^{13}C AND ^{119}Sn NMR SPECTRA OF DI-n-BUTYLTIN(IV) COMPOUNDS

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Summary

The ^{13}C and ^{119}Sn NMR spectra of a set of di-n-butyltin(IV) compounds and their complexes in coordinating and non-coordinating solvents have been studied. The results have shown that it is possible to describe semiquantitatively the shape of coordination polyhedra of these compounds from analysis of their $\delta(^{119}$Sn$)$ and $^1J(^{119}$Sn$-^{13}$C$)$ parameters. The values of $\delta(^{119}$Sn$)$ define the regions with different coordination numbers of the central tin atom, so that four-coordinate compounds have $\delta(^{119}$Sn$)$ ranging from about $+200$ to -60 ppm, five-coordinate compounds, -90 to -190 ppm, and six-coordinate compounds, -210 to -400 ppm. The values of $^1J(^{119}$Sn$-^{13}$C$)$ were used for the calculation of the C–Sn–C angle in the coordination polyhedron of individual compounds.

Introduction

In our previous papers [1,2] we manifested the advantage of the application of ^{13}C and ^{119}Sn NMR Spectra for the determination of the structure of triorganotin(IV) compounds and their complexes in solutions. For the triphenyl- and tri-n-butyl-tin(IV) compounds we have shown that different coordination numbers (four or five) of tin atoms and various geometrical arrangement of ligands (*cis* or *trans*), result in different values of the NMR parameters, especially of $\delta(^{119}$Sn$)$ and $^1J(^{119}$Sn$-^{13}$C$)$, having a relatively narrow range and are sharply resolved from one another. In papers [2,3] we also reported the mutual dependence of $\delta(^{119}$Sn$)$ and $^1J(^{119}$Sn$-^{13}$C$)$ parameters and their characteristic ranges on the three fundamental structural types of the various triorganotin(IV) compounds (trimethyl-, tri-n-butyl-, tricyclohexyl-, tribenzyl- and triphenyl-tin). Therefore we assume that the conclusions made in the papers [1–3] have a more general validity.

TABLE 1

$\delta(^{119}\text{Sn})$, $^nJ(^{119}\text{Sn}-^{13}\text{C})$ AND BASIC STRUCTURAL DATA OF DI-n-BUTYLTIN(IV) COMPOUNDS AT 300 K

No.	Compound [a]	Solvent	$\delta(^{119}\text{Sn})$ (ppm)	$^nJ(^{119}\text{Sn}-^{13}\text{C})$ [b], Hz			Coord. number	Angle θ, (°) [c]
				$n=1$	$n=2$	$n=3$		
1	Bu₂SnCl₂	CDCl₃	126.3	419.9	36.6	85.4	4	117
		hmpa	222.7	877.7	43.9	156.2	6	162
2	Bu₂SnBr₂	CDCl₃	89.7	391.8	34.2	85.4	4	114
		hmpa	−261.8	891.2	43.9	173.3	6	163
3	Bu₂SnI₂	CDCl₃	−56.1	347.9	33.0	83.6	4	109
		CDCl₃	−57.0	350.3	33.0	85.3	4	110
		hmpa	−259.4	795.8	37.8	159.9	6	154
4	Bu₂Sn(SBu)₂ [e,f]	CDCl₃	127.2 [e]	385.7 [f]	23.0 [f]		4	113
5	Bu₂Sn(OPr-i)₂ [g,h]	CCl₄	−31.0 [g]	520.0 [h]	38.0 [h]	88.0 [h]	4	126
6	Bu₂Sn(OBu-t)₂ [i,h]	CCl₄	−34.0 [i]	496.0 [h]	—		4	124
7	Bu₂SnCl₂·dppoe	CDCl₃	−66.6	598.2	36.6	104.8	4–5	(134)
8	Bu₂SnCl₂·NEt₄	CD₃NO₂	−120.2	673.8	37.8	109.8	5	142
		dmso-d₆	−169.4	839.8	42.8	147.7	5–6	(159)
9	Bu₂SnBr₂·NEt₄	CD₃NO₂	119.7	616.4	40.3	117.2	5	136
		dmso-d₆	235.2	869.8	47.0	168.4	6	162
10	Bu₂Sn(OMe)₂	—	164.2	645.3		87.2	5	139
		CDCl₃	155.8	637.2		96.4	5	138
		hmpa	186.3	700.7		97.7	5–6	(145)
11	Bu₂Sn(C₃H₅N₃O) [k]	CDCl₃	130.4	561.0	32.6	89.0	5	131
12	Bu₂Sn(C₁₀H₁₆N₂S₂O) [l]	CDCl₃	156.7	555.0	—		5	130
13	Bu₂Sn(OC(O)Me)₂	CDCl₃	161.1	618.3	36.6	97.7	6	136
		hmpa	−149.3	584.7	35.4	98.9	6	133
		hmpa	−334.7	891.1	36.6	147.7	6	163
14	Bu₂Sn(OC(O)Ph)₂	CDCl₃	−149.9	589.6	35.4	100.1	6	134
		hmpa	−348.6	920.4		149.0	6	167

