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Multinuclear NMR study of some diorgano(chloro)tin(IV) oxinates and thiooxinates

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Abstract

The ^{119}Sn, ^{15}N, ^{13}C and ^{1}H NMR as well as the solid state ^{119}Sn CP-MAS NMR spectra have been used to study the structures of four diorgano(chloro)tin(IV) oxinates and thiooxinates, $(C_6H_5)_2Sn(Cl)$-(oxin) and $R_2Sn(Cl)$(txin), where R = benzyl, phenyl or vinyl groups, oxin = 8-quinolinolate, txin = 8-quinolinethiolate, in deuteriochloroform solution and in the solid state. Both in a non-coordinating solvent ($CDCl_3$) and in the solid state the compounds studied are formed by monomeric molecular chelate complexes with a distorted *cis*-trigonal bipyramidal arrangement of coordination polyhedra centred on a five-coordinated tin atom.

The fine structure of the centre-bands in the ^{119}Sn CP-MAS spectra can qualitatively be explained as a result of the combined effect of residual dipolar coupling and scalar interaction of the ^{119}Sn nucleus with two different quadrupolar nuclei (^{14}N, $I = 1$; $^{35,37}Cl$, $I = 3/2$).

Introduction

In previous papers [1–3] we have reported a detailed analysis of the ^{1}H, ^{13}C, ^{15}N and ^{119}Sn NMR spectra of a group of triorganotin(IV) oxinates and diorganotin(IV) dioxinates, $R_3Sn(oxin)$ and $R_2Sn(oxin)_2$, where R = n-butyl(Bu), benzyl (Bz), phenyl (Ph) or vinyl (Vi), oxin = 8-quinolinolate, and analogous thiooxinates and dithiooxinates, $R_3Sn(txin)$ and $R_2Sn(txin)_2$, where txin = 8-quinolinethiolate. This

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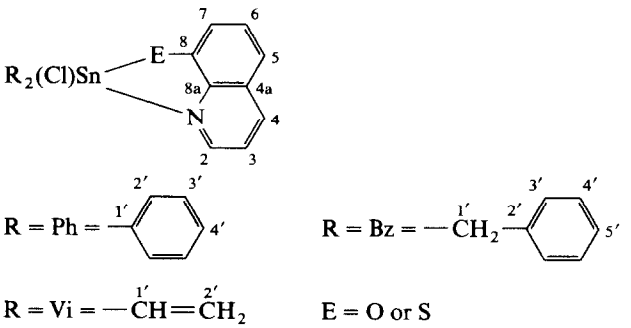
has shown that in non-coordinating solvent ($CDCl_3$) there is Sn · · · N bonding in these compounds. We have also discussed in qualitative terms their structures in non-coordinating solvents. All these compounds form chelate complexes. Triorganotin(IV) oxinates and thiooxinates form distorted trigonal bipyramids (coordinating number is 5, i.e. 4 + 1). Chelate complexes of diorganotin(IV) dioxinates and dithiooxinates exist in the form of trapezoidal bipyramids (skew), the central tin atom (coordinate number is 6, i.e. 4 + 2) being coordinated by two oxygen atoms or two sulphur atoms in what are close to *trans*-positions and two nitrogen atoms of the heterocyclic chelate ligand and two carbons C(1) of the substituent R in mutual *cis*-positions.

All compounds studied retain their structure as chelate complexes in the solid state as we have demonstrated [4] by means of ^{119}Sn and ^{15}N CP-MAS NMR spectra. In the same paper we described the pattern of a ^{119}Sn nucleus ($I = 1/2$) interacting with either one or two quadrupolar nuclei (^{14}N, $I = 1$).

This paper presents the results of a ^{119}Sn, ^{15}N and ^{13}C NMR study in deuteriochloroform solution of the following diorgano(chloro)tin(IV) oxinates and thiooxinates: $R_2Sn(Cl)(oxin)$ (R = Ph (**1**)) and $R_2Sn(Cl)(txin)$, respectively, where R = Bz (**2**), Ph (**3**) and Vi (**4**).



The results were compared with those of ^{119}Sn CP-MAS NMR spectroscopy of the same compounds. To the best of our knowledge, this is the first case where the interaction of a nucleus with spin number $I = 1/2$ with two different quadrupolar nuclei ^{14}N ($I = 1$) and ^{35}Cl and/or ^{37}Cl ($I = 3/2$) has been observed.

