5a				1 517	1 377	140
6a				1 713	1 279	434
1b	1 640	1 330	310	1 646	1 325	321
2b	1 568	1 341	227	1 568	1 337	231
3b	1 609 1 554	1 333 1 370	276 184	1 606 1 554	1 333	273 221
5b				1 552	1 409	143
6b				1 717	1 286	431
1c	1 593	1 360	233	1 593	1 358	235
2c	1 584	1 405	179	1 588	1 405	183
3c	1 569	1 408	161	1 576	1 429	147
5c				1 581	1 408	173
6c				1 664	1 271	393
1d	1 588	1 381	207	1 588	1 382	206
2d	1 584	1 402	182	1 589	1 402	187
3d	1 584	1 398	186	1 557	1 398	159
5d				1 574	1 411	163
6d				1 656	1 242	414
1e	1 657	1 386	271	1 657	1 386	271
2e	1 650	1 427	223	1 650	1 426	224
3e	1 554	1 391	163	1 554	1 403	151
5e				1 582	1 407	175
6e				1 691	1 282	409

compounds, their intensity and multiplicity agree with the presumed empirical formulas of the compounds. The ^{119}Sn NMR spectra of compounds **3** (Table VII) in deuteriochloroform solutions contain two signals of equal intensity and the ^{13}C NMR spectra (Table VII) contain two sets of signals of equal intensities for 1-butyl substituent and one set of equally intense signals due to naphthoate or hydroxynaphthoate groups (Table V). The presence of two different bis(1-butyl)tin(IV) groups in molecules of compounds **3** is connected with their structure (see below) which can also be derived from the presence of two distinctly resolved signals of hydrogen atoms in the methyl group of 1-butyl substituent in ^{1}H NMR spectra of compounds **3** in deuteriochloroform solutions (Table II). The ^{119}Sn NMR spectra of compounds **3c**–**3e** (Table VII) in solutions of a coordinating solvent (hexadeuteriodimethyl sulfoxide) only show one signal, and the ^{1}H and ^{13}C NMR spectra in the same solvent (Tables II, IV, VI) only show one set of signals whose number, intensity and multiplicity correspond to the empirical formulas of these compounds (compounds **3a** and **3b** are not sufficiently soluble in hexadeuteriodimethyl sulfoxide). The identity of all the compounds studied is further confirmed by the analysis of their IR spectra, in particular by the presence of the relevant bands due to valence vibrations of carboxylic groups ν_a(COO) and ν_s(COO) (Table VIII).

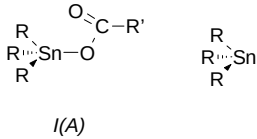
Structure of Compounds

It is worth mentioning that the ^{1}H NMR spectra (Tables III and IV) of all the compounds with hydroxynaphthoate groups exhibit signals in the region of *ca* 10–13 ppm which by their intensities correspond to one hydrogen atom per one hydroxynaphthoate group. The chemical shift values $\delta(^1H)$ of these signals are very close to those OH hydrogen atom in esters of hydroxynaphthoic acids. This finding excludes from further considerations the possibility of substitution of hydrogen atoms in hydroxyl groups by a tin atom (*cf.* refs[7,8,11,12]).

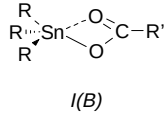
Tris(1-butyl)tin(IV) Naphthoates and Hydroxynaphthoates **1a**–**1e**

The chemical shift values $\delta(^{119}Sn)$ of compounds **1a**–**1e** in deuteriochloroform solutions (110.7–133.3 ppm) (Table VII) are typical of tris(1-butyl)tin(IV) compounds with the coordination number 4 at the central tin atom[13]. The coupling constant values $^1J(^{119}Sn,^{13}C)$ in the range of 352.4–358.8 Hz (Table VII) correspond to the magnitude of bond angles C–Sn–C of about 111° (ref.[14]). The values of chemical shifts $\delta(^{13}C)$ of carboxylic groups of compounds **1a**–**1e** are very close to the *average* values of the same parameters in the ^{13}C NMR spectra of organic esters **6a**–**6e** and sodium salts **5a**–**5e** of the respective naphthoic or hydroxynaphthoic acids (Table V) which – with a certain amount of caution – can be considered prototypes of mono- or bidentately bound carboxylic groups. Hence in compounds **1a**–**1e** the carboxylic groups are bound

