INFRARED AND ^{13}C, ^{15}N AND ^{119}Sn NMR SPECTRAL STUDY OF SOME TRI- AND DIORGANOTIN(IV) PYRIDINECARBOXYLATES

Tomáš LÉBL[a], Jaroslav HOLEČEK[a] and Antonín LYČKA[b]
[a]Department of General and Inorganic Chemistry
[b]Research Institute of Organic Syntheses, Pardubice-Rybitví

Eleven organotin(IV) pyridinecarboxylates of general formula $R_3SnOOCR'$ and $R_2Sn(OOCR')_2$ where R is 1-butyl or phenyl and R' is 2-, 3- or 4- pyridyl were prepared. Structures of these compounds in the solid state and in solutions of non-coordinating solvent ($CDCl_3$) and coordinating solvent (($CD_3)_2SO$) were studied using IR spectroscopy, multinuclear (^{13}C, ^{15}N, ^{119}Sn) NMR spectroscopy and ^{119}Sn CP MAS spectroscopy.

Introduction

We have been interested in the study of synthesis, properties, structure and reactivity of organotin(IV) compounds for severel years. The diagnostic method which enables to judge the structures of organotin(IV) compounds both in the solid state and in solutions of various types of solvents using the parameters of multinuclear NMR spectroscopy[1] was also developed here. At present our research is oriented to organotin(IV) compounds with cancerostatic effects. The basic approach consists of sythesis of chosen series of compounds and study of the relations of their structures and properties both in solutions of various types

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of solvents and in the solid state. The target is to complete the data of systematic research which would explain the relation between structure and composition of organotin(IV) compounds and their antitumor activity in the future.

Lately a series of works describing the great antitumor activity of tri- and diorganotin(IV) carboxylates has appeared[2-8]. One interesting group of organotin(IV) compounds of this type are organotin(IV) pyridinecarboxylates. The structure of triorganotin(IV) $R_3SnOOCR'$ and diorganotin(IV) $R_2Sn(OOCR')_2$ 2-pyridine, 3-pyridine and 4-pyridinecarboxylates, i.e. picolinates (pic), nicotinates (nic) and (isonicotinates (inic), where R is 1-butyl (Bu) or phenyl (Ph) and R' is 2-, 3- or 4-pyridyl

$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-$$

R = Bu   R = Ph   R'
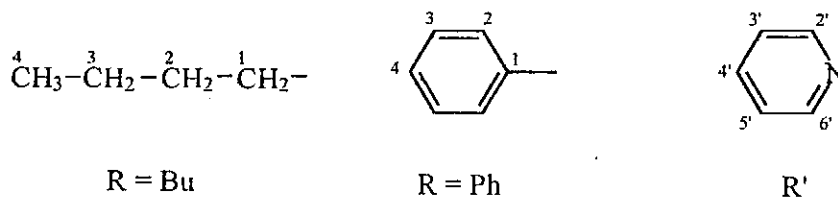
in the solid state and in solutions of various types of solvents was studied. Infrared spectroscopy and multinuclear (^{13}C, ^{15}N and ^{119}Sn) NMR were used as the experimental techniques to study the structures in both aggregation states.

It is necessary to mention that at present already exists a relatively considerable amount of information on structures of these compounds in solid state obtained either by using direct diffraction methods[9-11] or indirectly - on the basis of analysis and interpretation of Mössbauer, infrared and Raman spectra[12-19]. Especially in the last time, particular attention has been also paid to the structures of species of these compounds in solutions of various types of solvents[16-20]. The data are however isolated, most of them were obtained under different experimental conditions, most of them are incomplete and sometimes also unreliable. Whole set of these literary data is sufficient enough neither for any generalising nor for deeper mutual comparison.

Experimental

All the triorganotin(IV) pyridinecarboxylates studied (except for triphenyltin(IV) α-picolinate and diorganotin(IV) bis(picolinate) were prepared by the reaction of pyridinecarboxylic acid and organotin(IV) hydroxide (or oxide) in boiling benzene[13]. Triphenyltin(IV) picolinate and diorganotin(IV) bis(nicotinate) were prepared by reaction of organotin(IV) chloride with sodium salt of pyridine-carboxylic acid (from sodium methoxide and pyridinecarboxylic acid) in methanol cooled to 0 °C[13]. Dibutyltin(IV) bis(isonicotinate) was prepared by

reaction of dibutyltin(IV) dichloride with silver isonicotinate in acetone at laboratory temperature under inert atmosphere of argon. Diphenyltin(IV) bis(isonicotinate) was not prepared at all (it is most probably unstable and readily hydrolysed). Most of the prepared compounds were identified on the basis of melting points described in literature[12-17]. Other compounds were identified by elementary analyses and infrared and NMR spectra (see below).

The compounds Ph_3Snpik and $Bu_2Sninik_2$ are unstable. Triphenyltin(IV) picolinate disproportionates to diphenyltin(IV) bis(picolinate) and tetraphenyl-stannane. Dibutyltin(IV) bis(isonicotinate) hydrolyses very easily. Both these compounds were not prepared in pure state and were only identified by NMR spectroscopy in the reaction mixture

Table I   Analytical and physical data of compounds Bu_2Snnic_2, Ph_2Snnic_2, Ph_3Snnic and $Ph_3Sninic_2$

Compound	Found (Calculated)				Melting point
	% C	% H	% N	% Sn	°C
Bu_2Snnic_2	50.46	5.73	6.12	24.53	150 dec[a]
	(50.35)	(5.49)	(5.87)	(24.88)	
Ph_2Snnic_2	54.17	3.56	6.64	22.75	160 dec[a]
	(55.75)	(3.51)	(5.42)	(22.95)	
Ph_3Snnic	61.18	4.31	3.17	25.29	186 - 188
	(61.11)	(4.07)	(2.97)	(25.16)	
$Ph_3Sninic_2$	61.06	3.95	3.19	25.02	199 - 200
	(61.11)	(4.07)	(2.97)	(25.16)	

[a] Found by DTA. Decomposition is not combined with melting of the compound

The infrared spectra were measured using a Perkin-Elmer 684 apparatus. The samples were measured as liquid films, in the solid state (Nujol suspension) and in solution of $CHCl_3$.

