^{119}Sn AND ^{13}C NMR SPECTRAL STUDY OF SOME VINYLTIN(IV) COMPOUNDS INVOLVING THE Sn–S BOND

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The ^{13}C and ^{119}Sn NMR spectra were examined for two series of vinyltin(IV) compounds involving the Sn–S bond, of general formulas $(CH_2{=}CH)_nSn(SR)_{4-n}$ ($n = 0 - 4$) and $(CH_2{=}CH)_nSn(Cl)(SR)_{3-n}$ ($n = 0 - 3$) where R = 1-C_4H_9, $C(S)N(C_2H_5)_2$ or 8-quinolinyl C_9H_6N, or SR = ½(SCH_2CH_2S). Deuteriochloroform and hexadeuteriodimethyl sulfoxide served as non-coordinating and coordinating solvents, respectively. The ^{13}C and ^{119}Sn NMR data provided a basis for discussion of the nature and strength of the Sn–S bonding, coordination of the central tin atom including the shape of the coordination polyhedron, and the ability of the compounds to form donor–acceptor complexes.

Organotin(IV) compounds of the R_nSnX_{4-n} type where R is an organic substituent, X is a polar group, and $n = 1 - 4$, are known to form, more or less readily, complex compounds with electron pair donors, whereby they increase the number of bonding partners of the central atom, hence, its coordination number. How easily such donor-acceptor complexes are formed, and how thermodynamically stable they are, depends on a number of physical factors such as temperature and concentration but mainly on chemical factors. The most important of them include, in addition to the donor properties of the ligands, the nature of the organic substituents R and polar groups X in the organotin(IV) compounds R_nSnX_{4-n}, their proportion (parameter n), state of aggregation, and nature of solvent. Organotin(IV) compounds which involve the Sn–S bond generally exhibit a lower tendency to form complexes in which the coordination number of the central atom is higher than 4. This fact is attributed to the generally lower electronegativity of the sulfur atom as compared, e.g., to that of oxygen and light halogens, the usual partners of tin in the polar groups of organotin compounds predisposed to form complexes. It has been suggested, however, that steric phenomena associated with the higher effective size of the sulfur atom may play an equally important role[1].

In the present paper we attempt to answer some of the questions based on ^{13}C and ^{119}Sn NMR data of selected vinyltin(IV) compounds involving the Sn–S bond, whose general formulas are $(CH_2=CH)_nSn(SR)_{4-n}$ ($n = 0 - 4$) and $(CH_2=CH)_nSn(Cl)(SR)_{3-n}$ ($n = 0 - 3$) where R = 1-C_4H_9, $C(S)N(C_2H_5)_2$ or 8-quinolinyl, or SR = ½$(S(CH_2)_2S)$. Deuteriochloroform and hexadeuteriodimethyl sulfoxide served as non-coordinating and coordinating solvents, respectively. The choice of the organic substituent R (vinyl group) and the polar groups SR was deliberate: vinyltin(IV) compounds were chosen with regard to the relative simplicity and unambiguous identification and interpretation of their ^{13}C and ^{119}Sn spectra, and also for a higher group electronegativity of the vinyl group as compared, e.g., to alkyl groups, hence, for the higher Lewis acidity of the Sn centre, which is favourable to donor–acceptor complex formation. The polar SR groups were chosen so as to enable the problem of formation of complexes of organotin compounds involving Sn–S bonds to be treated on a broad basis, including the solvent effect, ligand nature, and donor atom properties.

EXPERIMENTAL

Compounds *I*, *II*, *IV*, *VI*, *VII*, *IX* – *XII*, *XVI*, and *XVII* (see Tables I and II) were prepared following published procedures[2 – 8].