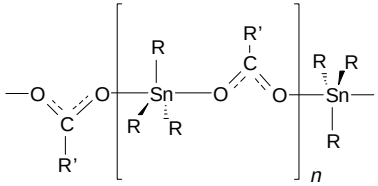
to tin atom either monodentately (see the $\delta(^{119}Sn)$ values) or more probably anisobidentately with a certain slight participation of bonding interaction between tin atom and carbonyl group oxygen atom. In principle the same conclusion about the way of bonding linkage between carboxylic group and tin atom can be made[15] from the comparison of values of valence vibrations $\nu_a(COO)$ and $\nu_s(COO)$ or their difference $\Delta\nu(COO)$ in the respective compounds **1**, **5** and **6** (Table VIII). Hence when dissolved in a noncoordinating solvent, compounds **1a**–**1e** are present either as more or less isolated monomeric (Table I) pseudotetrahedral molecules (*I*(*A*)) or as strongly deformed *cis*-trigonally bipyramidal molecular complexes with anisobidentate chelate carboxylic group (*I*(*B*)). The very close parameters of infrared spectra in chloroform solutions and paraffin suspensions of compounds **1a**–**1e** allow us to exclude the existence of polymeric forms of crystals of these compounds (*I*(*C*)) and hence to state that the crystals of compounds **1a**–**1e** are of molecular nature, being composed of the same particles as those occurring in solutions of noncoordinating solvents.



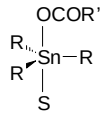
I(A)



I(B)



I(C)



I(D)

R = 1-C_4H_9, S = a molecule of coordinating solvent

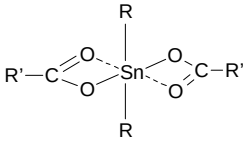
R' = 1-$C_{10}H_7$, 2-$C_{10}H_7$, 1-OH-2-$C_{10}H_6$, 2-OH-1-$C_{10}H_6$, 3-OH-2-$C_{10}H_6$

The general upfield shift in $\delta(^{119}Sn)$ values (Table VII) (values from –8.1 to –19.5 ppm are typical of pentacoordinated tris(1-butyl)tin(IV) compounds[13]) accompanying the change from deuteriochloroform solutions to solutions in the coordinating solvent hexadeuteriodimethyl sulfoxide is caused by the formation of donor–acceptor complexes of compounds **1a**–**1e** with one molecule of this solvent (*I*(*D*)). The coupling constant values $^1J(^{119}Sn,^{13}C)$ in the range of 470.4–485.5 Hz, corresponding to bond angles of about 122° (ref.[14]), indicate that the 1-butyl substituents in these complexes assume equatorial positions in *trans*-bipyramidal arrangement of bond partners of tin atom. The upfield shift of $\delta(^{13}C)$ values of carboxylic groups with the same change in solvents (Table VI) stands in accordance with the idea of a replacement at one coordination position in the polyhedron around tin atom: in deuteriochloroform solutions this posi-

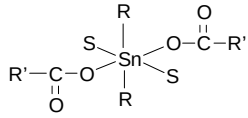
tion is probably occupied (see above) by the oxygen atom of carbonyl group which is bound to the tin atom by a weaker bond (the anisobidentate chelate function of carboxylic group in naphthoic or hydroxynaphthoic acids), whereas in a coordinating solvent this position is occupied by the solvent donor atom.