The NMR spectra of studied compounds were measured in solutions of $CDCl_3$, $(CD_3)_2SO$ and D_2O at 300 K using a Bruker AMX 360 apparatus. The ^{13}C (90.566 MHz) and ^{119}Sn (134.29 MHz) NMR spectra were measured in a 5 mm multinuclear tuneable probe and the ^{15}N (36,501 MHz) in a 10 mm multinuclear tuneable probe. The ^{13}C chemical shifts were referred to the appropriate signals of solvents (δ = 77.0 ($CDCl_3$) and 39.60 (($CD_3)_2SO$)) and recalculated to δ-scale. Internal dioxane (δ = 66.46) was used as the standard for the ^{13}C NMR spectra in D_2O. The ^{119}Sn chemical shifts were referred to external tetramethyl-stannane (δ = 0.0). The ^{15}N NMR spectra were measured using INEPT

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technique (Insensitive Nuclei Enhanced by Polarisation Transfer). When this technique could not be used, the ^{15}N NMR spectra were measured in standard way using inverse-gated mode. The ^{15}N chemical shifts were referred to external nitromethane (δ = 0.0). The ^{119}Sn CP MAS NMR spectra were run on a Bruker MSL 300 instrument using double bearing probes.

Results

NMR spectra

[119]Sn Chemical Shifts

Table II presents the $\delta(^{119}\text{Sn})$ values of studied compounds in the solid state and in solutions of non-coordinating solvent deuteriochloroform ($CDCl_3$) and coordinating solvent hexadeuteriodimethyl sulfoxide ($(CD_3)_2SO$). These values demonstrate that

a) the [119]Sn chemical shifts of all tributyltin(IV) pyridinecarboxylates in the solution of non-coordinating solvent $CDCl_3$ (108.8 ; 85.6 ; 96.5 ppm) are close to chemical shifts $\delta(^{119}\text{Sn})$ that is typical of tributyltin(IV) compounds with the coordination number of central tin atom equal to four[21]. The [119]Sn chemical shifts of these compounds in the solid state are situated in the limits from -38.9 to -63.4 ppm. So they show the $\delta(^{119}\text{Sn})$ upfield shift from 136.0 to 172.2 ppm as compared with the values in the $CDCl_3$ solution into the region of values that are characteristic of the coordination number equal to five. It means that while the central tin atoms of these compounds in the solution of deuteriochloroform are tetracoordinated and exist in distorted tetrahedral geometry, the Sn atoms exist in trigonal bipyramidal geometry in the solid state. Increasing coordination of the central tin atom at the transition from deuteriochloroform solutions to the solid state, which is connected to $\delta(^{119}\text{Sn})$ shift, is also supported by the finding that the values of this parameter shift in the same direction while replacing the non-coordinating solvent $CDCl_3$ by coordinating solvent $(CD_3)_2SO$. However, in these cases the $\delta(^{119}\text{Sn})$ upfield shift, being from 104.5 to 127.0 ppm, is not so distinct, which is the result of equilibrium formation of complex according to the equation

$$R_3SnOOR' + ((CD_3)_2SO) \rightleftharpoons R_3SnOOCR'.((CD_3)_2SO)$$

$$\text{coord. n. 4} \qquad\qquad \text{coord. n. 5}$$

(1)

which is not completely shifted to the side of products.

It is necessary to say that two signals at -38.9 ppm and -50.4 ppm with approximately identical integral intensities appear in the CP MAS spectrum of compound Bu_3Snnic, which agrees with the presece of two not very different isomer structures of trigonal bipyramidal surrounding of the central tin atom.

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This can be caused by different mutual orientation of the butyl groups in the crystal. These cases have already been described[22-23].

b) the central tin atoms of triphenyltin(IV) pyridinecarboxylates in solutions of non-coordinating solvent $CDCl_3$ exist also in distorted tetrahedral geometry according to the $\delta(^{119}Sn)$ values from -109.3 to -131.2 ppm[24]. However, the $\delta(^{119}Sn)$ values are near to the upper limit of the region typical of this coordination of triphenyltin(IV) compounds (from -40 to -120 ppm). Ph_3Snpic compound even slightly surpasses this limit. It is at least impossible to eliminate the very weak intra- or intermolecular interaction of tin atom with its ligand's donor atoms. The compounds Ph_3Snnic and $Ph_3Sninic$ in solid state exhibits the $\delta(^{119}Sn)$ upfield shift of 151.5 and 144.8 ppm, respectively, into the region typical of penta-coordinated triphenyltin(IV) compounds. The compounds Ph_3Snnik and $Ph_3Sninik$ in the solution of coordinating solvent $((CD_3)_2SO)$ form complex species according to the equation (1) analogous to tributyltin(IV) pyridinecarboxylates. It is interesting to note that the $\delta(^{119}Sn)$ values of these triphenyltin(IV) pyridinecarboxylates in solid state and in the $((CD_3)_2SO)$ solution are practically corresponding with each other so that the equilibrium (1) with triphenyltin(IV) compounds is more distinctly shifted to the side of products than that of tributyltin(IV) compounds.