15	Bu$_2$Sn(OCOCH$_2$OPh)$_2$ [l]	CDCl$_3$	−117.4	549.3	36.0	100.1	6	130
		hmpa	−298.3	811.8	34.2	140.4	6	156
16	Bu$_2$Sn(OCOCH$_2$OPh-2Me)$_2$ [l]	CDCl$_3$	−117.1	548.1	36.6	101.3	6	129
17	Bu$_2$Sn(OCOCH$_2$OPh-4Cl)$_2$ [l]	CDCl$_3$	−114.4	545.7	36.0	100.1	6	129
18	Bu$_2$Sn(OCOCH$_2$OPh-2,4Cl$_2$)$_2$ [l]	CDCl$_3$	−110.5	544.4	36.6	102.5	6	129
19	Bu$_2$Sn(OCOCH$_2$OPh-2OCH$_3$)$_2$ [l]	CDCl$_3$	−119.7	556.6	36.6	105.0	6	130
20	Bu$_2$Sn(OCOCH$_2$SPh)$_2$ [l]	CDCl$_3$	−135.8	559.7	34.8	102.5	6	130
21	(Bu$_2$SnOC(O)CCl$_3$)$_2$O	CDCl$_3$	−188.6	696.0	/	/	5	144
			−185.4	646.3	/	/	5	139
22	Bu$_2$Sn(oxin)$_2$	CDCl$_3$	−260.0	612.8	25.6	105.0	6	136
		hmpa	−272.6	/	/	/	6	
23	Bu$_2$Sn(Etdtc)$_2$	CDCl$_3$	−336.0	608.3	/	119.6	6	135
		hmpa	−350.8	643.2	40.3	116.9	6	139
24	Bu$_2$Sn(morf·dtc)$_2$	CDCl$_3$	−328.2	600.2	39.3	127.0	6	135
25	Bu$_2$Sn(acac)$_2$	–	−400.5	930.5	/	126.0	6	168
		CDCl$_3$	−397.9	943.7	/	140.7	6	169
		hmpa	−404.6	943.7	/	126.0	6	169
26	Bu$_2$Sn(dbzm)$_2$ [m]	CDCl$_3$	−385.1	880	41.3	126.0	6	163
27	Bu$_2$Sn(bzac)$_2$ [m]	CDCl$_3$	−390.4	902	41.2	129.9	6	165
28	Bu$_2$Sn(pic)$_2$ [m]	CDCl$_3$	−312±2	711	33.5	122.1	6	146
29	Bu$_2$Sn(Me·oxin)$_2$ [m]	CDCl$_3$	−248.7	805	45.3	122.1	6	155
30	Bu$_2$SnCl$_2$·bipy [m]	CDCl$_3$	−238.5±1	980	47.3	179.2	6	173
31	Bu$_2$SnCl$_2$·phen [m]	CDCl$_3$	−262.5±1	1016	47.3	185.1	6	176

[a] Abbreviations: hmpa = hexamethylphosphorotriamide, dmso-d_6 = hexadeuteriodimethyl sulphoxide, dppoe = 1,2-bis(diphenylphosphorylethane, oxin = 8-hydroxychinolinate, Etdtc = N,N-diethyldithiocarbamate, morf·dtc = O(CH$_2$CH$_2$)$_2$NC(S)S, acac = acetyl acetonate, dbzm = dibenzoylmethanoate, bzac = benzoyl acetonate, pic = 1-picolinate, Me·oxin = 2-methyl-8-hydroxychinolinate, bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline. [b] $^4J(^{119}$Sn–^{13}C) < 10 Hz. [c] ±4°, according to eq. 1 [15]. [d] At 330 K. [e] Ref. 16. [f] Ref. 17. [g] Ref. 18. [h] Ref. 19. [i] Ref. 7. [j] Undetermined. [k] Ref. 20. [l] Ref. 8. [m] Ref. 21.

The analysis of the structure of diorganotin(IV) compounds and their complexes in solutions from their ^{13}C and ^{119}Sn NMR spectra is substantially more complicated. In this case, there are more factors that have a considerable effect on the NMR parameters linked directly with structure. First of all, diorganotin(IV) compounds have a higher number of coordination types (coordination numbers of four, five, six and sometimes even seven) with a large number of different, yet corresponding polyhedra which are to be distinguished. NMR spectral parameters are also considerably influenced by various deformations of coordination polyhedra which occur frequently in diorganotin(IV) compounds. In some cases it is very difficult to determine the coordination number unambiguously, because, besides there being strong covalent bonds there are also weaker secondary coordination bonds in these compounds and their complexes. Fast equilibrating processes between different structural types with different NMR parameters, can also lead to erroneous results because we obtained only one parameter on the NMR time scale with the value given by a weighted average of the parameters corresponding to the compounds involved in the equilibrium. In spite of the above difficulties, ^{13}C and ^{119}Sn NMR spectra of diorganotin(IV) compounds and their complexes afforded valuable data which could be used for the determination of their structure.