Bis(1-butyl)tin(IV) Dinaphthoates and Bis(hydroxynaphthoates) **2a**–**2e**

The solutions of compounds **2a**–**2e** in deuteriochloroform exhibit the chemical shifts $\delta(^{119}Sn)$ in the range from –122.1 to –151.5 ppm (Table VII) which is a region of occurrence of $\delta(^{119}Sn)$ values of complexes of bis(1-butyl)tin(IV) compounds with the coordination number around the tin atom equal to five (trigonal bipyramid) or four plus two (deformed octahedron, or better, a trapezoidal bipyramid with four strong and two somewhat weaker bonds)[16]. The $\delta(^{13}C)$ chemical shift values of carboxyl groups in these compounds (Table V), which are practically identical with, or even higher than, the same parameters of the carboxylate anions, rather indicate the second eventuality, which is also supported by the magnitudes of bond angles of about 130–134° calculated[14] from the coupling constants $^1J(^{119}Sn,^{13}C)$ (553.6–594.1 Hz) (Table VII) as well as by the fact that always only one set of signals was found in both the ^1H and the ^{13}C NMR spectra for both naphthoate or hydroxynaphthoate groups. All compounds **2a**–**2e** are present in solutions in noncoordinating solvents as monomeric particles (Table I), hence the bidentate carboxyl groups form a chelate bond with the tin atom (*II*(*A*)).



II(A)



II(B)

R = 1-C_4H_9, S = a molecule of coordinating solvent

R' = 1-$C_{10}H_7$, 2-$C_{10}H_7$, 1-OH-2-$C_{10}H_6$, 2-OH-1-$C_{10}H_6$, 3-OH-2-$C_{10}H_6$

From the parameters of infrared spectra of these compounds in paraffin suspensions (Table VIII) it cannot be unequivocally decided what is the nature of bond link between carboxyl groups and tin atom in crystals of compounds **2a**–**2e**. Bidentate carboxyl groups occur both in molecular crystals composed of the same particles as those found in solutions in noncoordinating solvents and in polymeric macromolecular three-dimensional crystals in which they serve as bridges between two neighbouring tin atoms. Both the types of crystals have been described in literature[5]. With regard to the striking agreement between the IR spectral parameters of the discussed compounds in chloro-

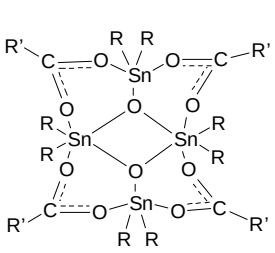
form solutions and in paraffin suspensions we are inclined to accept the first eventuality; for that matter, this eventuality distinctly predominates among the structures of diorganotin(IV) dicarboxylates described so far[5].

The values of $\delta(^{119}Sn)$ chemical shifts of compounds **2a**–**2e** in hexadeuteriodimethyl sulfoxide solutions (–262.5 to –318.3 ppm) (Table VII) are characteristic of complexes of bis(1-butyl)tin(IV) compounds with the coordination number at the tin atom equal to six[16]. Hence, compounds **2a**–**2e** dissolved in a coordinating solvent form complexes with two molecules of the solvent which are bound to the tin atom by their donor atom at a position which is occupied – in the deuteriochloroform solutions – by the less strongly bound oxygen atom of the chelate anisobidentate carboxyl group (*II*(*B*)). The destruction of chelate arrangement on going from a noncoordinating solvent to a coordinating one is accompanied – *inter alia* – by an upfield shift in the $\delta(^{13}C)(COO)$ values (Tables V and VI) *i.e.* in the direction toward values characteristic of the monodentately bound carboxyl group. In such a pseudooctahedral arrangement of the bonding partners of tin atom there also takes place an opening of C–Sn–C bond angles. The C–Sn–C bond angles calculated from the coupling constant values $^1J(^{119}Sn,^{13}C)$ (881.5–889.7 Hz) (Table VII) are about 165° (ref.[14]).

