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^{119}Sn, ^{15}N, ^{13}C and ^{1}H NMR study of some tri- and di-organotin(IV) 8-quinolinethiolates

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Abstract

Tin-119, nitrogen-15, carbon-13, and proton NMR spectroscopy has been used to study the structures of the triorganotin(IV) 8-quinolinethiolates $R_3Sn(txin)$ and the diorganotin(IV) di(8-quinolinethiolates) $R_2Sn(txin)_2$, (txinH=8-quinolinethiol; R=n-butyl, benzyl, phenyl or vinyl) in solutions of non-coordinating (deuteriochloroform) and coordinating (pyridine) solvents. Both types of compounds form molecular chelates having a weak Sn–N bond in solution. The molecules of $R_3Sn(txin)$ and $R_2Sn(txin)_2$ complex either form a distorted trigonal bipyramid or a distorted octahedron; the organic substituents R are in *cis*-skew positions. The strength of the Sn–N and Sn–O bonds and the degree of the distortion of coordination polyhedra of the compounds studied depend strongly on their composition, i.e. on the number and character of organic substituents R, whereas the type of solvent plays only a secondary role.

Introduction

8-Quinolinethiol (thiooxine, txinH), as well as its oxygen analogue 8-quinolinol (oxine, oxinH), forms relatively strong complexes with various metal ions, which are often utilized in analytical chemistry. Whereas the organotin(IV) oxinates have been studied extensively [1–3], the studies on organotin thiooxinates have been only sporadic. Significant results have been obtained [4] on the crystal and molecular structure of the compound $Ph_3Sn(txin)$. This compound forms a molecular chelate and has a weak Sn–N bond.

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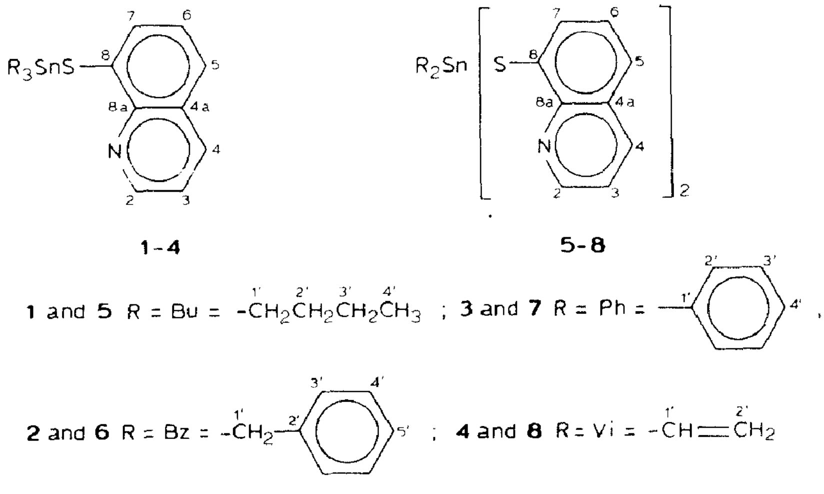


Scheme 1

This paper deals with the structures of triorganotin(IV) thiooxinates $R_3Sn(txin)$ and diorganotin(IV) dithiooxinates $R_2Sn(txin)_2$, resp., (Scheme 1) in solutions of non-coordinating (deuteriochloroform) and coordinating (pyridine) solvents studied by ^{119}Sn, ^{15}N, ^{13}C and ^{1}H NMR spectroscopy so as to characterize the Sn–N and Sn–O bonds with regard to the number and the type of R substituent.

Experimental

An equimolar mixture of sodium salt of 8-quinolinethiol (Reakhim, USSR) and the appropriate triorganotin(IV) chlorides in methanol yielded the compounds **1**–**4** (Table 1). The separated crude products (yields 70–85%) were crystallized from chloroform-ethanol solutions. For compound **2**, methanol was distilled from the reaction mixture and the residue was extracted with chloroform. The organic layer was dried over sodium sulphate and evaporated in vacuum to give a yellow oil. Compounds **5**–**8** were obtained by mixing the sodium salt of 8-quinolinethiol with the appropriate diorganotin(IV) dichlorides in a molar ratio of 2 : 1 in a methanol-acetone solvent mixture (in methanol only mixtures of $R_2Sn(txin)_2$ and $R_2Sn(txin)Cl$ were obtained). The separated crude products were crystallized from acetone-ethanol solution (yields 80–90%). Analytical and physical data of the compounds prepared are given in Table 1.