c) dibutyltin(IV) pyridinecarboxylates in the $CDCl_3$ solution have $\delta(^{119}Sn)$ values in the region typical of this type of compounds with coordination number equal to six[25]. (The compound $Bu_2Sninik_2$ even has two signals with the values of chemical shift $\delta(^{119}Sn)$ -205.0 and -209.9 ppm and with the ratio of integral intensity 1:1. However, this fact is impossible to interpret at present). In all the cases the coordination number six found in the molecules of these compounds in the solution of non-coordinating solvent, nevertheless, means that appropriate ligands have the bidentate function and form chelates. In the case of compound Bu_2Snnic_2, replacing of non-coordinating solvent ($CDCl_3$) by coordinating solvent $((CD_3)_2SO)$ is only accompanied by a small change in the $\delta(^{119}Sn)$ value 62.7 ppm which is probably connected with the destruction of chelate in the molecule of this compound and with simultaneous substitution of two coordination places in the original chelate by two molecules of coordinating solvent. The replacing of the types of solvents in the compound Bu_2Snpic_2 is connected with the $\delta(^{119}Sn)$ upfield shift of 161.6 ppm which is the value corresponding to the unit of coordination number. It means that the original chelate structure is preserved in this case and one molecule of solvent comes into the coordination sphere of the central tin atom. The tin atom should be hepta-coordinated in this case according the value of $\delta(^{119}Sn)$ = -467.6 ppm.

d) The ^{119}Sn chemical shift of compound Ph_2Snpic_2 in the non-coordinating solvent $CDCl_3$ is -427.2 ppm. The value of the same parameter obtained by measuring CP MAS in solid state is -411.7 ppm. The difference between these values is only 15.5 ppm, which means that this compound probably forms monomer species with the coordination number equal to six[27], both in the deuteriochloroform solution and in solid state. So the picolinate ligand should

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have the bidentate function in both cases. The $\delta(^{119}\text{Sn})$ upfield shift of 182.3 ppm caused by replacing the non-coordinating solvent ($CDCl_3$) by coordinating solvent (($CD_3)_2SO$) corresponds to the change in coordination number from six to seven. The coordination number equal to seven indicates that the original chelate structure remains preserved and one molecule of solvent comes into the coordination sphere of tin atom. The compound Ph_2Snnic_2 is insoluble in all common coordinating and non-coordinating solvents.

Table II $\delta(^{119}\text{Sn})$ values of studied compounds

Compound	$\delta(^{119}\text{Sn})$, ppm		
	Solid state[a]	$CDCl_3$ solution	$(CD_3)_2SO$ solution
Bu_3Snpic	-63.4	108.8	-18.2
Bu_3Snnic	-38.9; 50.4	85.6	-18.9
$Bu_3Sninic$	-58.2	96.5	-22.1
Ph_3Snpic	-	-131.2	-
Ph_3Snnic	-260.8	-109.3	-257.5
$Ph_3Sninic$	-256.2	-111.4	-257.9
Bu_2Snpic_2	-	-306.0	-467.6
Bu_2Snnic_2	-	-232.3	-295.0
$Bu_2Sninic_2$	-	-205.0; -209.9	-
Ph_2Snpic_2	-411.7	-427.2	-609.5

[a]Ref.[26]

^{13}C NMR Spectra Parameters

The parameters of the ^{13}C NMR spectra are given in Tables III - VI. The complete assigning of signals confirms the identity of compounds. The coupling constants $^1J(^{119}\text{Sn}, ^{13}C)$ and chemical shifts $\delta(^{13}C)(COO)$ are the most important for structure evaluation.

The coupling constants $^1J(^{119}\text{Sn}, ^{13}C)$ of organotin compounds correlate with the values of the interbond angle C-Sn-C (angle θ)[28,29]. The values of this parameter (Tab. III and V) demonstrate the following facts:
a) the coupling constants $^1J(^{119}\text{Sn}, ^{13}C)$ of three studied tributyltin(IV) pyridinecarboxylates in the deuteriochlorofom solutions lie in the relative narrow limits from 355.5 to 372.7 Hz which correspond to the average values of angles θ 110-112°. These values are only slightly higher than those corresponding to

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ideal tetrahedral angle confirming the pseudotetrahedral geometry of central tin atom. The coupling constants $^1J(^{119}Sn, ^{13}C)$ of tributyltin(IV) pyridinecarboxylates in the solution of coordinating solvent $(CD_3)_2SO$ are 479.0-482.7 Hz, which corresponds to angles θ 122-123°. These angles are near to those in equilateral triangle and, hence, well fulfil the idea of complexes of these compounds with one molecule of solvent having *trans*-trigonal bipyramidal geometry. In the coordination polyhedra of these compounds, the butyl substituents form the equatorial plane, and the apical places are occupied by donor atoms of pyridinecarboxylate group and molecule of solvent. Approximately the same conclusion can be made about triphenyltin(IV) pyridinecarboxylates whose coupling constants $^1J(^{119}Sn, ^{13}C)$ in the deuterio-chloroform solutions are almost conforming (from 653.4 to 656.8 Hz). The corresponding angles are approximately 116°. The coupling constants $^1J(^{119}Sn, ^{13}C)$ of the compounds Ph_3Snnic and $Ph_3Sninic$ in the $(CD_3)_2SO$ solution (from 653.4 to 656.8 Hz) correspond approximately to the angle of 120°.

b) The coupling constants $^1J(^{119}Sn, ^{13}C)$ of hexacoordinated butyltin(IV) pyridinecarboxylates (Bu_2Snpik_2 and Bu_2Snnik_2 in $CDCl_3$ solution and complex of Bu_2Snnik_2 in $(CD_3)_2SO$) are 615.5 - 842.0 Hz so that the angles which are clasped by the carbon atoms C(1) of both butyl substituents are 136-158°. Hence, the central tin atoms of these compounds exist in the trapezoidal bipyramidal (skew) geometry. The central tin atom of heptacoordinated complex $Bu_2Snpik_2.(CD_3)_2SO$) obviously exists in *trans*-pentagonal bipyramidal geometry with the butyl substituents in the *trans*-positions ($^1J(^{119}Sn, ^{13}C)$ = 1068.8; θ = 181°). The compound Bu_2Snpik_2 has the coupling constant $^1J(^{119}Sn, ^{13}C)$ 953.6 Hz. This value of coupling constant corresponds to the angle θ 135°, which indicates the trapezoidal bipyramidal (skew) geometry of central tin atom.