In this paper we have studied ^{13}C and ^{119}Sn NMR spectra of a selected series of di-n-butyltin(IV) compounds and their complexes. The set studied covered all structural types of these compounds. The NMR spectra of the compounds were studied in their pure state, in solutions of non-coordinating (deuteriochloroform, trideuterionitromethane), and coordinating (hexadeuteriodimethyl sulphoxide, hexamethylphosphorotriamide) solvents. Some di-n-butyltin(IV) compounds have been studied using ^{13}C or ^{119}Sn NMR spectra and there were also attempts to classify the forms of coordination polyhedra based on the measured NMR parameters. But only a few attempts were made to compare the results of the NMR spectra of both isotopes. Therefore our aim was also to summarize our results and literature data and to classify them so as to obtain a topical tool for the determination of the structure of the molecules and the complex ions of di-n-butyltin(IV) compounds.

Experimental

All the compounds studied were prepared by published methods [4–14]. The ^{13}C and ^{119}Sn NMR spectra were measured at 25.047 and 37.14 MHz, respectively, on a JEOL spectrometer JNM-FX 100 at 300 K. The compounds as measured were pure liquids or ca. 20% (w/v) or saturated (in the case of poor solubility), solutions. Chemical shifts, $\delta(^{119}\text{Sn})$, are related to external pure tetramethylstannane, $\delta(^{13}\text{C})$ were referred to a suitable solvent signal and converted to the δ-scale: deuteriochloroform (77.00 ppm), trideuterionitromethane (62.80 ppm), hexadeuteriodimethylsulphoxide (39.60 ppm) and hexamethylphosphorotriamide (36.00 ppm). Positive values denote down-field shifts. A more detailed description of the experimental conditions is given in refs. 1,2.

Results and discussion

The parameters of ^{13}C and ^{119}Sn NMR spectra of the studied di-n-butyltin(IV) compounds and their complexes, and other relevant di-n-butyltin(IV) compounds are summarized in Tables 1 and 2. The number of signals in the ^{13}C and ^{119}Sn NMR

TABLE 2

^{13}C NMR CHEMICAL SHIFTS OF DI-n-BUTYLTIN(IV) COMPOUNDS AT 300 K

Compound [a]	Solvent	$\delta(^{13}C)$ [b] (ppm)				
		C(1)	C(2)	C(3)	C(4)	others
1	CDCl$_3$	27.60	27.60	26.12	13.35	
	hmpa	36.63	27.28	25.72	13.19	
2	–	27.44	27.44	25.68	13.50	
	CDCl$_3$	27.04	27.53	25.92	13.45	
	hmpa	41.22	27.96	25.33	13.19	
3	–	25.59	28.61	24.90	13.50	
	CDCl$_3$	25.63	29.09	25.43	13.49	
	hmpa [c]	42.24	28.64	24.74	12.90	
7	CDCl$_3$ [d]	31.87	27.19	26.12	13.45	
8	CD$_3$NO$_2$	37.80	28.10	26.50	13.53	52.81(CH$_2$); 7.24(CH$_3$)
	dmso-d_6	40.28	27.71	25.26	13.87	51.46(CH$_2$); 7.29(CH$_3$)
9	CD$_3$NO$_2$	41.60	30.25	25.67	13.29	52.57(CH$_2$); 7.20(CH$_3$)
	dmso-d_6	43.35	28.49	25.32	13.87	51.69(CH$_2$); 7.48(CH$_3$)
10	–	19.00	27.54	26.98	13.50	51.84(CH$_3$)
	CDCl$_3$	19.10	27.19	26.75	13.35	51.95(CH$_3$)
	hmpa	20.06	27.13	26.45	13.14	51.26(CH$_3$)
13	–	24.87	26.85	26.32	13.50	181.45(COO); 20.03(CH$_3$)
	CDCl$_3$	24.36	26.17	25.83	13.06	181.10(COO); 19.98(CH$_3$)
	hmpa	29.13	26.74	25.96	13.19	176.56(COO); 20.65(CH$_3$)
14	CDCl$_3$	25.34	26.56	26.22	13.40	175.79(COO); 129.98(i); 130.37; 128.17; 133.00(p)
	hmpa	30.10	26.89	25.96	13.19	172.22(COO); 132.78; 129.18; 127.62; 131.38
21	CDCl$_3$	31.13	27.62	26.60	13.50	166.00(COO); 92.68(CCl$_3$)
		28.33	26.98	26.60	13.50	
22	CDCl$_3$	25.46	27.73	26.75	13.50	158.10($J(^{119}$Sn$-^{13}$C) = 26.9); 142.26; 138.16; 136.56; 130.03; 129.54; 120.91; 113.31; 112.48
	hmpa	24.69	27.42	26.25	13.09	157.70($J(^{119}$Sn$-^{13}$C) = 27.4); 142.10; 139.08; 136.01; 129.53(2C); 121.58; 112.37(2C)
23	CDCl$_3$	34.00	28.22	26.12	13.58	198.91(CSS); 48.80(CH$_2$); 11.86(CH$_3$)
	hmpa	33.42	27.80	25.71	13.22	197.69(CSS); 48.60(CH$_2$); 11.45(CH$_3$)
24	CDCl$_3$	34.33	28.27	26.18	13.63	200.69(CSS); 50.95(CH$_2$N); 65.90(CH$_2$O)
25	–	27.31	26.96	26.08	13.50	190.24(CO); 99.44(CH); 27.31(CH$_3$)
	CDCl$_3$	27.68	26.80	26.10	13.52	190.50(CO); 101.10(CH); 27.68(CH$_3$)
	hmpa	26.82	26.70	25.76	13.24	190.27(CO); 99.48(CH); 26.99(CH)$_3$)