The ^{1}H and ^{13}C NMR spectra were measured at 400.13 MHz and 100.61 MHz, respectively, using a Bruker AM 400 spectrometer and 5 mm dual probe as described in ref. 3 for the oxinate analogues. The ^{1}H and ^{13}C chemical shifts are from internal tetramethylsilane ($\delta = 0.00$). Approximately 20% solutions or saturated solutions (in case of poor solubility of a compound) in deuteriochloroform were used for the measurements at 300 K.

The ^{15}N NMR spectra were taken at the natural abundance level at 30.42 MHz on a Bruker AM 300 spectrometer in 10 mm tubes at 300 K. The ^{15}N chemical shifts were referred to external neat nitromethane ($\delta = 0.0$). The ^{15}N NMR spectra with $^{117/119}$Sn satellites were measured by use of a refocused selective INEPT [5] technique with polarization transfer from H(2) and WALTZ [6] type decoupling

Table 1

Analytical and physical data for **1**–**8**

Compound [a]	Elemental analysis (Found (calc) (%))					M.p. (°C)
	C	H	Sn	S	N	
1	55.01	7.73	26.54	7.31	2.97	55– 60 [b]
	(54.90)	(7.85)	(26.36)	(7.12)	(3.11)	
2	65.03	5.07	21.29	5.95	2.45	oil
	(65.24)	(4.93)	(21.49)	(5.81)	(2.54)	
3	63.79	4.01	23.40	6.08	2.62	174–175 [c]
	(63.56)	(4.15)	(23.26)	(6.28)	(2.74)	
4	49.87	4.19	33.12	8.70	3.96	65–66
	(50.04)	(4.20)	(32.97)	(8.91)	(3.89)	
5	57.13	5.85	21.86	11.22	5.22	213–214
	(56.44)	(5.46)	(21.45)	(11.59)	(5.06)	
6	61.89	4.58	19.51	10.14	4.74	154–158 [b]
	(61.85)	(4.21)	(19.10)	(10.32)	(4.50)	
7	61.00	3.94	20.23	10.50	4.59	219–220
	(60.73)	(3.74)	(20.00)	(10.81)	(4.72)	
8	53.59	3.40	24.39	12.97	5.86	156–158 [b]
	(53.58)	(3.68)	(24.06)	(13.00)	(5.68)	

[a] See Scheme 1. [b] Decomposition. [c] M.p. 174–175 °C (ref. 1).

during collection (number of scans 8000–15000). The coupling constants $^2J(^{15}N, ^1H(2))$ were measured by selective INEPT with polarization transfer from H(2) and selective decoupling from H(3) during collection ($\gamma B_2 = 100$ Hz, number of scans 200–1000). The evolution periods were optimized for measured coupling constants (50–70 ms).

The ^{119}Sn NMR spectra were measured at 37.14 MHz on a JEOL JNM-FX 100 instrument. The ^{119}Sn chemical shifts were relative to external neat tetramethylstannane ($\delta = 0.0$).

In all cases positive values of chemical shifts denote downfield shifts with respect to a standard.

Results and discussion

^{119}Sn NMR spectra

The values of chemical shifts $\delta(^{119}Sn)$ of compounds **1**–**4** (Table 2) in a solution of a non-coordinating solvent (deuteriochloroform) are rather unusual. They lie within a region of $\delta(^{119}Sn)$ values typical of four- and five-coordinated triorganotin(IV) compounds [7–10], but tending more towards those for five-coordinated compounds. In comparison with $\delta(^{119}Sn)$ values of analogous five-coordinated triorganotin(IV) oxinates R_3Sn(oxin) they are mainly shifted downfield by 6–40 ppm [3]. On the other hand the $\delta(^{119}Sn)$ value of compound **1** is shifted upfield by more than 50 ppm compared with those of isoelectronic (four-coordinated) 1-(tri-n-butylstannylthio)naphtalene, $Bu_3SnS(1\text{-}C_{10}H_7)$ ($\delta(^{119}Sn) = 89.1$ ppm [11]). The values of $\delta(^{119}Sn)$ are concentration independent and depend only slightly on the temperature in the range studied (240–330 K; $\Delta\delta(^{119}Sn)/\Delta T \sim 0.03\text{–}0.10$ ppm/K).