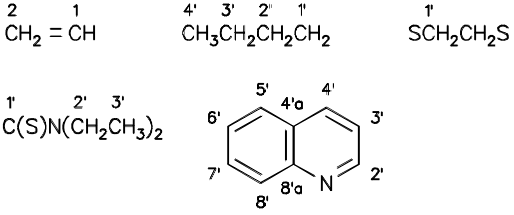
Compound *III* was synthesized by reacting vinyltrichlorostannane (4.0 g, 16 mmol) with butanethiol (4.3 g, 48 mmol) in alkaline medium at room temperature. The liquid product was dried with anhydrous calcium chloride and distilled in a vacuum. Compound *V* was prepared likewise from divinyldichlorostannane (4.9 g, 20 mmol) and ethane-1,2-dithiol (1.9 g, 20 mmol). Compound *XIII* was obtained by reacting vinyltrichlorostannane (3.0 g, 12 mmol) with disodium salt of ethane-1,2-dithiol (1.7 g, 12 mmol) in 30 ml of hexane (stirring for 1 h, 25 °C). The precipitated product was extracted with chloroform and allowed to crystallize, and the crystallized product was recrystallized from that solvent. Compound *VIII* was synthesized by reaction of vinyltrichlorostannane (3 g, 12 mmol) with sodium *N*,*N*-diethyldithiocarbamate trihydrate (8 g, 36 mmol) in 90 ml of ethanol (1 h, 25 °C). The precipitate was filtered out and extracted with chloroform, the extract was allowed to crystallize, and the crystals were recrystallized from ethyl acetate. Compounds *XIV* and *XV* were prepared likewise: *XIV* from 2.4 g (10 mmol) of divinyldichlorostannane and 2.2 g (10 mmol) of sodium *N*,*N*-diethyldithiocarbamate in 40 ml of ethanol, and *XV* from 3 g (12 mmol) of divinyldichlorostannane and 5.3 g (24 mmol) of sodium *N*,*N*-diethyldithiocarbamate in 70 ml of methanol. All of the compounds were analyzed chemically and their basic physical parameters were determined (Table III). The identity of the compounds was also confirmed by analysis of their ^{13}C and ^{119}Sn NMR spectra (see bellow).

^{13}C NMR spectra were measured at 100.61 MHz on a Bruker AM 400 instrument in a 5 mm dual tube. The $\delta(^{13}C)$ chemical shifts (in ppm) are relative to TMS as an internal standard ($\delta = 0$). ^{15}N NMR spectra were measured on the natural abundance level at 30.43 MHz on a Bruker AM 300 spectrometer in 10 mm tubes. The ^{15}N chemical shifts are relative to nitromethane as an external standard. ^{119}Sn NMR spectra were measured at 37.14 MHz on a JEOL JNM-FX 100 instrument, the $\delta(^{119}Sn)$ chemical shifts are relative to tetramethylstannane as an external standard. The ^{119}Sn CP/MAS NMR spectra were run on a Bruker 300 instrument using double bearing probes[9]. Coupling constants *J* are given in Hz.

TABLE I
Analytical and physical data of compounds *III* – *V*, *VIII*, *XIII* – *XV*

Compound	M.p., b.p., °C	Calculated/Found				
		% C	% H	% Sn	% S	other
III	153 – 155/200 Pa[a]	40.69	7.32	28.72	23.28	
		40.58	7.48	28.93	23.10	
V	85 – 87/50 Pa	27.20	3.80	44.80	24.20	
		27.97	3.98	44.69	24.32	
VIII	128 – 130	34.57	5.63	20.10	32.58	7.12[b]
		34.16	6.06	19.89	32.59	7.22
XIII	180 – 182	17.57	2.58	43.42	23.46	12.97[c]
		17.72	2.38	43.16	23.40	13.06
XIV	97 – 98	30.32	4.52	33.29	17.99	3.93[b]
		30.35	4.83	33.16	17.91	3.87
						9.94[c]
						9.89
XV	125 – 127	30.17	4.85	24.85	26.85	5.86[b]
		29.97	4.90	24.72	26.76	5.93
						7.42[c]
						7.58

[a] n_D^{25} 1.5505; [b] % N; [c] % Cl.



SCHEME 1

TABLE II
Parameters of ^{13}C and ^{119}Sn NMR spectra[a] of compounds $(CH_2{=}CH)_nSn(SR)_{4-n}$ (n = 0 – 3) at 300 K