[a] See Table 1. [b] $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2$. [c] At 330 K. [d] $\delta(^{31}$P) 34.8 ppm (standard 85% H$_3$PO$_4$).

spectra, the values of chemical shifts $\delta(^{13}$C) and $\delta(^{119}$Sn), and the coupling constants $^nJ(^{119}$Sn$-^{13}$C), confirm the chemical composition and constitution of the studied compounds. For the determination of the structure of the di-n-butyltin(IV) compounds, $\delta(^{119}$Sn) and $^1J(^{119}$Sn$-^{13}$C) are the most important parameters, and are thoroughly discussed in this paper. Basic structural data resulting from the analysis of the NMR spectra (coordination number of the central tin atom) and the values of C–Sn–C angles in coordination polyhedra of the di-n-butyltin(IV) compounds are also shown in Table 1.

Chemical shifts

The values of the chemical shift $\delta(^{119}Sn)$, of the compounds listed in Table 1 lie in a relatively broad range (from $+127.2$ to -404.6 ppm), this covers nearly the whole range of the hitherto known $\delta(^{119}Sn)$ values for di-n-butyltin(IV) compounds. Extreme values were obtained; $\delta(^{119}Sn)$ $+193$ ppm for $Bu_2SnSCH_2CH_2S$ [22] on the one hand, and $\delta(^{119}Sn)$ -469 ppm for $Bu_2Sn[OP(O)(OBu_2)_2]_2$ [23] on the other. From Table 1 a general trend of up-field shift of $\delta(^{119}Sn)$ with increasing coordination number of the tin atom can be seen. Moreover, the values of chemical shifts covers the whole of the above given range without dividing limits, which, from the boundaries of regions with characteristic values of $\delta(^{119}Sn)$, could be typical of various groups corresponding to particular coordination numbers of the tin atoms. Therefore we assume that the whole range from $+200$ to -470 ppm can be taken as characteristic of di-n-butyltin(IV) compounds. This range is a little broader than that for dialkyltin(IV) compounds with coordination numbers of four, five and six ($+200$ to -365 ppm) as given by Clark et al. [24].
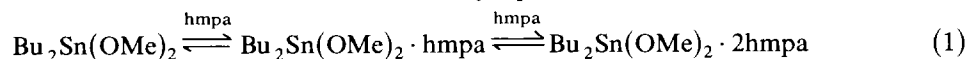
The values of chemical shifts for the dihalides (compounds 1–3), the dithiolate (compound 4) and the monomer alkoxides (compounds 5 and 6) in the pure state and in solutions of non-coordinating solvents ($CDCl_3$, CCl_4) give a range of $+127.2$ to -57.0 ppm. These compounds, which have a small tendency towards association, exist both in the pure state, and in solutions of non-coordinating solvents, as almost isolated quasi-tetrahedral molecules (see below), with a four-coordinate central tin atom. The value of $\delta(^{119}Sn)$ -57.0 ppm for compound 3 is an extreme value for four-coordinate di-n-butyltin(IV) compounds compared with the range $+200$ to 0 ppm as roughly delimited by Clark et al. [24]. We would like to add that our proposed region includes all hitherto known values of $\delta(^{119}Sn)$ of quasi-tetrahedral four-coordinate di-n-butyltin(IV) compounds those mentioned above and other compounds, e.g. simple and cyclic dithiolates, monomer dialkoxides, halogenothiolates, halogenoalkoxides, diamides and the compounds with a tin–transition metal bond [16,18,25,26].