Results and discussion

Multinuclear NMR spectra of compounds 1–4 in deuteriochloroform

The chemical shift $\delta(^{119}Sn)$ of compound **1** in deuteriochloroform solution (Table 1) is typical of five-coordinated diphenyltin(IV) compounds [5]. However $\delta(^{119}Sn)$ of compounds **2–4** lie either in the upper part of a region characteristic of four-coordinated compounds or between the $\delta(^{119}Sn)$ regions characteristic of four- and five-coordinated diorganotin(IV) compounds which is typical of tin coordination number 4 + 1 [2,5,6]. There is no doubt that the increased coordination number of tin (5 or 4 + 1, respectively) in compounds **1–4** is caused first of all by the existence of donor-acceptor interaction Sn · · · N, regardless of the fact that in the ethyl analogue of compound **1** ($Et_2sn(Cl)(oxin)$) a weak association through bridges formed by chlorine atoms [7] has been demonstrated using X-ray diffraction in the solid state. Considerable high-field shift of $\delta(^{15}N)$ with respect to the same parameter in 8-methoxyquinoline and 8-methylthioquinoline, respectively [1,2], is

Table 1

Parameters of ^{13}C (organic substituents), ^{15}N and ^{119}Sn NMR spectra of compounds **1–4** ($CDCl_3$ or solid, 300 K)

Compound	$\delta(^{119}Sn)$ $CDCl_3$ (solid)	$\delta(^{13}C)$ ($^nJ(^{119}Sn, ^{13}C)$, Hz)				
		C(1′)	C(2′)	C(3′)	C(4′)	C(5′)
$Ph_2Sn(Cl)(oxin)$	−243.8	142.12	136.65	128.70	130.32	
(1)	(−245 ± 1)	(991.0)	(66.5)	(92.3)	(18.4)	
$Bz_2Sn(Cl)(txin)$ [a]	−151.0	35.01	137.72	127.76	128.00	124.60
(2)	(−145 ± 1)	(499.2)	(61.2)	(43.1)	(23.9)	(29.1)
$Ph_2Sn(Cl((txin)$ [b]	−197.1)	143.27	135.21	128.78	129.70	
(3)	(−186 ± 1)	(1080.0)	(57.1)	(84.0)	(17.0)	
$Vi_2Sn(Cl)(txin)$	−201.3	140.70	136.83			
(4)	(−210 ± 1)	(852.9)	(3.3)			

[a] $\delta(^{15}N) = -128.0$ ppm, $J(^{119}Sn, ^{15}N) = 198.2$ Hz, $^2J(^{15}N, ^1H(2')) = 7.80$ Hz. [b] $\delta(^{15}N) = -122.3$ ppm, $J(^{119}Sn, ^{15}N) = 164.2$ Hz, $^2J(^{15}N, ^1H(2')) = 7.28$ Hz.

significant for the existence of donor-acceptor interactions Sn · · · N. This difference $\Delta\delta(^{15}N)$ is −42.9 ppm in compound **3** (while $\delta(^{15}N)$ of 8-methylthioquinoline is −79.4 [2]) and it is higher than those for compounds $Ph_3Sn(txin)$ (−15.7 ppm) and $Ph_2Sn(txin)_2$ (−31.4 ppm). A still larger high-field shift is observed for compound **1** ($\Delta\delta(^{15}N) = -48.6$ ppm in comparison with the values −15.5 and −37.4 ppm for $Bz_3Sn(txin)$ and $Bz_2Sn(txin)_2$, respectively [1,2]). By analogy, the coupling constants $J(^{119}Sn, ^{15}N)$ of compounds **2** and **3** (198.2 and 164.2 Hz) are substantially greater than those for corresponding $Bz_3Sn(txin)$ and $Bz_2Sn(txin)_2$ (92.5 and 99.8 Hz) and $Ph_3Sn(txin)$ and $Ph_2Sn(txin)_2$ (99.3 and 89.0 Hz), respectively [2]. This enormous increase of $J(^{119}Sn, ^{15}N)$ in compounds **2** and **3** can be ascribed in part to the increase of *s*-electron character of the appropriate orbital of tin in the Sn · · · N bond, as a result of the decrease of *p*-electron density through formation of the polar Sn–Cl bond (contrary to the Sn–C bond and the donor–acceptor interaction Sn · · · N in compounds $R_3Sn(txin)$ and $R_2Sn(txin)_2$, respectively). It seems, however, that this is not the decisive factor. Comparison of the considerably different values for $J(^{119}Sn, ^{15}N)$ in compounds **2** and **3** on the one hand and the very similar values of the same parameter in compounds $R_3Sn(txin)$ and $R_2Sn(txin)_2$ makes this clear. The most important factor contributing to $J(^{119}Sn, ^{15}N)$ is the greater strength of the donor–acceptor Sn · · · N bond in compounds **2** and **3**. If this effect is of general occurrence, the structure of such compounds (at least on the NMR time scale) should clearly be more rigid than that of triorganotin(IV) chelates and diorganotin(IV) dichelates. This is further supported by the observation of two different signals in ^1H NMR spectrum for magnetically nonequivalent protons of methylene group of the benzyl substituents in compound **2** (Table 2).