Table 2

Parameters of ^{119}Sn and ^{15}N NMR spectra of compounds **1**–**8** in deuteriochloroform at 300 K

Compound [a]	$\delta(^{119}\mathrm{Sn})$	$\delta(^{15}\mathrm{N})$ $(\Delta\delta(^{15}\mathrm{N}))$ [b]	$J(^{119}\mathrm{Sn}, ^{15}\mathrm{N})$ (Hz)	$^2J(^{15}\mathrm{N}, ^1\mathrm{H})$ [c] (Hz) $(\Delta^2J(^{15}\mathrm{N}, ^1\mathrm{H}))$ [d] (Hz)
1	36.2	−82.1	53.4	10.3
		(−2.7)		(1.1)
2	−63.9	−94.9	92.5	9.6
		(−15.5)		(1.8)
3	−150.5	−95.1	99.3	8.6
		(−15.7)		(2.8)
4	−167.9	−94.5	93.3	9.0
		(−15.1)		(2.4)
5	−145.4	−92.3	88.6	9.4
		(−12.9)		(2.0)
6	−235.2	−116.8	99.8	6.9
		(−37.4)		(4.5)
7	−273.6	−110.8	89.0	6.8
		(−31.4)		(4.6)
8	−282.4	−101.4	90.2	8.2
		(−22.0)		(3.2)

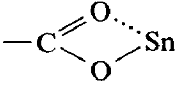
[a] See Scheme 1. [b] The differences of $\delta(^{15}\mathrm{N})$ of compounds **1**–**8** and $\delta(^{15}\mathrm{N})$ of 8-methylthioquinoline (−79.4 ppm). [c] Data corrected for off-resonance decoupling effect. [d] The differences between the $^2J(^{15}\mathrm{N}, ^1\mathrm{H})$ of 8-methylthioquinoline (11.4 Hz) and the $^2J(^{15}\mathrm{N}, ^1\mathrm{H})$'s of compounds **1**–**8**.

The data reveal an increased coordination of the central tin atom (coordination number greater than 4; i.e. 4 + 1) as a result of weak intramolecular Sn–N bonding (the intermolecular interaction and/or existence of the equilibrium of two particles with different coordination numbers of tin atoms can be excluded). Thus, chelate complexes having anisobidentate thiooxinate ligands and a relatively weak intramolecular bonding interaction of the central tin atom with the nitrogen atom of the quinoline skeleton are present in non-coordinating solvents as well as in the solid state [1].

The organotin(IV) thiolates show a lower tendency to form the complexes with electron-pair donors (e.g. with molecules of coordinating solvents) than the corresponding oxocompounds [12]. In spite of this it is of interest to compare the $\delta(^{119}\mathrm{Sn})$ vs. T plots for isoelectronic compounds $\mathrm{Bu_3Sn(txin)}$ and $\mathrm{Bu_3SnS(1\text{-}C_{10}H_7)}$ as was carried out recently for the analogous pair of compounds $\mathrm{R_3Sn(oxin)}$ and $\mathrm{R_3SnO(1\text{-}C_{10}H_7)}$ [13]. From the Fig. 1 it is evident that differences in $\delta(^{119}\mathrm{Sn})$ of both the isoelectronic thiocompounds in deuteriochloroform and in pyridine are very small. The variation of $\delta(^{119}\mathrm{Sn})$ with T for the compounds $\mathrm{Bu_3SnS(1\text{-}C_{10}H_7)}$ in pyridine is at first a sigmoidal curve (with point of inflexion at a temperature below the measured range), which is typical of the equilibrium

$$\mathrm{R_3SnER'} + \mathrm{D} \rightleftharpoons \mathrm{R_3SnER'} \cdot \mathrm{D} \tag{1}$$

and of the formation of the complex $\mathrm{Bu_3SnS(1\text{-}C_{10}H_7)} \cdot \mathrm{D}$ (D = pyridine). On the other hand the linear course of this dependence for compound **1** (nearly parallel to the dependence in deuteriochloroform solution and shifted only ~ 14 ppm downfield) excludes the existence of such an equilibrium (1). Compound **1** (and obviously also **2**, **3** and **4**) are resistant to attack by an electron pair donor.