Compound	R [SR]	n	$\delta(^{119}Sn)$	$\delta(^{13}C)/(J(^{119}Sn, ^{13}C))$		
				C(1)	C(2)	other (R)
I[b]	1-C_4H_9	3	−73.8	134.99 (539.0)	136.76 [c]	ref.[2]
I[d]	1-C_4H_9	3	−99.5	136.82 (570.1)	135.72 [c]	ref.[2]
II[b]	1-C_4H_9	2	16.3	134.90 (571.3)	137.29 [c]	ref.[3]
II[d]	1-C_4H_9	2	−24.2	138.34 (636.0)	136.05 [c]	ref.[3]
III[b]	1-C_4H_9	1	87.6	135.95 (601.8)	137.72 [c]	C(1′): 36.06 (20.8) C(2′): 27.53 (18.3) C(3′): 21.44 C(4′): 13.35
III[d]	1-C_4H_9	1	31.5	138.99 (682.1)	136.21 [c]	C(1′): 35.80 (19.1) C(2′): 27.10 (17.1) C(3′): 21.12 C(4′): 13.37
IV[b]	1-C_4H_9	0	140.9	–	–	C(1′): 35.96 (21.9) C(2′): 28.30 (19.7) C(3′): 21.52 C(4′): 13.39
V[b]	[1/2$(SCH_2)_2$S)]	2	67.9	135.88 (571.7)	137.49 [c]	C(1′): 35.86
V[d]	[1/2$(SCH_2)_2$S)]	2	−59.1	142.66 (727.8)	134.08 (7.0)	C(1′): 33.62
VI[b]	C(S)N$(C_2H_5)_2$	3	−202.1	140.01 (587.6)	134.86 [c]	ref.[2]
VII[b]	C(S)N$(C_2H_5)_2$	2	−471.7	145.45 (956.9)	130.65 [c]	ref.[3]
VIII[b]	C(S)N$(C_2H_5)_2$	1	−819.0	156.74 (1 271.9)	124.97 [c]	C(1′): 199.30 C(2′): 49.80 C(3′): 11.83
IX[b]	C(S)N$(C_2H_5)_2$	0	−767.4	–	–	C(1′): 192.64, 186.38 C(2′): 49.84, 49.30, 48.87, 47.54 C(3′): 13.28, 12.14 10.95
X[b]	8-quinolinyl	3	−168.3	142.83 (587.4)	138.20 (8.9)	ref.[2,4]

TABLE II
(*Continued*)

Compound	R [SR]	*n*	$\delta(^{119}Sn)$	$\delta(^{13}C)/(J(^{119}Sn, ^{13}C))$		
				C(1)	C(2)	other (R)
XI[b]	8-quinolinyl	2	–282.4 –306.3[e]	149.58 (841.7)	131.04 (3.0)	ref.[4,5,10]
XII[b,f]	8-quinolinyl	1	–313.3 –319 ± 1[e]	153.89 (842.3)	129.24 (< 3)	ref.[5]

[a] Numbering of atoms is depicted in Scheme 1; [b] solvent: deuteriochloroform; [c] not found; [d] solvent: hexadeuteriodimethyl sulfoxide; [e] $\delta(^{119}Sn)$ in the solid state (CP/MAS); [f] $\delta(^{15}N) = -101.75$, $^{3}J(^{119}Sn),^{1}H) = 8.15$ Hz.

RESULTS AND DISCUSSION

The parameters of the ^{13}C and ^{119}Sn NMR spectra of the compounds $(CH_2{=}CH)_nSn(SR)_{4-n}$ (*I* – *XII*) and $(CH_2{=}CH)_nSn(Cl)(SR)_{3-n}$ (*XIII* – *XVII*) are given in Tables II and III, respectively.

Compounds $(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n}$ (I – IV) *and* $(CH_2{=}CH)_2Sn(SCH_2CH_2S)$ (V)

The $\delta(^{119}Sn)$ value indicates that compounds *I* and *II* in deuteriochloroform solutions occur[2,3] as monomeric pseudotetrahedral molecules. The positive $\delta(^{119}Sn)$ value of compound *III*, as well as the fact that this parameters does not change more than by

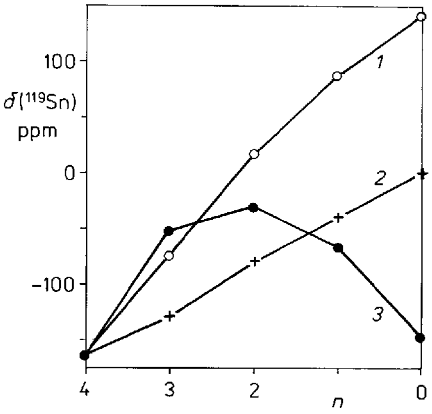


FIG. 1
Chemical shifts $\delta(^{119}Sn)$ of compounds $(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n}$ (*1*), $(CH_2{=}CH)_n$–$Sn(CH_3)_{4-n}$ (*2*) and $(CH_2{=}CH)_nSnCl_{4-n}$ (*3*) in dependence on parameter *n*; the values were taken from refs[5,11,12] and from this work