Significant changes in the bond relationships in the heterocyclic ligands, which are manifested by changes in the ^1H and ^{13}C NMR spectra, also support the existence of a relatively strong Sn · · · N bond in compounds **1–4** (Table 2 and 3).

The values of the ^1H chemical shifts in compound **1** are very close to those in the *N*-protonated form of 8-hydroxyquinoline ($oxinH_2^+$). It is well known that oxinate complex formation with metal–nitrogen bond and *N*-protonation show the same direction of changes in the ^1H (and also in the ^{13}C) NMR spectra of oxinates. According to the classification [8] of oxinate complexes by means of ^1H NMR

Table 2

Chemical shifts $\delta(^1H)$ of compounds **1–4** ($CDCl_3$, 300 K)

Compound [a]	$\delta(^1H)$										
	H(1′)	H(2′)	H(3′)	H(4′)	H(5′)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
1		8.03	7.31	7.32		9.46	7.48	8.31	7.09	7.54	7.36
2	3.12 [b] 3.31 [b]		6.83	6.95	6.95	7.20	7.05	8.20	7.47	7.43	7.83
3		7.54	7.27	7.27		8.23	7.41	8.37	7.59	7.51	7.96
4	6.50	6.28 [c] 6.07 [d]				8.64	7.65	8.45	7.59	7.53	7.95

[a] See Table 1. [b] AB-system, $J_{gem} = 12.1$ Hz. [c] Atom H in positions *trans* to the Sn atom. [d] Atom H in position *cis* to the Sn atom.

spectra, compound **1** can be characterized as a chelate complex with a relatively strong donor–acceptor Sn · · · N bond.

The information derived from the ^{13}C NMR spectra of oxinate and thiooxinate ligands has been discussed in detail in our previous papers [1,2]. By comparing the ^{13}C chemical shifts of C(4), C(5) and C(8) atoms (Table 4) to the appropriate data for the neutral forms of the ligands (oxinH, txinH), their *N*-protonated forms ($oxinH_2^+$, $txinH_2^+$) and their anions ($oxin^-$, $txin^-$), it is possible to demonstrate the existence of relatively strong Sn · · · N bonding and of a partially ionic character of Sn–O and Sn–S bonds. Increasing values of $|J(^{119}Sn, ^{13}C(2))|$ and $|J(^{119}Sn, ^{13}C(3))|$ correspond to an increasing strength of the Sn · · · N bond. The common tendency towards decreasing values of $|J(^{119}Sn, ^{13}C(7))|$ and $|J(^{119}Sn, ^{13}C(8))|$ is in accord with an increasing ionic character of the Sn–O and Sn–S bond, respectively. The coupling constants $|J(^{119}Sn, ^{13}C(8a))|$ reflect both the effects. Some discrepancies in the order of the $J(^{119}Sn, ^{13}C(7))$ and $J(^{119}Sn, ^{13}C(8))$ values can be ascribed to coincidence of ionic effects of Sn–O and Sn–S bond, effects of s-electron character of tin orbitals on these bonds and transfer

Table 3

^{13}C NMR data of the heterocyclic ligands in compounds **1–4** ($CDCl_3$, 300 K)