The values of chemical shift $\delta(^{13}C)(COO)$ (Tables IV and VI) reflect the structure and the way of bonding connection of carboxylate group with central tin atom. The organic esters of appropriate pyridinecarboxylic acids can be the prototypes of monodentately bonded COO group and the alkali salts of these acids can be used as models of bidentate group COO. Ethyl picolinate, nicotinate and isonicotinate have the values of chemical shift $\delta(^{13}C)(COO)$ in the range of 164.27 - 164.66 ppm, while the values of this parameter of sodium pyridinecarboxylates are shifted downfield by 7 ppm (173.28 - 173.86 ppm). The values $\delta(^{13}C)(COO)$ of the organotin(IV) compounds studied are between these two limits and the actual values in this range can be used as the rate of denticity of carboxylate group.

a) The values of chemical shift $\delta(^{13}C)(COO)$ of compounds Bu_2Snpik_2 and Ph_2Snpik_2 in both types of solvents (165.50 and 164.53 ppm) approach the value of chemical shift $\delta(^{13}C)(COO)$ of ethyl picolinate (164.66 ppm), hence these compounds have the monodentate carboxylate groups in both types of solvents.

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Table III ^{13}C NMR parameters of butyl and phenyl substituents in triorganotin(IV) pyridinecarboxylates studied

Compound	δ(^{13}C), [ppm]/(J(^{119}Sn, ^{13}C), [Hz])			
(Solvent)	C (1)	C (2)	C (3)	C (4)
Bu₃Snpic				
(CDCl₃)	16.60	27.08	26.28	12.84
	(364.6)	(20.1)	(67.8)	
(CD₃)₂SO	18.84	27.81	26.61	13.63
	(479.0)	(27.4)	(76.3)	
Bu₃Snpic				
(CDCl₃)	16.71	27.78	26.97	13.59
	(355.5)	(20.8)	(65.0)	
(CD₃)₂SO	18.63	27.72	26.44	13.55
	(479.5)	(27.9)	(72.6)	
Bu₃Sninic				
(CDCl₃)	16.86	27.67	26.78	13.62
	(372.7)	(22.3)	(65.6)	
(CD₃)₂SO	18.61	27.62	26.32	13.53
	(482.7)	(28.0)	(73.7)	
Ph₃Snpic				
(CDCl₃)	137.91	136.61	128.76	129.87
	(624.0)	(48.5)	(64.6)	
Ph₃Snnic				
(CDCl₃)	137.89	136.84	128.98	130.29
	(653.8)	(48.0)	(64.0)	(13.3)
(CD₃)₂SO	143.23	136.49	128.58	129.18
	(835.9)	(45.6)	(69.8)	(14.6)
Ph₃Sninic				
(CDCl₃)	137.78	136.85	129.05	130.38
	(656.8)	(47.9)	(65.0)	(13.4)
(CD₃)₂SO	142.87	136.16	128.30	128.91
	(836.0)	(45.7)	(70.0)	(13.4)

ᵃ The NMR spectrum (CD₃)₂SO was not measured. The compound decomposes during dissolving

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Table IV Chemical shifts $\delta(^{13}C)$ of pyridinecarboxylate groups in triorganotin(IV) pyridinecarboxylates studied

Compound (Solvent)	$\delta(^{13}C)$, [ppm]					
	(COOH)	C (2')	C (3')	C (4')	C (5')	C (6')
Bu$_3$Snpic						
(CDCl$_3$)	168.60	149.13	128.27	136.12	125.27	148.27
(CD$_3$)$_2$SO	168.44	152.72	124.16	136.55	125.18	148.85
Bu$_3$Snnic						
(CDCl$_3$)	169.12	151.5	128.03	137.54	123.03	152.34
(CD$_3$)$_2$SO	167.87	150.43	130.32	136.55	123.12	151.40
Bu$_3$Sninic						
(CDCl$_3$)	169.14	149.70	123.58	140.33	123.58	149.70
(CD$_3$)$_2$SO	167.61	149.95	122.87	142.36	122.87	149.95
Ph$_3$Snpic						
(CDCl$_3$)	168.48	148.28	125.38	139.67	126.78	148.24
Ph$_3$Snnic						
(CDCl$_3$)	170.73	151.76	126.94	137.93	123.04	152.83
(CD$_3$)$_2$SO	168.07	150.70	130.13	136.99	123.56	152.02
Ph$_3$Sninic						
(CDCl$_3$)	170.40	150.24	123.84	138.71	123.84	150.24
(CD$_3$)$_2$SO	167.55	150.07	122.95	141.81	122.95	150.07

b) The values of chemical shift $\delta(^{13}C)(COO)$ of compounds Bu$_2$Snnik$_2$ and Bu$_2$Sninik$_2$ in CDCl$_3$ (174.18 and 171.42 ppm) approach the value of chemical shift $\delta(^{13}C)(COO)$ of sodium nicotinate and isonicotinate (173.28 and 173.52 ppm), hence the COO groups in these compounds can be considered practically bidentale. It is important to notice that the changeover from non-coordinating solvent CDCl$_3$ to coordinating solvent (CD$_3$)$_2$SO of compound Bu$_2$Snnik$_2$ is connected with the destruction of chelate function of carboxylate group as a result of coordination of two molecules of a coordinating solvent to the central tin atom.

c) The values of chemical shift $\delta(^{13}C)(COO)$ of all other compounds are in the region of 167.55 - 170.83 ppm. The carboxylate groups in these complexes can be denoted as anisobidentate which means a transient state between bidentate and monodentate COO group. This fact can be interpreted in such a manner that the carboxylate group is bonded with the tin atom via one stronger and one weaker Sn-O bond.