3 ppm within the concentration region of approximately 5 – 25% and temperature region of –30 °C to +50 °C, indicates that compound *III*, also, occurs in deuteriochloroform solutions in the form of single isolated pseudotetrahedral molecules without any appreciable tendency to associate into larger units. The $\delta(^{119}Sn)$ values of the compounds $(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n}$ with $n = 0 - 4$ (compounds *I* – *IV*, respectively) and of $(CH_2{=}CH)_4Sn$ ($\delta(^{119}Sn) = -164.4$, ref.[5]), plotted against *n*, give a monotonous, slightly bent line, with no indication of the so-called U-shape (Fig. 1). This is usual if the electronegativities of the organic substituents and the polar groups X and Y in compounds of the SnX_nY_{4-n} type do not differ significantly, such as in the $(CH_2{=}CH)_nSn(CH_3)_{4-n}$ (ref.[11]) and $SnBr_nI_{4-n}$ (ref.[12]) series (Fig. 1). An appreciable U-shape, on the other hand, is observed in the $\delta(^{119}Sn)$ vs n plot for compounds with different electronegativities, as in the $(CH_2{=}CH)_nSnCl_{4-n}$ series[5] (Fig. 1). The nearly strictly linear and, in particular, monotonous shape of the plot for the $(CH_2{=}CH)_nSn(SC_4H_9\text{-}1)_{4-n}$ series in deuteriochloroform can be regarded as evidence of the same coordination of the tin atom, i.e. of its coordination number 4, in all of the

TABLE III
Parameters of ^{13}C and ^{119}Sn NMR spectra[a] of compounds $(CH_2{=}CH)_nSn(Cl)(SR)_{3-n}$ (n = 1, 2) at 300 K

Compound	R [SR]	*n*	$\delta(^{119}Sn)$	$\delta(^{13}C)/(J(^{119}Sn, ^{13}C))$		
				C(1)	C(2)	other (R)
XIII[b]	[1/2(S(CH$_2$)$_2$S)]	1	–29.6	135.34 (787.4)	139.49 [c]	C(1′): 35.82
XIII[d]	[1/2(S(CH$_2$)$_2$S)]	1	–250.0	152.28 (1 289.4)	129.64 [c]	C(1′): 32.40
XIV[b]	C(S)N(C$_2$H$_5$)$_2$	2	–338.2	140.77 (854.5)	136.32 [c]	C(1′): 194.71 C(2′): 50.56 C(3′): 11.95
XV[b]	C(S)N(C$_2$H$_5$)$_2$	1	–655.1 –663 ± 1[e]	155.32 (1 219.2)	127.28 [c]	C(1′): 196.35 C(2′): 50.92 C(3′): 11.80
XVI[b]	8-quinolinyl	2	–201.3 –210 ± 1[e]	140.70 (852.9)	136.83 (3.3)	ref.[5,6]
XVII[b]	8-quinolinyl	1	–336.0 –335 ± 1[e]	153.78 (990.8)	129.98 (< 3)	ref.[5]

[a] Numbering of atoms is depicted in Scheme 1; [b] solvent: deuteriochloroform; [c] not found; [d] solvent: hexadeuteriodimethyl sulfoxide; [e] $\delta(^{119}Sn)$ in the solid state (CP/MAS).

compounds in the series, and hence, of a pseudotetrahedral shape of the isolated molecule *III* in the deuteriochloroform solution (see above).

Thus, the $(1\text{-}C_4H_9)_SS$ substituent must be expected to only slightly contribute to the Lewis acidity of compounds of this kind, as also indicated by the nearly identical values of the group electronegativities of the $(1\text{-}C_4H_9)S$ and $CH_2{=}CH$ groups (about 2.6 and 2.7, respectively[13]). The weakly polar character of the Sn–S bonding is also documented by the $^1J(^{119}Sn,^{13}C(1))$ coupling constants in the $(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n}$ series, which increase only very slightly with decreasing *n*. The increase is comparable to that in the $(CH_3)_nSn(CH{=}CH_2)_{4-n}$ series[11]. In this respect the two series differ markedly from the $(CH_2{=}CH)_nSnCl_{4-n}$ series where the $^1J(^{119}Sn,^{13}C(1))$ values increase much more steeply (Fig. 2). Since in the first (Fermi) approximation the $^1J(^{119}Sn,^{13}C(1))$ values are a measure of the *s*-character of the tin atom orbitals in the Sn–C bond and hence, of the *p*-character of the tin atom orbitals in the Sn–S bond (and according to Bent's rule[14], also of the polarity of that bond), the increase in the Lewis acidity in the $(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n}$ series with increasing number of $(1\text{-}C_4H_9)S$ groups (decreasing *n*) will be as low as the increase in the acidity of the $(CH_3)_nSn(CH{=}CH_2)_{4-n}$ compounds with increasing number of $CH_2{=}CH$ groups. In contrast to the compounds $(CH_2{=}CH)_nSnCl_{4-n}$, which readily form donor–acceptor complexes where the coordination number of the central tin atom is higher than 4 (ref.[5]), the compounds $(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n}$ will be very reluctant to form such complexes. The compounds $(CH_3)_nSn(CH{=}CH_2)_{4-n}$ will not form them at all.