Chemical shifts $\delta(^{119}Sn)$ of six-coordinate chelate complexes (compounds 22–31) lie in the range -260 to -404.6 ppm. Lower values (-222.7 to -348.6 ppm) were found for dihalides (1–3) and dicarboxylates (compounds 13–15) in a solution of hexamethylphosphorotriamide due to the formation of adducts with two molecules of this coordinating solvent. The chemical shifts of other six-coordinate complexes and adducts of di-n-butyltin(IV) compounds such as the dithiocarbamates and some higher aggregates of the cyclic dialkoxides, also lie in the range -210 to -340 ppm [26–29]. The value $\delta(^{119}Sn)$ -469 ppm [23] found for the compound, $Bu_2Sn[OP(O)(OBu_2)_2]_2$, seems to be very high. As it is unusual and atypical of six-coordinate di-n-butyltin(IV) compounds, we therefore assume that the region roughly bounded by -210 to -400 ppm of $\delta(^{119}Sn)$ to a good approximation can be taken as being characteristic of six-coordinate di-n-butyltin(IV) compounds. This region is a little broader, and is shifted a little up-field compared with those given in other papers [24,29].

The middle part of the range of $\delta(^{119}Sn)$ values of di-n-butyltin(IV) compounds and be ascribed to compounds with a coordination number for the central tin atom equal to five, this can be both real and/or apparent (average). In Table 1 both such compounds can be found. The complex anions $Bu_2SnX_3^-$ of compounds 8 and 9, the chelate complexes 11 and 12 and the dimer of compound 10 in non-coordinating

solvents such as deuteriochloroform, in weakly coordinating trideuterio-nitromethane or in the pure state represent compounds with a real coordination number of five [6,18,26]. Their chemical shifts range from -119.7 to -164.2 ppm. The values $\delta(^{119}Sn)$ of other compounds with a confirmed five-coordinate tin atom such as chelate $Bu_2Sn(oxin)Cl$ ($\delta(^{11(}Sn)$ -112 ppm [30]), dimeric alkoxides ($\delta(^{119}Sn)$ from ca. -105 to -165 ppm) [7,16,18,25,26] and their complexes with some N- or O-donor ligands [31] are also close to or fall within this range. The value of $\delta(^{119}Sn)$ -189 ppm for $Bu_2\overline{SnOCH_2CH_2O}$ seems to be "unnatural". This value is a weighted average for two different groupings (with coordination numbers five and six) as a result of a fast equilibrating process on the NMR time scale [29]. Relatively high values of $\delta(^{119}Sn)$ for poly(di-n-butyltin(IV) oxides) [32] could be the result of the same effect. We assume that their interpretation will be revised. Chemical shifts of compound **21** and the other tetranuclear dimer distannoxanes of the type $(Bu_2Sn(X)OSnBu_2Y)_2$, range from -82.8 to -218.4 ppm [33]. For these compounds it is possible to observe two distinctly resolved signals corresponding to two non-equivalent groups Bu_2SnO_2X and Bu_2SnOXY. Chemical shifts of the first group (-131.3 to -175.5 ppm) correspond to the five-coordinate Bu_2SnO_2X, except in the compounds where $X = Y = CH_3COO$, where $\delta(^{119}Sn)$ -202.2 ppm. Also most of the chemical shifts of Bu_2SnOXY lie in the region typical of five-coordinate di-n-butyltin(IV) compounds (-138.4 to -168.2 ppm). There are exceptions, for Bu_2SnOBr_2 and Bu_2SnOCl_2 (-82.8, -92.0 ppm, respectively) and for $Bu_2SnO(OH)NCS$, $Bu_2SnO(OPh)NCS$ and $Bu_2SnO(CH_3COO)_2$ where $\delta(^{119}Sn)$ are -211.8, -202.9 and -218.4 ppm, respectively. For the first two groups this could be caused by a weak intramolecular interaction of halogen atoms with the central tin atom in dimers of the compounds. The value of $\delta(^{119}Sn)$ -82.8 ppm is the lowest value hitherto found for five-coordinate di-n-butyltin(IV) compounds. According to our previous papers [8,34], in groups of the second type we assumed the presence of a six-coordinate tin atom and a bidentate function of the carboxyl (and perhaps also the NCS) ligand. In such a case, the value of -149.0 ppm for the monomeric 1,3-diacetoxytetrabutyldistannoxane, $(Bu_2SnCH_3COO)_2O$ [33], would correspond well to a five-coordinate central tin atom. Thus, a five-coordinate di-n-butyltin(IV) compound, according to the above discussion, can be characterized by chemical shifts $\delta(^{119}Sn)$ between -90 to -190 ppm. This is also different from the range given by Clark et al. [24], but its lower limit is in accordance with the results of Otera et al. [30,35]. Roelens and Taddei [29] consider the values of $\delta(^{119}Sn) \sim -190$ ppm as the upper limit for five-coordinate dialkyltin(IV) compounds.