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Table V ^{13}C NMR parameters of butyl and phenyl substituents in diorganotin(IV) pyridinecarboxylates studied

Compound	$\delta(^{13}C)$, [ppm]\(J(^{119}Sn, ^{13}C), [Hz])			
(Solvent)	C (1)	C (2)	C (3)	C (4)
Bu$_2$Snpic$_2$				
(CDCl$_3$)	28.27	27.19	26.06	13.19
	(729.8)	(34.9)	(125.7)	
(CD$_3$)$_2$SO	32.66	27.21	25.39	13.31
	(1068.8)	(45.1)	(166.5)	
Bu$_2$Snnic$_2$				
(CDCl$_3$)	26.27	26.65	26.14	13.45
	(615.5)	(35.3)	(38.6)	
(CD$_3$)$_2$SO	29.96	29.96	25.73	13.62
	(842.0)	(37.6)	(135.4)	
Bu$_2$Sninic$_2$[a]				
(CDCl$_3$)		25.94 - 30.28[b]		13.42
				13.47
Ph$_2$Snpic$_2$				
(CD$_3$)$_2$SO	146.31	134.44	128.49	129.12
	(953.6)	(57.2)	(86.7)	(17.8)
(CD$_3$)$_2$SO	149.58	133.51	128.24	128.38
	[c]	(63.1)	(109.6)	[d]

[a] The NMR spectrum in (CD$_3$)$_2$SO was not measured. The compound decompose during dissolving
[b] The signals cannot be assigned unambiguously
[c] Low solubility in (CD$_3$)$_2$SO
[d] The half signal width is larger than 20 Hz

Table VI Chemical shifts $\delta(^{13}C)$ of pyridinecarboxylate groups in diorganotin(IV) pyridinecarboxylates studied

Compound (Solvent)	$\delta(^{13}C)$, [ppm]					
	(COOH)	C (2')	C (3')	C (4')	C (5')	C (6')
Bu_2Snpic_2						
$(CDCl_3)$	165.50	147.14	125.50	140.43	127.47	145.49
$(CD_3)_2SO$	165.40	149.38	124.51	140.41	126.97	147.66
Bu_2Snnic_2						
$(CDCl_3)$	174.18	151.61	126.24	137.86	123.25	153.38
$(CD_3)_2SO$	170.83	150.53	128.41	137.06	123.65	152.57
$Bu_2Sninic_2$						
$(CDCl_3)$	171.42	150.31	123.15	140.48	123.15	150.31
Ph_2Snpic_2						
$(CD_3)_2SO$	164.53	145.68	125.75	141.37	128.32	144.11
	a	b	c			
$(CD_3)_2SO$	164.78	147.61	124.99	141.45	128.31	146.82

a $^{2+3}J(^{119}Sn,^{13}C)$ = 22.9 Hz
b $^{3+2}J(^{119}Sn,^{13}C)$ = 19.4 Hz
c $^{3+4}J(^{119}Sn,^{13}C)$ = 11.4 Hz

^{15}N chemical shift

The values of ^{15}N chemical shift and $^2J(^{15}N, {}^1H)$ coupling constants of some organotin(IV) pyridinecarboxylates are given in Table VII. The parameter $\delta(^{15}N)$ is important for estimating the structure of organotin(IV) pyridine-carboxylates because the donor-acceptor interaction of nitrogen atom with tin atom is reflected in the significant ^{15}N upfield shift[30,31]. The table shows that only the compounds Bu_2Snpic_2 and Ph_2Snpic_2 exhibit the significant upfield shift (40.4 and 42.7 ppm, respectively) towards the respective comparative ethyl pyridinecarboxylates. So, the bidentate character of picolinate ligand is realized via pyridine N atom and via one O atom of COO group. As a rule, the shifts of $\delta(^{15}N)$ values of the other compunds studied do not reach over 10 ppm, which can be ascribed to the influence of association of molecules of the compounds studied.

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Table VII ^{15}N NMR parameters of some studied compounds

Compound	$\delta(^{15}N)$, ppm		$^2J(^{15}N.^1H)$, Hz	
	(CDCl$_3$)	(CD$_3$)$_2$SO	(CDCl$_3$)	(CD$_3$)$_2$SO
Etpic [a]	-67.5	-64.29	5.9	6.1
Bu$_3$Snpic	-70.4			
Bu$_2$Snpic$_2$	-107.9			
Ph$_2$Snpic$_2$	-110.2			
Etnic [a]	-67.3	-61.9[b]	10.9	
Bu$_3$Snnic	-80.6	-66.4	9.67	11.3
Ph$_3$Snnic	-74.9	-65.9	10.3	11.2
Bu$_2$Snnic$_2$	-77.1		9.9	
Etinic [a]	-54.5	-51.8	10.9	11.0
Bu$_3$Sninic	-65.7		10.3	
Ph$_3$Sninic	-62.5	-57.1	9.6	10.7

[a] Etpic., Etnic., Etinic - Ethyl picolinate, nicotinate and isonicotinate
[b] Ref.[32]

Infrared Spectra

It is known that denticity of COO group can be determined with a high level of probability on the basis of values v_{as}(COO) and v_s(COO) and/or their difference Δv(COO) = v_{as}(COO) – v(COO) (Ref.[33]). Ethyl pyridinecarboxylates (Δv(COO) from 423 to 448 cm^{-1}) (Tab. VI) were used as the model compounds with the monodentately bonded carboxylate group. Sodium pyridinecarboxylates (Δv(COO) from 156 to 179 cm^{-1}) (Tab. VIII) were used as prototypes of bidentate bonded carboxylate group. The values Δv(COO) of organotin(IV) compounds studied (Tab. IX) lie between these two limits and their actual values serve for evaluation of denticity of carboxylate group both in CHCl$_3$ solution and in solid state (Nujol suspension).