The values of $\delta(^{119}Sn)$ for **5–8** (Table 2) in non-coordinating solvent (deuteriochloroform) lie within the region characteristic of five-coordinated diorganotin(IV) compounds [12–14]. The temperature dependences of $\delta(^{119}Sn)$ for these compounds ($\Delta\delta(^{119}Sn)/\Delta T \sim 0.02$–$0.11$ ppm/K) in both solvent types are linear and are nearly parallel to each other. The values of $\delta(^{119}Sn)$ in pyridine solution are shifted only slightly upfield (by 7–10 ppm) as opposed to those in deuteriochloroform solutions. We assume that **5–8** form chelates containing a six-coordinated central tin atom and two anisobidentate thiooxinate ligands (two weaker Sn–N bonds). That the Sn–N bond is weaker, is revealed by a fall in the effective coordination number (apparent coordination number of Sn is 5) analogous to the case discussed previously [15,16] for tri- and diorganotin(IV) carboxylate chelates with a weak  $-\mathrm{C}\langle^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Sn}$ connection. Hence the upfield shift of $\delta(^{119}Sn)$ is less than that expected for an actual six-coordinated Sn atom. The $\delta(^{119}Sn)$ chemical shifts of diorganotin(IV) dioxinate chelates $R_2Sn(oxin)_2$ having the same substituents R [3] are shifted more upfield (by 100–125 compared with the corresponding thiooxinates), mainly up to regions typical of six-coordinate diorganotin(IV) compounds.

^{15}N NMR spectra

Some parameters of the ^{15}N NMR spectra (namely $\delta(^{15}N)$, $^2J(^{15}N, ^1H)$ and $J(^{119}Sn, ^{15}N)$) can clearly be used (i) to evaluate the nature of the chelate bonding of the thiooxinate ligands to the central tin atom in the studied compounds **1–8** and (ii) to evaluate of the Sn–N bond strength, as described for the organotin(IV) oxinates [2].

Stader and Wrackmeyer [17,18] have reported on the application of the basic INEPT pulse sequence [19] for recording proton-coupled ^{15}N NMR spectra with $^{117/119}Sn$ satellites at the natural abundance level. We have used non-refocused

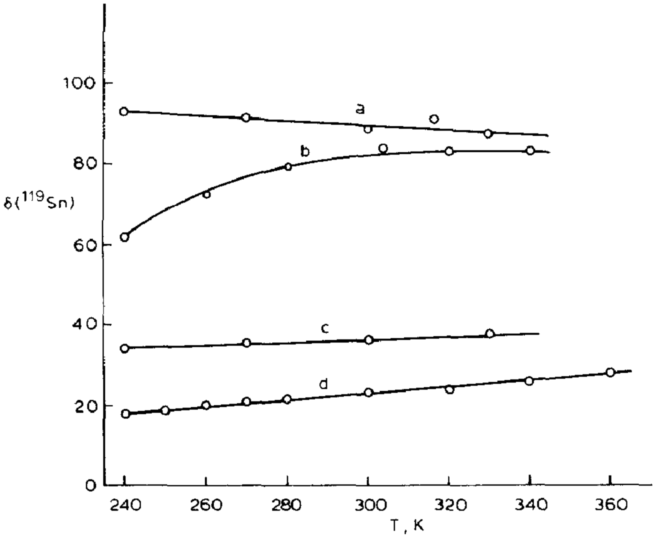


Fig. 1. Temperature dependence of $\delta(^{119}Sn)$ of $Bu_3Sn(txin)$ ((c) in $CDCl_3$, (d) in pyridine) and of $Bu_3SnS(1\text{-}C_{10}H_7)$ ((a) in $CDCl_3$, (b) in pyridine).

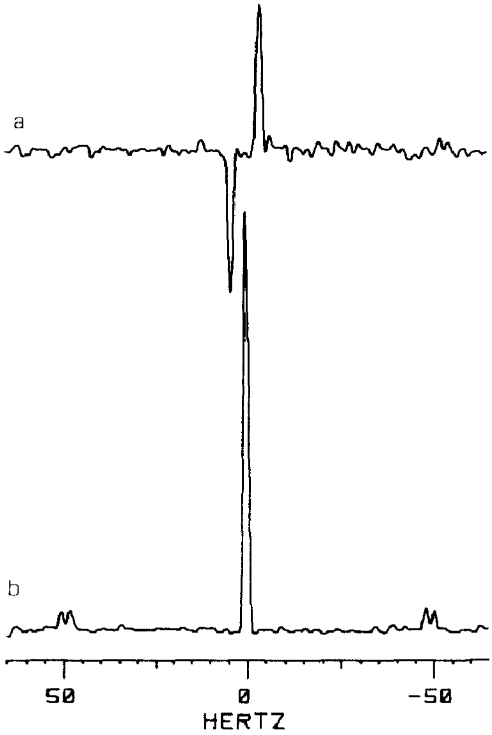


Fig. 2. ^{15}N NMR spectra of $Ph_3Sn(txin)$ in deuteriochloroform; (a) non-refocused selective INEPT, selective decoupling of H(3) ($\gamma B_2 = 100$ Hz), relaxation time 3 s, evolution period 52 ms ($D2 = 16$ ms), 1000 scans, Gaussian multiplication, digital resolution 0.1 Hz/point. (b) refocused selective INEPT with broad-band ^{1}H decoupling, ^{1}H-90°-soft pulse 10 ms ($\gamma B_2 = 25$ Hz), relaxation time 4 s, evolution and refocusing period 52 ms ($D2 = 16$ ms, $D3 = 21$ ms), 9200 scans, Gaussian multiplication, digital resolution 0.2 Hz/point.