Compound [a]	$\delta(^{13}C)$ ($^nJ(^{119}Sn, ^{13}C)$, Hz)								
	C(2)	C(3)	C(4)	C(4a)	C(5)	C(6)	C(7)	C(8)	C(8a)
1	146.54 (9.6)	121.54 (10.2)	141.95 (4.2)	129.69 (14.2)	113.43 (< 5)	131.03 (< 5)	114.76 (14.6)	157.09 (22.3)	136.65 (37.8)
2	147.01 (< 5)	120.82 (5.9)	140.31 (< 5)	129.07 (6.0)	123.02 (< 5)	127.63 (4.9)	129.96 (35.4)	136.84 (15.7)	141.54 (7.7)
3	147.41 (5.0)	121.72 (4.3)	141.31 (< 5)	129.44 (2.7)	123.65 < 5)	128.58 (5.7)	130.69 (46.4)	137.24 (20.0)	141.99 (19.2)
4	146.36 (3.3)	121.62 (3.9)	141.08 (< 5)	129.75 (2.9)	123.21 (< 5)	128.68 (6.7)	130.84 (44.7)	138.12 (19.7)	142.21 (19.1)

[a] See Table 1.

Table 4

Comparison of selected NMR data of compound **1–4** with those of similar compounds

Compound	$\Delta\delta(^{13}C(8,5))$ [a]	$\Delta\delta(^{13}C(4))$ [b]	$J(^{119}Sn, ^{13}C)$ Hz				
			C(2)	C(3)	C(7)	C(8)	C(8a)
$(oxin^-)$ [c]	53.9	0.4	–	–	–	–	–
oxinH [c]	34.8	0	–	–	–	–	–
$(oxinH_2^+)$ [c]	27.2	10.3	–	–	–	–	–
$Ph_2Sn(Cl)(oxin)$	43.66	5.25	9.6	10.2	14.6	22.3	37.8
$Ph_3Sn(oxin)$ [c]	41.99	1.19	3.6	5	27.6	31.9	25.5
$Ph_2Sn(oxin)_2$ [c]	44.58	2.16	7.3	6.2	23.0	24.1	44.1
$(txin^-)$ [d]	29.17	4.00	–	–	–	–	–
txin [a]	10.2	0	–	–	–	–	–
$(txinH^+)$ [d]	−6.64	14.95	–	–	–	–	–
$Bz_2Sn(Cl)(txin)$	13.82	3.61	< 5	5.9	35.4	15.7	7.7
$Bz_3Sn(txin)$ [d]	14.77	1.30	< 6	4.4	18.8	< 6	5.6
$Bz_2Sn(txin)_2$ [d]	18.50	2.86	6.1	3.0	8.3	10.0	18.2
$Ph_2Sn(Cl)(txin)$	13.59	4.61	5.0	4.3	46.4	20.0	19.2
$Ph_3Sn(txin)$ [d]	13.86	1.40	2.4	3.3	28.7	20.4	14.1
$Ph_2Sn(txin)_2$ [d]	18.41	3.11	10.1	4.6	20.9	13.6	29.9
$Vi_2Sn(Cl)(txin)$	14.91	4.38	3.3	3.9	44.7	19.7	19.1
$Vi_3Sn(txin)$ [d]	14.98	1.46	< 6	3.5	28.0	19.2	13.3
$Vi_2Sn(txin)_2$ [d]	18.67	2.39	5.4	< 6	18.5	14.3	14.7

[a] $\delta(^{13}C(8)) - (^{13}C(5))$. [b] Difference between $\delta(^{13}C(4))$ of compounds and those of the 8-quinolinol. [c] Ref. 1. [d] Ref. 2.

of these effects further along the purely carbon ring of the heterocyclic ligand.

Remembering that the tin atom is bound to five atoms (atoms C(1′) of the organic ligands, chlorine, sulphur or oxygen and nitrogen of the heterocyclic ligand), and noting Bent's rule, the most probable spatial arrangement of chelate complexes **1–4** seems to be *cis*-trigonal bipyramidal with the organic substituents in the equatorial plane. Heterogeneous coordination sphere and different strengths of bonds cause considerable deformations from the ideal shape. We use the value of the C–Sn–C angle which can be determined from $^1J(^{119}Sn, ^{13}C(1'))$ data [5] to measure these deformations. For compounds **1** and **3** we have determined this angle to be 138 and 144°, respectively. This is in good agreement with the value of the C–Sn–C angle in $Et_2Sn(Cl)(oxin)$ (140.94°) determined from X-ray data [7].