In the region of the values of chemical shifts typical of five-coordinate compounds we also find other compounds from Table 1. A slight up-field shift for compound **10** observed during its transition from non-coordinating solvents into coordinating hexamethylphosphorotriamide corresponds to the formation of five-coordinate complexes of the monomer with one solvent molecule, as in the case of the other dialkoxides [31]. This reaction, linked with a dedimerization of the initial dialkoxide, proceeds without a change in coordination number. As the chemical shift of the complex lies at the upper limit of five-coordinate di-n-butyltin(IV) compounds, it is suggested that the formation of the adduct of these compounds with two solvent molecules is described by eq. 1.

$$Bu_2Sn(OMe)_2 \overset{hmpa}{\rightleftharpoons} Bu_2Sn(OMe)_2 \cdot hmpa \overset{hmpa}{\rightleftharpoons} Bu_2Sn(OMe)_2 \cdot 2hmpa \qquad (1)$$

The small differences between $\delta(^{119}Sn)$ of the six-coordinate chelates **22, 23** and **25** in deuteriochloroform and hexamethylphosphorotriamide solutions, give similar equilibrium reactions without changes in coordination number of the central tin atom. Values of chemical shifts of compounds **8** and **9** in hexadeuteriodimethyl sulphoxide also correspond to the equilibrium of formation of the complexes. The value of $\delta(^{119}Sn)$ of compound **9** (-225.2 ppm) belongs in the range of six-coordinate compounds, the chemical shift of compound **8** in hexadeuteriodimethyl sulphoxide is only slightly higher than that in trideuterionitromethane. Thus, in the first case the octahedral complex anion $[Bu_2SnBr_3 \cdot dmso]^-$ predominates in the equilibrium mixture, while in the second case the equilibrium is substantially shifted in favour of the five-coordinate anion $Bu_2SnCl_3^-$. The $\delta(^{119}Sn)$ value for compound **7** is also "unnatural". It corresponds to the equilibrium of the four-coordinate di-n-butyltin(IV) dichloride and the five-coordinate complex $Bu_2SnCl_2 \cdot dppoe$ [15].

Dibutyltin(IV) carboxylates (compounds **13–20**) represent an apparent five-coordinate group, $\delta(^{119}Sn)$ ranging from -110.5 to -161.1 ppm. As we found earlier [8,34], in these compounds every carboxyl group is bidentately linked to the tin atom thus forming an asymmetric chelate arrangement with Sn–O bonds of various strengths. The two types of bonding can be considered to be a transition state of four-coordination and six-coordination, showing an average coordination number of five. We assume that similar situations can be found in other asymmetric chelates such as diorganotin(IV) *O,O*-alkylenedithiophosphates [36].

Coupling constants $^1J(^{119}Sn-^{13}C)$

Important information relating to the structure of coordination polyhedra of di-n-butyltin(IV) compounds and their complexes can be obtained from the values of the coupling constants $^1J(^{119}Sn-^{13}C)$, because they are directly linked to the size of the C–Sn–C angle (θ) according to the equation given in our recent paper [15]:

$$|^1J(^{119}Sn-^{13}C)| = (9.99 \pm 0.73)\theta - (746 \pm 100) \ (r = 0.989, \ n = 9) \tag{2}$$

The values of θ of the studied compounds, calculated from this equation, are given in Table 1.

Four-coordinate di-n-butyltin(IV) dihalides (compounds **1–3**) give values of θ in range 109–117°, i.e. tetrahedral or slightly greater angles. Comparing these angles with those obtained by direct diffraction methods is not possible owing to the lack of data for di-n-butyltin(IV) compounds. However, monomer molecules of $(CH_3)_2SnCl_2$ in the vapour state reveal the angle 109.5°, while in the solid state this angle is 123.5° due to the formation of six-coordinate polymers [37,38]. Not only the values of θ of other polymer dihalides, R_2SnX_2 (X = Cl, R = C_2H_5, $ClCH_2$, C_6H_5 and cyclo-C_6H_{11}: R = C_2H_5, X = Br and I), but also of the monomer, bis(biphenylyl-2)tin(IV) dichloride, lie in the range 125–135° [39,40]. Therefore it is evident that the values of θ and the coupling constant $^1J(^{119}Sn-^{13}C)$ are determined not only by the coordination number of the central tin atom [19], but also by steric and electronic factors. In the case of compounds **1–3** we assume that there is deformation of the tetrahedral structure of the monomer molecule caused by the repulsion of differentially polarized n-butyl and halide ligands, because this deformation increases in the order Bu_2SnI_2 (θ 109°) < Bu_2SnBr_2 ($\theta \sim 114°$) < Bu_2SnCl_2 (θ 117°), with increasing electronegativity of halogen atoms. Compound **4** and other

simple di-n-butyltin(IV) thiolates [17] give $^1J(^{119}Sn-^{13}C)$s similar to those of di-halides (342.0 to 385.7 Hz) which correspond to near-tetrahedral angles (109–113°). However, calculated values of θ for four-coordinate compounds **5** and **6** are a little higher (θ 126° and 124°, respectively), nevertheless they are 10–15° lower than those of dialkoxide dimers (see below). It is possible that beside the repulsion effect (θ of dialkoxides $> \theta$ of dithiolates) steric and coordination effects (the equilibria, monomer $\leftrightarrows$ dimer $\leftrightarrows$ polymer) are also involved.