(proton-coupled) and refocused (proton-decoupled) selective INEPT [5] for this purpose. Typical spectra are shown in Fig. 2. The values of $\delta(^{15}N)$, $J(^{119}Sn, ^{15}N)$ and $^2J(^{15}N, ^1H)$ of **1**–**8** are listed in Table 2 together with those of a comparable compound (8-methylthioquinoline) and the differences in $\Delta\delta(^{15}N)$ and $\Delta^2J(^{15}N, ^1H)$ and their respective definitions.

The values of $\delta(^{15}N)$ for **1**–**8** are shifted upfield by ~ 3–38 ppm compared with that of 8-methylthioquinoline. The differences in $\Delta\delta(^{15}N)$ for analogous triorganotin(IV) oxinates and diorganotin(IV) dioxinates vary from −27 to −53 ppm [3]. These values provide further evidence for the existence of an Sn–N bond in the thiooxinates **1**–**8**. In accordance with the conclusions drawn from the analysis of $\delta(^{119}Sn)$ values (see above) this bond is weaker than that in the analogous triorganotin(IV) oxinates and diorganotin(IV) dioxinates. The same conclusions are obtained from the analysis of $^2J(^{15}N, ^1H)$ values, which lie between 10.3 and 6.8 Hz, whereas those for the analogous oxinates lie between 9.3 to 6.0 Hz [3], and also lie further from the values of $J(^{119}Sn, ^{15}N)$, which increase with the upfield shift of $\delta(^{15}N)$, and with the increasing difference of $\Delta^2J(^{15}N, ^1H)$.

All the ^{15}N NMR spectral parameters also indicate unambiguously that the Sn–N bond is generally stronger in the diorganotin(IV) dithiooxinates **5**–**8** than in the triorganotin(IV) thiooxinates and that the Sn–N bond is markedly weaker in both compounds having 1-butyl substituents (compounds **1** and **5**) than that in other $R_3Sn(txin)$ and $R_2Sn(txin)_2$ compounds. A more detailed differentiation in the bonding strength between the thiooxinates **2–4** and the dithiooxinates **6–8** cannot be obtained from the ^{15}N NMR spectral parameters because the differences in individual parameters are not distinct and in addition the trends in the $\delta(^{15}N)$, $J(^{119}Sn, ^{15}N)$ and $^2J(^{15}N, ^1H)$ values are not related in any way. We assume that this is due to other factors that influence the values of these parameters, namely: electronic and steric effects of substituents R, N–C(2) bond order, the degree of distortion of the coordination polyhedra etc.

^1H and ^{13}C NMR spectra

The ^1H and ^{13}C chemical shifts in **1–8** are listed in Tables 3–5. A combination of one-dimensional (selective INEPT [20], NOE difference spectroscopy [21]) and two-dimensional [22,23] (H,H-COSY,H,C-COSY) NMR techniques was used to unambiguously assign the ^1H and ^{13}C chemical shifts as described elsewhere [3].

The ^1H NMR parameters and especially the results of the NOE difference spectroscopy are of great importance for determining the conformation of compounds studied. A paper describing such a study is in preparation.

In the ^1H and ^{13}C NMR spectra of the compounds **1–8** there is only one set of NMR signals for both the substituents R and for the thiooxinate ligands which provides evidence for the magnetic equivalence of both the R substituents and the oxinate ligands on the NMR time scale, and indicates their relative symmetrical arrangement in the coordination sphere of the central tin atom.

The chemical shifts $\delta(^{13}C)$ of the carbon atoms in the R substituents (Table 4) are not very sensitive to changes in the coordination of the central tin atom. Nevertheless, the $\delta(^{13}C(1'))$ values, which are shifted mostly by 2–4 ppm downfield in comparison with those in the compounds having a four-coordinated central tin atom [7–10,12,13], are in a good agreement with the weak Sn–N interaction model.