Nevertheless, the characteristic shifts of the $\delta(^{119}Sn)$ values and $\delta(^{13}C)$ values of the carbon atoms of the vinyl group as well as the $^1J(^{119}Sn,^{13}C)$ coupling constants of compounds *I*, *II* and *III* when passing from a non-coordinating solvent, deuteriochloroform, to a coordinating solvent, hexadeuteriodimethyl sulfoxide[2,3], do not rule out the

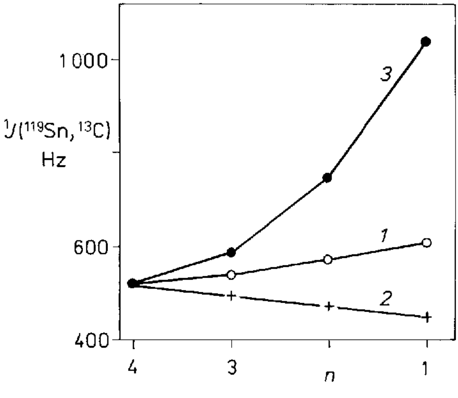


FIG. 2
Coupling constants $^1J(^{119}Sn,^{13}C)$ of compounds $(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n}$ (*1*), $(CH_2{=}CH)_nSn(CH_3)_{4-n}$ (*2*) and $(CH_2{=}CH)_n$–$SnCl_{4-n}$ (*3*) in dependence on parameter *n*; the values were taken from refs[5,11] and from this work

possibility of formation of relatively weak complexes as a result of the chemical equilibrium

$$(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n} + (CD_3)_2SO \rightleftharpoons$$

$$(CH_2{=}CH)_nSn[S(1\text{-}C_4H_9)]_{4-n} \cdot (CD_3)_2SO \qquad (A)$$

which is probably shifted appreciably towards the substrate. The differences in the values of the relevant parameters of the ^{13}C and ^{119}Sn NMR spectra of the compounds in the two solvents, which increase with increasing number of (1-C_4H_9)S groups and a shift of the equilibrium towards products in order *I* < *II* < *III*, suggest that the reluctance of compounds *I* – *III* to form strong complexes is a consequence of the low, though observable, polarity of the Sn–S bond, rather than of the steric effects of the bulky sulfur atoms. In fact, the latter effect would have to give rise to an opposite trend with increasing number of (1-C_4H_9)S groups.

Compound *V* in deuteriochloroform is also pseudotetrahedral, as the δ(^{119}Sn) and ^1J(^{119}Sn,^{13}C) values indicate[3]. Owing to the chelating effect of the –SCH_2CH_2S– group, however, this compound is better fitted to a change in the structure of the coordination polyhedron from the tetrahedron to a trigonal bipyramid[15] (coordination number increases from 4 to 5), so that the equilibrium of the complex formation with a molecule of hexadeuteriodimethyl sulfoxide (Eq. (*A*)) is more shifted towards products than in the case of compound *II*. This is evidenced by the difference between the δ(^{119}Sn) values in deuteriochloroform and hexadeuteriodimethyl sulfoxide (Δδ(^{119}Sn) = 127.0 ppm).

Compounds $(CH_2{=}CH)_nSn[SC(S)N(C_2H_5)_2]_{4-n}$ (VI – IX)

Tri- and divinyltin(IV) *N,N*-diethyldithiocarbamates (compounds *VI* and *VII*, respectively) in deuteriochloroform solutions occur as isolated monomeric molecular complexes with the anisobidentate chelating function of the dithiocarbamate CS_2 group (^{13}C and ^{119}Sn NMR data, refs[2,3]). The coordination polyhedron of the pentacoordinated tin atom in *VI* has the shape of a distorted *cis*-trigonal bipyramid[2], whereas the molecular chelating complex of hexacoordinated tin in *VII* is a trapezoidal (*skew*) bipyramid[3]. For compound *VIII*, the facts that the δ(^{119}Sn) value is markedly shifted upfields (–819.0 ppm) and that the ^{13}C NMR spectrum exhibits only one series of signals for all of the three $(C_2H_5)_2NCS_2$ ligands, suggests that this compound involves a central tin atom coordinated by seven bonding partners, viz. the C(1) carbon atom of the vinyl group and six sulfur atoms of the three bidentate $(C_2H_5)_2NCS_2$ ligands. The parameters of the ^{13}C NMR spectra, i.e. the ^1J(^{119}Sn,^{13}C) coupling constants and δ(^{13}C) chemical shifts of the two carbon atoms in the vinyl group, also correspond with the high coordination number of the tin atom[2,3]. It can be inferred that the units of compound *VIII* possess the shape of a pentagonal bipyramid, probably distorted slightly. In view of the high $^1J(^{119}Sn,^{13}C)$ value, the C(1) carbon atom occupies the axial position (in place of the higher *s*-electron contribution of the tin orbitals to the Sn–C bond). We have been able to prove such shape of the molecular complex of the analogous phenyltin(IV) compound in the crystal state[16], and such shape has also been evidenced by X-ray diffraction study for other $RSn[SC(S)N(C_2H_5)_2]_3$ compounds in the solid state (R = CH_3, ref.[17]; R = 1-C_4H_9, ref.[18]).