The values of Δv(COO) of the organotin(IV) pyridinecarboxylates studied in solid state (Nujol suspension) can be divided into three groups like those of $\delta(^{13}C)$(COO).

a) The Δv(COO) value of the compound Ph$_2$Snpik$_2$ in solid state (352 cm^{-1}) approaches the Δv(COO) value of ethyl picolinate (423 cm^{-1}), hence this compound contains, with high probability, the monodentate carboxylate group. However, other very weak intra- or intermolecular interactions cannot be

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excluded.

b) The $\Delta v(COO)$ values of the compounds Bu_3Snpic, Bu_2Snnik_2 and Ph_2Snnik_2 in solid state (from 162 to 187 cm^{-1}) approach the $\Delta v(COO)$ values of sodium pyridinecarboxylates, hence the COO group of these compounds can be considered to be practically bidentate.

c) The $\Delta v(COO)$ values of all other compounds studied are in the range from 295 to 315 cm^{-1}. That is why these cases can be described as an intermediate state between monodentate and bidentate carboxylate groups which is called anisobidentate.

The $\Delta v(COO)$ values of the organotin(IV) compounds studied in $CHCl_3$ solution confirm the results obtained by analysis of $\delta(^{13}C)(COO)$ parameter.

Table VIII The $v_{as}(COO)$, $v_s(COO)$ and $\Delta v(COO)$ values in cm^{-1} of ethyl and sodium pyridinecarboxylates

	Ethyl			Sodium		
	$v_{as}(COO)$	$v_s(COO)$	$\Delta v(COO)$	$v_{as}(COO)$	$v_s(COO)$	$\Delta v(COO)$
picolinates	1730[a]	1307	423	1580	1401[a]	179
nicotinates	1731	1288	443	1572[a]	1404	168
isonicotinates	1732	1284	448	1570[a]	1414	156

[a] The band is split. The value is an average of wavenumber of bands raised by splitting

Conclusions

Triorganotin(IV) pyridinecarboxylates

All triorganotin(IV) pyridinecarboxylates in solid state are probably composites of polymeric chains with trans-trigonal bipyramidal environment of central tin atom. The planar fragments R_3Sn of nicotinate and isonicotinate are connected by a bridging carboxylate group which is bonded to tin atoms via one O atom of COO group and via pyridine N atom. This proposed structure is in accord with the measurements of ^{119}Sn NMR CP MAS spectra and IR spectra but also with the parameters of Mössbauer spectra[9]. In the case of compounds Ph_3Snnic (Fig. 1) and $Ph_3Sninic$ this fact was also confirmed by X-ray structural analysis[9,10]

The central tin atom of compound Bu_3Snpic (Fig. 2) is also pentacoordinate. However, this compound in solid state forms trans-R_3SnO_2 polymeric chains with bridging function of COO group ($\Delta v(COO) = 169$ cm^{-1}). The coordination polyhedron is based on trans-trigonal bipyramide, with the equatorial plane being defined by butyl substituents and O atoms occupying the axial positions (high value Q.S. = 3.75 mm.s^{-1}). (As the compound Ph_3Snpic
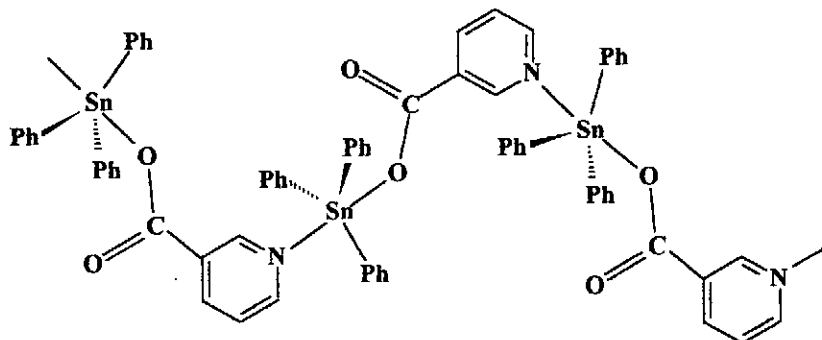
Fig. 1 Structure of compound Bu_3Snnic in solid state

Table IX The $v_{as}(COO)$, $v_s(COO)$ and $\Delta v(COO)$ values in cm^{-1} of organotin compounds studied

	Solid state (Nujol suspension)			$CHCl_3$ solution		
	$v_{as}(COO)$	$v_s(COO)$	$\Delta v(COO)$	$v_{as}(COO)$	$v_s(COO)$	$\Delta v(COO)$
Bu_3Snpic	1561[a]	1397	164	1651	1354	297
Bu_2Snpic_2	1650[a]	1351[a]	299	1672	1345	327
Ph_3Snpic [c]	1628	1369	259	-	-	-
Ph_2Snpic_2	1686[a]	1334	352	1676	1339	337
Bu_3Snnic	1647	1344	303	1648	1344	304
Bu_2Snnic_2	1573[a]	1411	162	1614	1367	247
Ph_3Snnic	1654	1352	302	1646	1345	301
Ph_2Snnic_2 [b]	1601[a]	1414	187	-	-	-
$Bu_3Sninic$	1649	1354	295	1651	1354	297
$Bu_2Sninic_2$ [c]	1643[a]	1347	296	-	-	-
$Ph_3Sninic$	1658[a]	1343[a]	315	1652	1345	307