More conclusive information is obtained from the values of the coupling constants $^nJ(^{119}Sn, ^{13}C)$ (the spin–spin coupling between Sn atom and carbon atoms of

Table 3

Chemical shifts $\delta(^1H)$ of compounds **1–8** in deuteriochloroform at 300 K

Compound [a]	$\delta(^1H)$										
	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(1′)	H(2′)	H(3′)	H(4′)	H(5′)
1	8.70	7.29	8.02	7.39	7.25	7.91	1.11	1.53	1.27	0.80	
2	8.19	7.20	8.04	7.39	7.28	7.83	2.47 [b]		6.74	7.06	6.92
3	8.01	7.07	7.99	7.43	7.35	7.97		7.49	7.22	7.22	
4	8.63	7.37	8.11	7.41	7.30	7.87	6.47	6.17 [c] 5.82 [d]			
5	8.85	7.46	8.21	7.42	7.35	7.94	1.49	1.31	1.07	0.50	
6	9.26	7.10	8.04	7.37	7.42	8.04	2.59 [e]		6.65	6.81	6.73
7	9.70	7.15	7.98	7.31	7.38	8.08		7.60	7.11	7.08	
8	9.18	7.38	8.17	7.40	7.42	7.99	6.57	5.86 [c] 5.62 [d]			

[a] See Scheme 1. [b] $^2J(^{119}Sn, ^1H) = 64.5$ Hz. [c] *cis*-H with respect to –C*H*=. [d] *trans*-H. [e] $^2J(^{119}Sn, ^1H) = 71.6$ Hz.

substituents R), and especially from the values of ${}^1J({}^{119}\mathrm{Sn}, {}^{13}\mathrm{C}(1'))$ (Table 4). They provide information on the spatial arrangement of substituents (and thus indirectly also that of the ligands) around the central tin atom. We have calculated the value of the angle θ (the mean C–Sn–C angle) to be 110 ± 3° from the value of coupling constants ${}^1J({}^{119}\mathrm{Sn}, {}^{13}\mathrm{C}(1'))$ of **1**, and applied in the expression given in ref. [24]. For the compounds **2–4**, a comparison of their ${}^1J({}^{119}\mathrm{Sn}, {}^{13}\mathrm{C}(1'))$ values with those for various R_3SnCl compounds and their complexes [7–10] reveals that the value of θ is near to 110°. The value of θ in the crystalline compound **3** is 108.9° [4]. If we regard the compounds **1–4** as molecular chelates with a five-coordinated central tin atom, we can propose a distorted *cis*-trigonal bipyramid arrangement for the coordination sphere of the central tin atom. Two C(1′) atoms lie in the equatorial plane and the third is located at the apex. The sulphur and the nitrogen atoms occupy the remaining positions of this distorted *cis*-trigonal bipyramid.

The C–Sn–C angle in compound **5**, calculated as described in ref. 24, is 135 ± 3° and such a value for complexes with a six-coordinated central tin atom (see above) corresponds to a skew trapezoidal bipyramid [25] arrangement of the C(1′) atoms of substituents R, the sulphur, and the nitrogen donor atoms of thiooxinate ligands in this complex. For complexes **6–8** we have estimated the C–Sn–C angle to be is 120°, from a comparison of their coupling constants ${}^1J({}^{119}\mathrm{Sn}, {}^{13}\mathrm{C}(1'))$ with those of R_2SnX_2 compounds having the corresponding substituents (R = benzyl, phenyl or vinyl) and their complexes [11–13]. Thus we can assume that the coordination polyhedra of compounds **6–8** are severely distorted octahedra with the C(1′) atoms of the R substituents being *cis*-skew to each other.

To elucidate the nature of the thiooxinate ligand bonding in metal complexes, it is useful to compare their chemical shifts $\delta({}^{13}\mathrm{C})$ with those in 8-quinolinethiol, its anion and its protonated form (protonization and the formation complexes having an Sn–N bond is manifested in ^{13}C NMR spectra in the same way [26,27] (Table 5).