Electronic, steric, and perhaps, stereochemical effects cause the deviation of the real structure of all the organotin(IV) compounds and ions of the type R_2SnX_3 from ideal *cis*-trigonal-bipyramidal structure. These deformations result in the opening of θ angles compared with the ideal angle of 120°. All five-coordinate compounds given in Table 1 give values of $^1J(^{119}Sn-^{13}C)$ above ca. 452 Hz which is the value corresponding to the angle of 120° as derived from eq. 2. The value of θ in compound **8**, 142° is in good agreement with the C–Sn–C angle of the $(CH_3)_2SnCl_3^-$ anion (140 ± 2°) in the compound $[(CH_3)_2SnCl \cdot terpy]^+$ $[(CH_3)_2SnCl_3]^-$ [41]; the C–Sn–C angle in the $Bu_2SnBr_3^-$ anion (136°) is a little lower owing to repulsion. The values of θ calculated from $^1J(^{119}Sn-^{13}C)$ values for compound **10** ($\sim$ 138° and 139°, respectively) are almost identical with θ for the related compound $Bu_2\overline{Sn(OCH_2CH_2O)}$, as determined by diffraction measurements (138.6° [42]). Lower values of θ ($\sim$ 130°) were found for the compounds **11** and **12** due to a characteristic geometry of the tridentate ligand [20]. The values of θ and $^1J(^{119}Sn-^{13}C)$ of compound **21** were used for the correlation of eq. 2 [15].

Also the structure of six-coordinate diorganotin(IV) complexes cannot be simply described in terms of *cis*- or *trans*-symmetry owing to the effects discussed above. The values of θ of the di-n-butyltin(IV) compounds calculated from eq. 2 vary in a broad region (129–176°), but most lie in the range 129–146° (carboxylates **13–20** in the pure state or in a $CDCl_3$ solution, oxinate **22**, picolinate **28** and dithio-carbamates **23** and **24**) or are close to 180° (162–176°). In accordance with the literature [43] we designated the first group as irregular trapezoidal-bipyramidal (skew) and the second as a slightly distorted *trans*-octahedral structure (compounds **1**, **2**, **13**, **14** in hexamethylphosphorotriamide, **9** in hexadeuteriodimethyl sulphoxide, **25**, **26**, **27**, **30** and **31**). The other six-coordinate complexes listed in Table 1 possess a transition structure between skew- and *trans*-types. Moreover, we should remark here that there is also good agreement between the values of θ calculated from eq. 2 and those determined by other methods within their limits of accuracy (see ref. 15). This can be shown by the compounds **13** and **14** where the angles, θ 133° and 134° as calculated from eq. 2, are in good agreement with those calculated from the quadrupole splitting of Mössbauer spectra (141° and 143°, respectively) (mean values QS 3.47 and 3.52 mm s^{-1}, resp.) [44] using the equation of Sham and Bancroft [45].

Conclusion

From the results of our study of ^{13}C and ^{119}Sn NMR spectra of di-n-butyltin(IV) compounds and their complexes we have found that it is possible to describe semiquantitatively the shape of coordination polyhedra of these compounds by analysis of their chemical shifts $\delta(^{119}Sn)$ and their coupling constants $^1J(^{119}Sn-^{13}C)$. As these parameters are only slightly dependent on the types of alkyl substituents, it

is possible to use these results for a rough estimation of the structure of other dialkyltin(IV) compounds.