[a] The band is split. The value is an average of wavenumber of bands raised by splitting
[b] Little soluble compound
[c] Unstable compound

is unstable, see Experimental, the amount of information about the structure of this compound in solid state is little, hence it is impossible to make more reliable conclusions.)
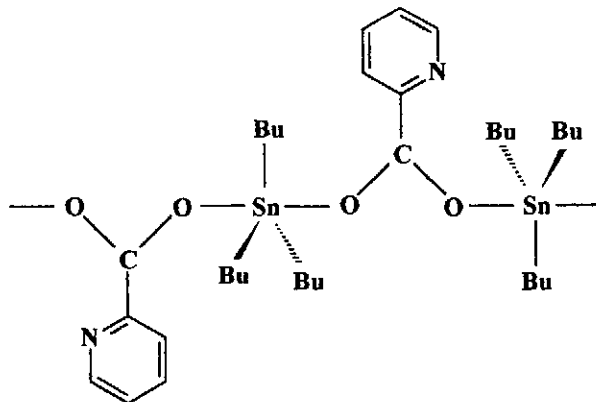
Fig. 2 Structure of compound Bu₃Snpic in solid state

While dissolving triorganotin(IV) pyridinecarboxylates in non-coordinating solvent $CDCl_3$, the polymeric chains are destroyed and the pseudotetrahedral isolated molecules are formed (Fig. 3). It is indicated by the value of coordination number (equal to four), monodentate or at most anisobidentate carboxylate group, bonding angle θ from 110 to 112° (butyltin(IV) compounds) or ~ 116° (triphenyltin(IV) compounds), and the fact that the values $\delta(^{15}N)$ are not so different from those of the same parameter of the corresponding ethyl pyridinecarboxylates (the significant interaction is not between tin and nitrogen atoms).

trans-trigonal bipyramid (c. n. 5)   tetrahedron (c. n. 4)
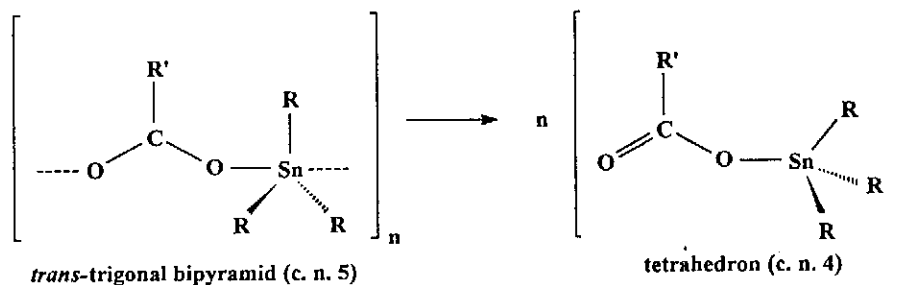
Fig. 3 The change of coordination polyhedron due to dissolving triorganotin(IV) pyridinecarboxylates

The compound Ph₃Snpic makes an exception. The value $\delta(^{119}Sn)$ = -131.2 ppm corresponds to a little higher coordination number than four, hence the other type of coordination cannot be excluded. It is impossible, on basis of existing results, to exactly determine whether this coordination is via oxygen or nitrogen atom.

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All studied triorganotin(IV) pyridinecarboxylates in solution of coordinating solvent $(CD_3)_2SO$ are present as *trans*-trigonal bipyramidal molecular complexes with one molecule of solvent $R_3SnX.(CD_3)_2SO$ (Fig. 4). This is indicated by the $\delta(^{119}Sn)$ upfield shift (the increase of coordination), the downfield ^{13}C chemical shift of carboxylate group (the lowering of denticity) and the increasing of coupling constants $^1J(^{119}Sn.^{13}C)$ (the increasing bonding angles C-Sn-C) at all studied triorganotin(IV) pyridinecarboxylates while changeover from non-coordinating $CDCl_3$ to coordinating solvent $(CD_3)_2SO$.
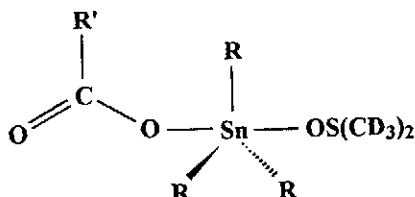
Fig. 4 The structure of triorganotin(IV) pyridinecarboxylates in coordinating solvent $(CD_3)_2SO$

Diorganotin(IV) pyridinecarboxylates

According to the results of X-ray structural analysis[11], the crystals of compound Ph_2Snpic_2 are composed of isolated pseudooctahedral molecules with phenyl substituents and nitrogen atoms in *cis*-positions; oxygen atoms are in *trans*-positions. This structure corresponds to the results following from Mössbauer spectra (I.S. = 0.81 mm s^{-1} Q.S. = 2.01 mm s^{-1})[17] and to our results obtained by ^{119}Sn NMR CP MAS ($\delta(^{119}Sn)$ = -411.7 ppm; the typical value of coordination number six) and IR spectra ($\Delta v(COO)$ = 352 cm^{-1}; monodentate carboxylate group). It is impossible to make any final conclusion from the existing information about homologous compound Bu_2Snpic_2. On the basis the Mössbauer spectra parameters of (I.S. = 1.45 mm s^{-1} and Q.S. = 4.35 mm s^{-1})[15], especially the high value of quadrupole splitting and on the basis of the value $\Delta v(COO)$ = 229 cm^{-1}, which is 53 cm^{-1} lower than that of analogous compound Ph_2Snpic_2, it is possible to suppose that it is a polymer. In this case the coordination number of central tin atom would be equal to seven

According to the parameters of Mössbauer spectra (I.S. = 1.60 or 1.29 mm s^{-1}, Q.S. = 3.93 or 3.86 mm s^{-1})[13,18], the central tin atoms of compounds Bu_2Snnic_2 and Ph_2Snnic_2 in solid state exist in *trans*-octahedral geometry. According to the IR spectra of these compounds in Nujol suspension, the carboxylate groups are clearly bidentate. However, it is impossible to decide whether they have chelateing or bridging function and wheteher these compounds form molecular or polymeric crystals.