The sets of $\delta({}^{13}\mathrm{C})$ data for the thiooxinate ligands of complexes **1–8** are generally similar to those of the neutral 8-quinolinethiole. The $\delta({}^{13}\mathrm{C})$ values for the carbon atoms C(5) and C(8) are shifted a little more towards the $\delta({}^{13}\mathrm{C})$ values of the thiooxinate anion, whereas the $\delta({}^{13}\mathrm{C})$ values for the C(2) carbon atoms shift towards values typical of the protonized 8-quinolinethiole. This fact provides evidence for the formation of a Sn–N bond on the one hand, but also for the greater ionic character of Sn–S bond on the other. The $\delta({}^{13}\mathrm{C})$ values for the C(4) carbon atom C(4), (Table 5), though not very sensitive to the protonization change at the sulphur atom, are very sensitive to the same change at the nitrogen atom. Therefore, they can be used as another criterion of the formation of chelates and partly as a measure of the strength of their Sn–N bond. The compounds **1–8** have $\delta({}^{13}\mathrm{C})$ in the range 137.19–139.81, i.e. they are shifted somewhat downfield from those of 8-quinolinethiole and towards the $\delta({}^{13}\mathrm{C})$ value of protonized 8-quinolinethiole. The magnitude of these shifts and the fact that the changes in $\delta({}^{13}\mathrm{C})$ for the C(4) carbon atoms of compounds **1–8** parallel the changes in the coupling constants ${}^2J({}^{15}\mathrm{N}, {}^1\mathrm{H})$, lend support to the conclusions about the formation and strength of the Sn–N bond in the compounds we have studied (see above). The Sn–N bonding interaction is also indicated by the $\delta({}^{13}\mathrm{C})$ values of the C(2) carbon atom, but we do not recommend to their application to evaluate the Sn–N bond strength, because they are determined by at least two opposing effects. A positive charge on the nitrogen atom, as a consequence of the Sn–N interaction, results in the shift of the π-electron

Table 4

Parameters $\delta(^{13}C)$ and $^{n}J(^{119}Sn, ^{13}C)$ of compounds **1–8** for substituent R in deuteriochloroform at 300 K

Compound [a]	$\delta(^{13}C)/(^{n}J(^{119}Sn, ^{13}C)$, Hz)				
	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)
1	17.92	28.60	26.90	13.40	
	(355.1)	(20.5)	(65.7)	[b]	
2	27.58	141.22	127.9	128.20	123.62
	(311.7)	(40.0)	(30.7)	(16.0)	(19.5)
3	144.99	136.04	128.21	128.46	
	(600.0)	(45.0)	(60.0)	(13.9)	
4	142.83	138.16			
	(587.4)	(8.9)			
5	29.48	27.98	26.00	13.27	
	(635.9)	(39.2)	(111.8)	(5.6)	
6	41.17	141.69	127.36	127.17	122.79
	(444.2)	(62.6)	(39.1)	(26.1)	(31.0)
7	154.49	134.35	127.84	127.65	
	(728.6)	(55.6)	(74.7)	(17.7)	
8	149.58	131.04			
	(841.7)	[b]			

[a] See Scheme 1. [b] < 6 Hz.

density from C(4) and C(3) towards C(2) and thus in the upfield shift of $\delta(^{13}C)$ for the C(2) carbon atom. But simultaneously the protonization and especially the formation of Sn–N bond lead to a decrease in bond order of N–C(2) which results in the downfield shift of $\delta(^{13}C)$ value for the C(2) carbon atom [28]. The result is a compromise between the effects but their relative proportions cannot be determined.

The $\delta(^{13}C)$ chemical shifts for the carbon atoms C(5) and C(8) of the chelates **1–8** lie in the region between the values of $\delta(^{13}C)$ for the same carbon atoms in 8-quinolinethiole and for the same in its anion. The difference $\Delta\delta(^{13}C)$, defined as $\Delta\delta(^{13}C) = \delta(^{13}C)(C(8)) - \delta(^{13}C)(C(5))$, is recommended for chelate oxinates [2,26,17] as a criterion of the ionic character of the Sn–O bond. The value of $\Delta\delta(^{13}C)$ of the thiooxinate anion is 29.17 ppm and decreases steeply with increasing protonization. For the neutral 8-quinolinethiole, the $\Delta\delta(^{13}C)$ value is 10.2 ppm and for its protonized form it is −6.04 ppm. The $\Delta\delta(^{13}C)$ values for triorganotin(IV) thiooxinates **2–4** lie between 14.36 and 14.98 ppm (for compound **1** this difference is higher, 15.92 ppm); for the diorganotin(IV) dithiooxinates **6–8** $\Delta\delta(^{13}C)$ varies from 18.41 to 18.67 ppm (compound **5** has a $\Delta\delta(^{13}C)$ of 20.51 ppm). Thus, we can say that the Sn–S bond is generally more ionic in diorganotin(IV) dithiooxinates than in triorganotin(IV) thiooxinates. In both compounds with 1-butyl substituents (**1** and **5**) there is a higher ionic character of the Sn–S than in other compounds of the same type (**2–4** and **6–8**). From a comparison of the $\Delta\delta(^{13}C)$ values of compounds **1–8** with those of analogous organotin(IV) oxinates ($\Delta\delta(^{13}C) = \sim 45$ ppm [3]) it is evident that the ionic character of the Sn–O bond is higher than that of Sn–S bond, a fact which is consistent with the difference in electronegativity between oxygen and sulphur.