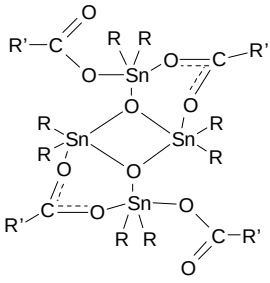
Tetrakis(1-butyl)dinaphthoato- and Tetrakis(1-butyl)bis(hydroxynaphthoato)-distannoxanes **3a**–**3e**

From the results of cryoscopic measurements (Table I) it follows that compounds **3a**, **3b** and **3e** are present as dimeric isolated molecules if dissolved in a noncoordinating solvent (benzene) (compounds **3c** and **3d** are not sufficiently soluble in benzene). According to the results obtained by analysis of ^1H, ^{13}C and ^{119}Sn NMR spectra of deuteriochloroform solutions (Tables II, III, V, VII), compounds **3a**–**3e** contain two pairs of structurally different bis(1-butyl)tin(IV) groups and four equivalent naphthoate or hydroxynaphthoate groups. The $\delta(^{119}Sn)$ values of both the $(1\text{-}C_4H_9)_2Sn$ groupings in all compounds **3a**–**3e** (–188.9 to –213.4 ppm) are characteristic of complexes of bis(1-butyl)tin(IV) compounds with the coordination number of the central tin atom equal to five or four plus two[16]. The magnitudes of C–Sn–C bond angles in compounds **3a** and **3b** calculated from the coupling constant values[14] $^1J(^{119}Sn,^{13}C)$ (694.0 to 739.4 Hz) are about 145° (it was not possible to determine the coupling constants $^1J(^{119}Sn, ^{13}C)$ of compounds **3c**–**3e**). Hence the environment of tin atom has a shape of strongly deformed trigonal bipyramid or strongly deformed octahedron (*skew*-trapezoidal bipyramid). These results fully agree with the common basic feature of all the so far known structures of tetraorganodicarboxylatodistannoxanes, *viz.* the existence of dimeric unit $R_8Sn_4O_2$ (R = organic residue) built around the four-membered cyclic nucleus Sn_2O_2 whose tin atoms are connected with other two (external) tin atoms by means of the oxygen atoms. Each of the tin atoms carries two R groups. The structures known so far only differ by the way of linking of carboxylate ligands to this fragment. According to the

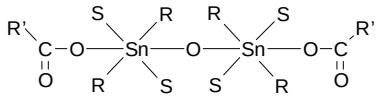
$\delta(^{13}C)$(COO) values of compounds **3c**–**3e**, which are identical with, or even higher than, the same values of alkali salts of the respective acids (compounds **5c**–**5e**) (Table V), as well as according to the $\Delta\nu$ values (Table VIII), the carboxyl groups in these compounds are bound bidentately, the two oxygen atoms of a carboxyl group forming a bridge between one cyclic and one external tin atoms (*III*(*A*)).



III(A)



III(B)



III(C)

R = 1-C_4H_9, S = a molecule of coordinating solvent

R' = 1-$C_{10}H_7$, 2-$C_{10}H_7$, 1-OH-2-$C_{10}H_6$, 2-OH-1-$C_{10}H_6$, 3-OH-2-$C_{10}H_6$

The pairs of bands due to valence vibrations ν_a and ν_s and the $\delta(^{13}C)$(COO) values of compounds **3a** and **3b**, which are lower than the corresponding values of compounds **5a** and **5b**, probably indicate that one part of carboxyl groups (probably one half according to the integral intensities of bands in the infrared spectra) in particles of these organotin(IV) compounds are bound monodentately, whereas the other part is bound bidentately (*III*(*B*)). The existence of only one signal in ^{13}C NMR spectra for the carboxyl group in this case would be due to rapid (in the NMR time scale) exchange between mono- and bidentate carboxyl groups. The low value of $\delta(^{13}C)$(COO) chemical shifts would naturally be an *average* value of the same parameters for both types of differently bound carboxyl groups[17]. Both these structural motives have already been proved several times in molecular crystals of tetraorganodicarboxylatodistannoxanes[5].