For compounds *VI* – *VIII*, the chemical shifts $\delta(^{13}C(1'))$ of the $(C_2H_5)_2NCS_2$ ligands, which are 195.35 (ref.[2]), 197.28 (ref.[3]), and 199.30, respectively, lie between those of the organic ester $(C_2H_5)_2NC(S)SC_2H_5$ (194.5, ref.[19]), which we consider a prototype of the monodentate $-CS_2$ group, and the $(C_2H_5)_2NCS_2^-$ anion (209.0 for the ammonium salt[19]), which serves as a prototype of its purely bidentate function. It can be deduced that in the three compounds studied, the $(C_2H_5)_2NCS_2$ ligands are bonded anisobidentately to the tin atom, i.e. by one strong and one weaker Sn–S bond. The latter grows stronger in order *VI* < *VII* < *VIII*. In crystals of the analogous compounds $(CH_3)_nSn[(C_2H_5)_2NCS_2]_{4-n}$, this phenomenon gives rise to a gradual shortening of the weaker bond from 3.16 Å for $n = 3$ (ref.[20]) to 3.06 and 2.95 Å for $n = 2$ (ref.[21]) to 2.817, 2.772 and 2.749 Å for $n = 1$ (ref.[17]). The shift of the $\delta(^{13}C(1'))$ values of compounds *VI* – *VIII* to the limit of approximately 209.0 for the *N,N*-diethyldithiocarbamate anion, and hence, the evidence of the increasing importance of its bidentating function, would be even more pronounced if correction for the weight of the central atom was applied. For organosilicon esters of carboxylic acids with an unambiguously monodentate function of the carboxy group, the $\delta(^{13}C(COO))$ values are shifted appreciably upfields as compared to organic esters of those acids[22,23]. Thus, it is reasonable to assume that the chemical shift $\delta(^{13}C(1'))$ of the purely monodentate CS_2 group bonded through one sulfur atom to the tin atom would be lower than the value of 194.5 ppm for $(C_2H_5)_2NC(S)SC_2H_5$. For this reason, compound *IX*, which in the solid state involves two monodentate and two bidentate $(C_2H_5)_2NCS_2$ groups[7], exhibits two series of signals in the ^{13}C NMR spectrum, with $\delta(^{13}C(1'))$ = 186.38 ppm for the monodentate CS_2 group and 192.64 ppm for the bidentate group.

Compounds $(CH_2{=}CH)_nSn(SC_9H_6N)_{4-n}$ (X – XII)

As follows from the above text, the chemical shifts $\delta(^{119}Sn)$ of compounds *VI* – *IX* can be considered characteristic of tri-, di-, and monovinyltin(IV) compounds in which the coordination numbers of the central tin atom are 5, 6, and 7, respectively. Such complexes are comparatively rigid and the chelating bonding of the two sulfur atoms to the tin atom is sufficiently strong[24]. As compared to those compounds, for compounds *X* – *XII* the $\delta(^{119}Sn)$ chemical shifts are shifted downfields, indicating lower effective coordination numbers. Nevertheless, ^{1}H, ^{13}C, ^{15}N, and ^{119}Sn NMR spectra[2 – 5,10] provide sufficient evidence that in compounds *X* and *XI*, the quinolinethiolate ligands SC_9H_6N are bonded to the tin atom through a strong Sn–S bond and a relatively weaker donor–acceptor Sn ← N bond, so that the SC_9H_6N groups function as anisobidentate ligands in these compounds as well[2,3]. The δ(^{119}Sn), δ(^{13}C(1)) and δ(^{13}C(2)) values of *XII* are sufficiently indicative of a tin coordination number higher than 4. The δ(^{13}C) parameters of the carbon atoms (particularly the C(2′), C(5′) and C(8′) atoms) of the quinolinethiolate ligand as well as the values of δ(^{15}N) = –101.75 ppm and $^{2}J(^{119}\text{Sn},^{1}\text{H})$ = 8.15 Hz give evidence of a moderate Sn ← N interaction[4]. The occurrence of a single series of signals for the C(2′) – C(8′a) carbon atoms is a proof of magnetic equivalence of the three quinolinethiolate ligands on the NMR time scale. Thus, compound *XII* can be regarded as a chelating complex with anisobidentate SC_9H_6N ligands, where the coordination number of the central tin atom is 7, or more precisely, 4 + 3. With regard to the different strength of the Sn–S and Sn ← N bonds, the environment of the tin atom will form a highly distorted pentagonal bipyramid. The lower δ(^{119}Sn) values for compounds *X* – *XII* are due to a low effective increase in the electron density at the tin atom because of the weak Sn ← N interaction, rather than to lower coordination numbers of the tin atom. The structure of the species of *XI* and *XII* in deuteriochloroform solutions and in crystals is apparently identical, as evidenced by the virtually identical δ(^{119}Sn) values in the two states of aggregation*.