Table 5

The $\delta(^{13}C)$ and $^{n}J(^{119}Sn, ^{13}C)$ parameters for compounds **1–8** for the thiooxinate ligands in deuteriochloroform at 300 K

Compound [a]	$\delta(^{13}C)/(J(^{119}Sn, ^{13}C)$, Hz)								
	C(2)	C(3)	C(4)	C(4a)	C(5)	C(6)	C(7)	C(8)	C(8a)
txin^{-} [b]	151.45	123.74	140.70	131.95	121.40	129.27	136.30	150.57	151.39
txinH [c]	149.2	121.5	136.7	128.6	124.4	126.4	126.9	134.6	143.6
txinH$_2^{+}$ [d]	147.50	125.04	151.65	132.97	132.05	132.83	143.70	125.41	140.65
1	146.74	120.72	137.19	128.73	123.17	126.35	131.02	139.09	145.16
	[e]	(2.8)	[e]	(3.4)	[e]	[e]	(15.7)	(8.6)	(5.6)
2	147.16	120.84	138.00	129.00	123.23	126.91	130.60	138.00	143.69
	[e]	(4.4)	[e]	(3.7)	[e]	[e]	(18.8)	[e]	(5.6)
3	147.19	121.19	138.10	128.62	123.36	127.18	130.23	137.72	143.18
	(2.4)	(3.3)	[e]	(2.2)	[e]	(3.0)	(28.7)	(20.4)	(14.1)
4	146.35	121.09	138.16	128.91	123.04	126.99	130.09	138.02	143.23
	[e]	(3.5)	[e]	(2.4)	[e]	[e]	(28.0)	(19.2)	(13.3)
5	145.01	120.99	138.41	129.30	121.97	127.38	130.82	142.48	144.97
	[e]	(3.4)	[e]	(6.0)	[e]	[e]	(7.3)	(12.5)	(5.4)
6	147.28	120.86	139.56	129.55	121.91	127.27	131.23	140.41	141.00
	(6.1)	(3.0)	[e]	(5.1)	[e]	[e]	(8.3)	(10.0)	(18.2)
7	147.65	121.18	139.81	129.45	122.34	127.47	131.34	140.75	140.23
	(10.1)	(4.6)	[e]	(7.2)	[e]	[e]	(20.9)	(13.6)	(29.9)
8	146.70	121.07	139.09	129.45	122.23	127.54	130.98	140.90	142.74
	(5.4)	[e]	[e]	[e]	[e]	[e]	(18.5)	(14.3)	(14.7)

[a] See Scheme 1. [b] Measured as the sodium salt in deuteriumoxide (referred to TSPA-d_4; $\delta = 0.00$). [c] Measured in deuteriochloroform. [d] Measured in 1 *M* deuterioperchloric acid in deuteriumoxide (referred to TSPA-d_4). [e] $^{n}J(^{119}Sn, ^{13}C) < 6$ Hz.

Interaction of the tin atom with the carbon atoms of the thiooxinate ligand

The values of some of the coupling constants $^nJ(^{119}Sn, ^{13}C)$ of the thiooxinate ligand carbon atoms are given in Table 5. According to our knowledge it is a rare case of the determination of parameters of a long-range interaction of tin and carbon atoms with an inserted electronegative atom in the bonding pathway [29–31]. The interpretation of the coupling constants is complicated because they represent an algebraic sum of the contributions of various bonding vectors between tin atom and the individual carbon atoms the signs of which are not known and for which absolute values cannot be determined. Moreover, it is important to note that the individual contributions will be influenced significantly not only by the Sn–N and Sn–S bond strength, but also by the number and nature of organic substituents on tin atom (substituents R), by the geometrical arrangement of substituents R and the ligands around the central tin atom, by the mutual positions of the donor atoms of the ligands, and other factors.

In spite of these difficulties it is noteworthy that the coupling constants of the tin atoms with carbon atoms C(8) and C(7), which reflect in highest measure the bonding vectors via the sulphur atom, are inversely proportional to the ionic character of Sn–S bond. Generally higher values were obtained for $R_3Sn(txin)$ than for $R_2Sn(txin)_2$ and lower values for compounds with 1-butyl substituents (compounds **1** and **5**) than those for compounds with other substituents (compounds **2**–**4**, **6**–**8**). On the other hand the coupling constants $^2J(^{119}Sn, ^{13}C(2))$ are directly proportional to the Sn–N bond strength.

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