In contrast to the deuteriochloroform solutions, compounds **3c**–**3e** dissolved in hexadeuteriodimethyl sulfoxide (compounds **3a** and **3b** are not sufficiently soluble in this solvent) exhibit only one signal in the ^{119}Sn NMR spectrum and only one set of signals in the ^1H and ^{13}C NMR spectra, both for the 1-butyl substituents and for hydroxynaphthoate groups (Tables II, IV, VI, VII). The $\delta(^{119}Sn)$ values of compounds

3c–**3e** dissolved in this solvent (–270.3 to –275.7 ppm) are typical of hexa-coordinated bis(1-butyl)tin(IV) compounds. The upfield shift in $\delta(^{13}C)$(COO) values (Tables V and VI) as compared with the same values found in deuteriochloroform indicates a decreasing denticity of carboxyl groups. The changes in character of ^{1}H, ^{13}C and ^{119}Sn NMR spectra, the increase in coordination number of central tin atom, and the decrease in denticity of carboxyl groups on going from a noncoordinating solvent to a coordinating one are obviously caused by a molecule of coordinating solvent entering the coordination sphere of tin atom in such a way that the solvent molecules assume not only free coordination positions but also the positions of less strongly bound oxygen atoms of carbonyl group in bridging carboxylate ligands and the oxygen atoms in Sn_2O_2 cycle. In this way, at the same time the dimeric character of original molecules disappears. Hence the tin atom of monomeric particles of these compounds is surrounded in pseudooctahedral way by two 1-butyl substituents, one monodentate COO group of hydroxynaphthoate torso, an oxygen atom of Sn–O–Sn grouping, and two solvent molecules (*III*(*C*)). In this coordination polyhedron the 1-butyl groups form a C–Sn–C angle of 150° (ref.[14]) (the $^{1}J(^{119}Sn,^{13}C)$ values of 747.0–785.5 Hz). The idea of monomeric character of particles of these compounds in a coordinating solvent is also supported by the fact that the molecular weight of compound **3e** determined in (slightly coordinating) camphor is substantially lower that that measured in (noncoordinating) benzene (Table I).

Bis(1-butyl)chlorotin(IV) Compounds **4a**–**4e**

According to chemical shift values $\delta(^{119}Sn)$ (0.3 to –33.4 ppm) and coupling constants $^{1}J(^{119}Sn,^{13}C)$ (491.2 to 522.4 Hz; C–Sn–C bond angles about 125°) (Table VII), the bis(1-butyl)chlorotin(IV) compounds dissolved in deuteriochloroform are present as simple molecular complexes with the coordination number of the central tin atom equal to five and with a *cis*-trigonally bipyramidal geometry in its neighbourhood. Two of the coordination positions in this arrangement are occupied by oxygen atoms of (aniso)bidentate chelate carboxyl group of naphthoate or hydroxynaphthoate ligands as it follows from the $\delta(^{13}C)$ values of carboxyl groups, which are mostly very close to the corresponding values of alkali salts of the respective acids (Table V). The upfield shift in $\delta(^{119}Sn)$ values (–206.1 to –329.2 ppm for compounds **4a** and **4b**) (Table VII) into a region typical of hexa-coordinated bis(1-butyl)tin(IV) compounds, and the upfield shift in $\delta(^{13}C)$ values of carboxyl groups on going from the original solvent to the coordinating hexadeuteriodimethyl sulfoxide (Table VI) indicate formation of complexes of compounds **4a**–**4e** with two solvent molecules with concomitant disappearance of chelate bond in the original compounds. In the new complexes the 1-butyl groups form angles of *ca* 140°, hence the resulting shapes of coordination polyhedrons of these complexes can be considered as trapezoidal bipyramides.