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Regardless of the structure of compounds Ph_2Snpic_2 and Bu_2Snpic_2 in solid state, these compounds in solution behave like trapezoidal bipyramidal molecular chelate complexes in $CDCl_3$. The chelate bond is mediated by one O atom of carboxylate group and by pyridine N atom. There are the following proofs for that: the coordination number of central tin atom is equal to six, angles $\theta = 148°$ or $135°$, carboxylate group is monodentate, between tin and nitrogen atoms there is a strong donor-acceptor interaction.

The compound Bu_2Snnic_2 forms also trapezoidal bipyramidal complexes in $CDCl_3$ solution. In contrast to the compound Bu_2Snpic_2, the chelate connection in this case is realized via two oxygen atoms of carboxylate group. The prospective consideration about donor-acceptor interaction between tin and nitrogen atoms contradicts with the $\delta(^{15}N)$ values. The large difference between the $\Delta v(COO)$ values in solid state (162 cm^{-1}) and in $CHCl_3$ solution (247 cm^{-1}) indicates that the denticity of carboxylate group becomes lower upon dissolving.

Owing to the problems during preparation of the compound $Bu_2Sninic_2$ (see Experimental), the information about the structure of this compound in $CDCl_3$ solution is incomplete. However, it seems that the structure of this compound resembles that of the analogous compound Bu_2Snnic_2.

While dissolving in coordinating solvent, diorganotin(IV) pyridinecarboxylates form the complexes with one or two molecules of the solvent. Both bis(picolinates) add one molecule of solvent, thus increasing the coordination number of central tin atom by unit. The resulting complex takes the shape of *trans*-pentagonal bipyramid (Fig. 5).
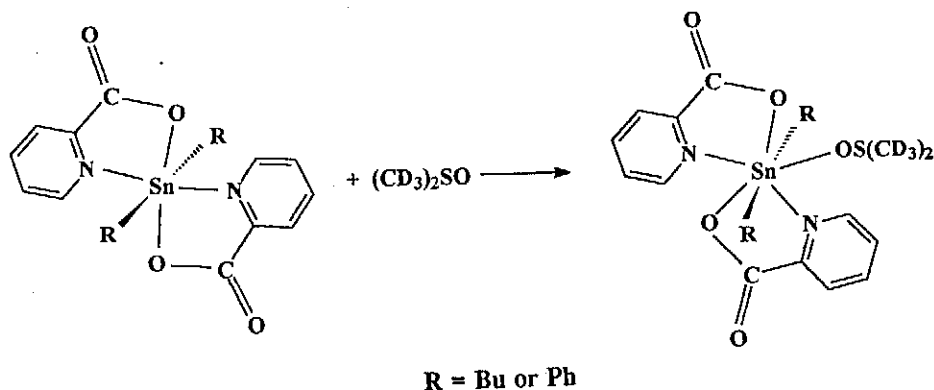

R = Bu or Ph

Fig. 5 The change of shape of coordination polyhedron of compounds Bu_2Snpic_2 and Ph_2Snpic_2 due to replacement of non-coordinating solvent $CDCl_3$ by coordinating solvent $(CD_3)_2SO$

On the other hand dibutyltin(IV) bis(nicotinate) forms the complex with two molecules of solvent. The coordination number of central tin atom, six, is

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retained (little change in $\delta(^{119}\text{Sn})$ parameter while replacing the solvent type). In this case, however, the addition of $(CD_3)_2SO$ molecules into the coordination sphere of tin atom is connected with lowering of denticity of carboxylate group and thereby with the destruction of chelate bond (Fig. 6)
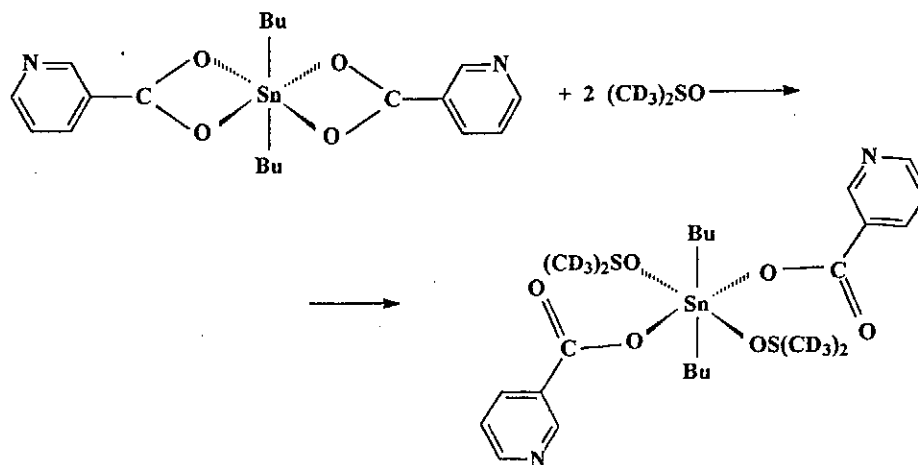

Fig 6 The change of shape of coordination polyhedron of the compound Bu_2Snnic_2 due to replacement of non-coordinating solvent $CDCl_3$ by coordinating solvent $(CD_3)_2SO$

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