Compounds $(CH_2{=}CH)_nSn(Cl)(SR)_{3-n}$ (XIII – XVII)

The δ(^{13}C) chemical shifts of the two carbon atoms in the vinyl group[2,3] (δ(^{13}C(2)) > δ(^{13}C(1)) indicate that in compound *XIII* in deuteriochloroform solution, the coordination number of tin is 4. The isolated molecule thus possesses the pseudotetrahedral shape. The shift of the δ(^{119}Sn) value upfields as compared to compound *V* (a $CH_2{=}CH$ group being replaced by chlorine) apparently mirrors the “U-shape” effect. The presence of chlorine (a strongly polar entity) in compound *XIII* is the cause of a marked Lewis acidity of the substance, as documented by an approximately 220 ppm shift upfields accompanying the replacement of deuteriochloroform by hexadeuteriodimethyl sulfoxide. Equilibrium (*A*) is shifted appreciably towards the product. The difference between the δ(^{119}Sn) values in the two solvents agrees well with the increase in the coordination number of the central tin atom by 1 (refs[2,3]), hence, the complex of compound *XIII* with a molecule of hexadeuteriodimethyl sulfoxide can be assumed to be

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* In contrast to compounds *XI* (ref.[10]) and *XVI* (ref.[6]), for compounds *XII* and *XVII* the fine structure of the ^{119}Sn NMR CP/MAS spectra in the solid state could not be analyzed because the high half band widths did not permit the $J(^{119}\text{Sn},^{14}\text{N})$ and $J(^{119}\text{Sn},^{35,37}\text{Cl})$ coupling constants to be determined.

trigonally bipyramidal, where – in view of the high value of the coupling constant $^1J(^{119}Sn,^{13}C)$ – the vinyl group is in one of the axial positions.

For compound *XVI*, the ^{13}C and ^{119}Sn NMR data indicate the occurrence of molecular chelating complexes with a distorted *cis*-trigonally bipyramidal arrangement of the environment of the pentacoordinated central tin atom[6], both in the solid state and in deuteriochloroform solution. The $\delta(^{119}Sn)$ value of *XIV* is typical of divinyltin compounds where the coordination number of tin is 5 (ref.[2]), the value of the interaction constant $^1J(^{119}Sn,^{13}C) = 854.5$ is virtually identical with that of *XVI*, and the $\delta(^{13}C(1'))$ value is indicative of the anisobidentate function of the CS_2 group (see above). From this it can be concluded that compound *XIV* in deuteriochloroform solution is also present in the form of isolated molecules with the *cis*-trigonally bipyramidal structure. For compound *XV*, our X-ray investigation on single crystals[16] revealed a molecular chelating complex with the structure of a highly distorted octahedron with the carbon and chlorine atoms in a mutual *cis* position. The four Sn–S bonds are nearly identical in length, which is from 2.552 to 2.613 Å. The $\delta(^{119}Sn)$ value of *XV* in deuteriochloroform solution and in the solid state is −655.1 ppm and −663 ± 1, respectively, hence, shifted more than 150 ppm downfields as compared to *VIII*. This corresponds well with the concept of octahedral arrangement about the tin atom (coordination number 6). Also consistent with this are the $\delta(^{13}C)$ values of the C(1) and C(2) carbon atoms (coordination number higher than 4, refs[2,3]) and, in particular, $\delta(^{13}C(1'))$ (bidentate function of the two CS_2 groups of the $(C_2H_5)_2NCS_2$ ligand, which are equivalent on the NMR time scale).