CONCLUSION

The tris(1-butyl)tin(IV) naphthoates and hydroxynaphthoates studied in the present paper are present in solutions of noncoordinating solvents as monomeric isolated pseudotetrahedral molecules or as strongly deformed *cis*-trigonally bipyramidal complexes with anisobidentate chelate carboxyl group. The same particles also form their molecular crystals. In solutions of coordinating solvents these compounds form *trans*-trigonally bipyramidal complexes with one solvent molecule. Bis(1-butyl)tin(IV) dinaphthoates and bis(hydroxynaphthoates), which form monomeric chelate *skew*-trapezoidally bipyramidal complexes in solutions of noncoordinating solvents and probably also in solid state, react with two molecules of coordinating solvent to give complexes in which the positions of carbonyl oxygen atoms of chelate carboxyl groups of original compounds are assumed by donor atoms of solvent. Similar changes in function of carboxyl group and structure of coordination sphere of tin atoms, and formation of complexes with two molecules of coordinating solvent at tin atom take place also in tetrakis(1-butyl)bis(hydroxynaphthoato)distannoxanes and bis(1-butyl)chlorotin naphthoates. In the former case the reaction with a coordinating solvent also leads to monomerization of the original dimeric structural units.

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REFERENCES

1. Blunden S. J., Cussack P. A., Hill R.: *The Industrial Use of Tin Compounds*. Royal Society of Chemistry, London 1985.
2. Gielen M., Lilieveld P., de Vos D., Willem R. in: *Metal-Based Antitumor Drugs* (M. Gielen, Ed.), Vol. 2, p. 29. Freund Publishing House, Tel Aviv 1992.
3. Zubieta J. A., Zuckerman J. J. in: *Progress in Inorganic Chemistry* (S. J. Lippard, Ed.), Vol. 24, p. 251. Wiley, New York 1978.
4. Cussack P. A., Smith P. J., Donaldson J. D., Grimes S. M.: *A Bibliography of X-Ray Crystal Structures of Tin Compounds*. Publication No. 588, International Tin Research Institute, Uxbridge 1984.
5. Tiekink E. R. T.: Trends Organomet. Chem. *1*, 71 (1994); and references therein.
6. Dunn P., Norris T.: Australia, Commonwealth, Dept. Supply, Defence Std. Lab., Rept. *269*, 21 (1994); Chem. Abstr. *61*, 3135 (1994).
7. Manral D., Shah R., Chandra M.: Chim. Acta Turc. *21*, 229 (1993).
8. Manral D., Chandra M.: Asian J. Chem. *6*, 514 (1993).
9. Begley M. J., Sowerby P. B., Kapoor P., Kapoor R.: Polyhedron *14*, 1937 (1995).
10. Davies A. G., Smith P. J. in: *Comprehensive Organometallic Chemistry* (G. Wilkinson, Ed.), Vol. 2, Chapter 11, p. 519. Pergamon Press, Oxford 1984.
11. Boualam M., Willem R., Gelan J., Sebald A., Lilieveld P., de Vos D., Gielen M.: Appl. Organomet. Chem. *4*, 335 (1990).
12. Gielen M., Vanbellinghen C., Gelan J., Willem R.: Bull. Soc. Chim. Belg. *97*, 873 (1988).

13. Nadvornik M., Holecek J., Handlir K., Lycka A.: J. Organomet. Chem. *275*, 43 (1984).
14. Holecek J., Lycka A.: Inorg. Chim. Acta *118*, L15 (1986).
15. Deacon G. B., Phillips R. J.: Coord. Chem. Rev. *33*, 227 (1980).
16. Holecek J., Nadvornik M., Handlir K., Lycka A.: J. Organomet. Chem. *315*, 229 (1986).
17. Tiekink E. R. T., Gielen M., Bouhdid A., Biesemans M., Willem R.: J. Organomet. Chem. *494*, 247 (1995).