References

1 J. Holeček, M. Nádvorník, K. Handlíř and A. Lyčka, J. Organomet. Chem., 241 (1983) 177.
2 M. Nádvorník, J. Holeček, K. Handlíř and A. Lyčka, J. Organomet. Chem., 275 (1984) 43.
3 J. Holeček, K. Handlíř, M. Nádvorník, A. Lyčka and R. Wagener, Proc. Xth Conf. Coord. Chem., June 4, 1985, Smolenice-Bratislava (Czechoslovakia).
4 D.L. Alleston and A.G. Davies, J. Chem. Soc., (1962) 2050.
5 M.A. Mullins and C. Curran, Inorg. Chem., 6 (1967) 2017.
6 J.W. Nicholson, J.A. Douek and A.J. Crowe, J. Organomet. Chem., 219 (1981) 309.
7 P.J. Smith, R.F.M. White and L. Smith, J. Organomet. Chem., 40 (1972) 341.
8 J. Holeček, K. Handlíř, A. Lyčka, T.K. Chattopadhyay, B. Majee and A.K. Kumar, Collect. Czech. Chem. Commun., 51 (1986) 1100.
9 T. Tanaka, M. Kamura, Y. Kawasaki and R.I. Okawara, J. Organomet. Chem., 1 (1964) 484.
10 J.L.K.F. de Vries and R.H. Herber, Inorg. Chem., 11 (1972) 2458.
11 J. Lokaj, V. Kettmann, V. Vrábel and E. Kellö, Acta Crystallogr., in press.
12 G. Domazetis, R.J. Magee and B.D. James, J. Inorg. Nucl. Chem., 41 (1979) 1547.
13 R. Graziani, G. Bombieri, E. Forsellini, P. Furlan, V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 125 (1977) 43.
14 P.G. Harrison, N.W. Sharpe, C. Pelizzi, G. Pelizzi and P. Tarasconi, J. Chem. Soc., Dalton Trans., (1983) 921.
15 J. Holeček and A. Lyčka, Inorg. Chim. Acta, 118 (1986) L17.
16 V.S. Petrosyan, Prog. NMR Spectrosc., 11 (1977) 115 and references therein.
17 G. Domazetis, R.J. Magee, B.D. James and J.D. Cashion, J. Inorg. Nucl. Chem., 43 (1981) 1351.
18 P.J. Smith and L. Smith, Inorg. Chim. Acta Rev., 7 (1973) 11.
19 T.N. Mitchell, J. Organomet. Chem., 59 (1973) 189.
20 A. Saxena and J.P. Tandon, Polyhedron, 2 (1983) 443.
21 W.F. Howard, R.W. Crecely and W.H. Nelson, Inorg. Chem., 24 (1985) 2204.
22 W. McFarlane, J.C. Maire and M. Delmas, J. Chem. Soc., Dalton Trans., (1972) 1862.
23 J. Otera, T. Yano, E. Kunimoto and T. Nakata, Organometallics, 3 (1984) 426.
24 H.C. Clark, V.K. Jain, R.C. Mehrotra, B.P. Singh, G. Srivastava and T. Birchall, J. Organomet. Chem., 279 (1985) 385.
25 P.J. Smith and A.P. Tupčiauskas, Annu. Rep. NMR Spectrosc., 8 (1978) 291 and references therein.
26 B. Wrackmeyer, Annu. Rep. NMR Spectrosc., 16 (1985) 73 and references therein.
27 A.G. Davies and J.A.A. Hawari, J. Chem. Soc., Perkin Trans., 1, (1983) 875.
28 A.G. Davies, A.J. Price, H.M. Dawes and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1986) 297.
29 S. Roelens and M. Taddei, J. Chem. Soc., Perkin Trans., 2, (1985) 799.
30 J. Otera, J. Organomet. Chem., 221 (1981) 57.
31 A.G. Davies and A.J. Price, J. Organomet. Chem., 258 (1983) 7.
32 A.G. Davies, J.A.A. Hawari and P. Hua-de, J. Organomet. Chem., 251 (1983) 203.
33 T. Yano, K. Nakashima, J. Otera and R. Okawara, Organometallics, 4 (1985) 1501 and ref. therein.
34 A. Lyčka and J. Holeček, J. Organomet. Chem., 294 (1985) 179.
35 J. Otera, A. Kusaba, T. Hinoishi and Y. Kawasaki, J. Organomet. Chem., 228 (1982) 223.
36 R.J. Rao, G. Srivastava, R.C. Mehrotra, B.S. Saraswat and J. Mason, Polyhedron, 3 (1984) 485.
37 H. Fujii and M. Kimura, Bull. Chem. Soc. Jpn., 44 (1971) 2643.
38 A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, J. Chem. Soc. A, (1970) 2862.
39 K.C. Molloy, K. Quill and I.W. Nowell, J. Organomet. Chem., 289 (1985) 271 and ref. therein.
40 J.L. Baxter, E.M. Holt and J.J. Zuckerman, Organometallics, 4 (1985) 255 and ref. therein.
41 F.W.B. Einstein and B.R. Penfold, J. Chem. Soc. A, (1968) 3019.
42 A.G. Davies, A.J. Price, H.M. Dawes and M.B. Hursthouse, J. Organomet. Chem., 279 (1984) C1.
43 D.L. Kepert, Inorg. Chem., 12 (1977) 1.
44 J.J. Zuckerman, Adv. Organomet. Chem., 9 (1970) 21.
45 T.K. Sham and G.M. Bancroft, Inorg. Chem., 14 (1975) 2281.