Most probably, compound *XVII* is also pseudooctahedral, although its $\delta(^{119}Sn)$ value is considerably lower than for *XV*, due to the weak donor–acceptor Sn ← N bonding as discussed above. The strength of the bonding and the structure of the tin atom environment in *XVII*, however, remain preserved in deuteriochloroform solutions as they are in the solid state. This is evidenced by the virtually identical $\delta(^{119}Sn)$ values in the two states of aggregation (Table III). The ^{13}C NMR parameters are consistent with the concept of pseudooctahedral coordination of the tin environment in this compound[2,3].

CONCLUSIONS

The results obtained give evidence that vinyltin(IV) compounds involving weakly polar $(1\text{-}C_4H_9)S$ groups are very weak Lewis acids, with no pronounced tendency to form complexes with electron pair donors. Increase in the number of such “polar” groups contributes very slightly to the Lewis acidity. Considerably more marked is the role of the chelating effect, as follows from a comparison of the relevant NMR spectral parameters for compounds involving the $(1\text{-}C_4H_9)S$ group on the one hand and the SCH_2CH_2S group on the other hand. This conclusion is, moreover, borne out by the fact that cyclic compounds of the $R_2\overline{SnSCH_2CH_2S}$ type in the solid state form associates with intermolecular Sn· · ·S bonding[25], whereas no reliable information concerning the association of analogous acyclic compounds of the $R_2Sn(SR')_2$ type occurs in the literature. The existence and thermodynamic stability of chelating complexes of organotin(IV) compounds involving the Sn–S bond undoubtedly depends on the geometry of that part of the ligand which forms the chelating ring with the central tin atom, as well as on the electron density at the donor atoms of the ligands and at the central atom[24]. Equally important is the mutual arrangement of the organic substituents, polar groups, and ligand donor atoms in the tin coordination sphere. In organotin compounds R_nSnX_{4-n}, where the Sn–R and Sn–X bond energies (R and X electronegativities) are not very different, the tetrahedron→trigonal bipyramid or tetrahedron→octahedron coordination change is facilitated by mutual *cis* arrangement of the polar groups[15]. This requirement is satisfied automatically by bidentate ligands. Thus, in organotin compounds involving the Sn–S bond the formation of chelating complexes is preferred markedly. Owing to this it is possible to isolate and identify organotin 8-quinolinethiolate chelating complexes, with the N and S atoms in the *cis* position, whereas this is impossible for the similar complexes with the C_6H_5S polar group and the C_5H_5N ligand, in which the donor N and S atoms are expected in the mutual trans position[26] by Bent's rule[14].

As expected, replacement of the vinyl group by a chlorine atom (*V–XIII*, *VI–XIV* and *VII–XV* pairs) is associated with an upfields shift of the $\delta(^{119}Sn)$ values in deuteriochloroform solutions. This shift does not imply a change in the coordination number of the central tin atom, it only mirrors increase in the effective negative charge at that atom due to electron density withdrawal from its bonding partners as a result of increase in the Lewis acidity. Replacement of the SCH_2CH_2S, $(C_2H_5)_2NCS_2$ or 8-quinolinethiolate ligands by chlorine atoms (*VII–XIV*, *VIII–XV* and *XI–XVI* pairs), on the other hand, gives rise to shifts of the $\delta(^{119}Sn)$ values downfields as a consequence of decrease in the coordination number of tin by 1. The *XII–XVII* pair is an exception where the replacement of one bidentate 8-quinolinethiolate ligand by a chlorine atom and decrease in the coordination number of the central tin atom (from 4 + 3 to 6) are accompanied by a small shift of $\delta(^{119}Sn)$ upfields. Apparently, the effect of the polar chlorine substituent bringing about increase in the electron density at the central tin atom ultimately predominates over the contribution of the weak $Sn \leftarrow N$ donor–acceptor interaction, despite the decrease in the coordination number of the central atom.

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Note added in proof:

While this paper is in press, Dakternieks et al. (Dakternieks D., Zhu H., Masi D., Mealli C.: Inorg. Chim. Acta *211*, 155 (1993)) published a paper dealing with similar compounds containing –S–Sn–S– fragments. X-Ray structure of $(C_6H_5)Sn[S_2CN(C_2H_5)_2]_3$ was determined and it is in agreement with our data (ref.[16]). Chemical shift $\delta(^{119}Sn)$ for this compound moved from −813 at 25 °C to −888 at −100 °C in dichloromethane. The later value is very close to ^{119}Sn chemical shift of the same compound in the solid state (–894 ppm). Similar behaviour can also be expected for analogous vinyl compound mentioned in this our paper (e.g. in $CH_2=CH–Sn[S_2CN(C_2H_5)_2]_3$ the value of $\delta(^{119}Sn)$ is −819 ppm in deuteriochloroform at 300 K.