^{119}Sn CP-MAS NMR spectra of compounds 1–4

The chemical shifts $\delta(^{119}Sn)$ for the solid compounds **1–4** are given in Table 1. The ^{119}Sn CP-MAS NMR spectrum of compound **3** is shown in Fig. 1, together with an expansion of the centre band region. All compounds **1–4** display one centre band in their ^{119}Sn CP-MAS spectra, consistent with one molecule in the asymmetric unit. The great similarity of $\delta(^{119}Sn)$ for compounds **1–4** in solution and in the solid state, shows that their solid state structure is retained in $CDCl_3$ solution. In particular, any intermolecular chlorine-bridging in the solid state can be ruled out, as this would cause substantial low-frequency (high-field) shifts in the solid state ^{119}Sn NMR spectra. Qualitatively, all the ^{119}Sn CP-MAS spectra of compounds **1–4** show anisotropies of the order of 600–700 ppm, and the overall shape of the shielding patterns is typical of a fairly asymmetric shielding tensor (quantitative

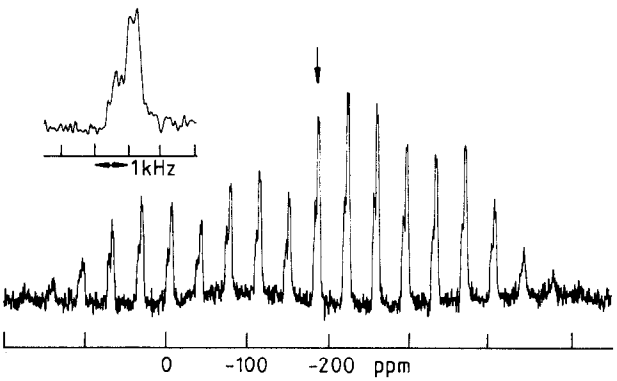


Fig. 1. ^{119}Sn CP-MAS spectrum of compound **3**. An expansion of the centre band region is shown in the insert. The spinning rate was 4 kHz, 3624 transients were accumulated, with a 1 ms contact time and 20 s recycle delay. No exponential line broadening was used for the data processing. The centre band is marked with an arrow.

analysis of the tensorial components of the shielding tensors would require better S/N ratios). These shielding patterns are in accord with a strongly distorted environment for the tin-atom, as had been concluded from the solution-state NMR data.

Apart from these considerations, the fine structure observed for the centre band (see Fig. 1) and all the associated spinning sidebands, deserve some further comment. Similar splittings are observed for all compounds **1–4**. The centre-band in Fig. 1 consists of (at least) five lines with approximate relative intensity ratios of 1 : 2 : 1 : 4 : 4. The splitting between these resonances amounts to 229, 168, 229 and 214 Hz, respectively. The only way to explain this irregular line shape is to assume the combined effects of two quadrupolar nuclei (i.e. ^{14}N, $I = 1$ and ^{35,37}Cl, $I = 3/2$) coupled to ^{119}Sn ($I = 1/2$). This coupling includes scalar and dipolar interaction, as well as quadrupolar coupling. Recently, Harris et al. [9–11] have shown that similar splittings in the ^{119}Sn CP-MAS NMR spectra of compounds R_3SnCl can be rationalized in terms of these three parameters, including information on the anisotropy of the J-term and, possibly, on the sign of the quadrupolar coupling constant. This analysis used perturbation theory to describe the observed effects. Some simplifications have been used in this process: an axially symmetric J-tensor has been assumed, and the possible effects of the second, less abundant, chlorine isotope, ^{37}Cl, on the ^{119}Sn–^{35,37}Cl pair have been ignored. A more complete description of the underlying theory is to be found in the literature [12,13]. Olivieri et al. [14–16] have recently published some more general applications of perturbation theory for the description and analysis of quadrupolar effects on the solid-state NMR spectra of spin-1/2 nuclei.

Such splittings, as described by Harris et al. [9–11] for the Sn–Cl case, are generally to be expected if second-order quadrupolar effects have to be taken into account. For the specific case of Sn–Cl this seems to be true if one operates at magnetic field strengths of 4.7 or 7 T. More precisely, under these operating conditions with magic angle spinning a 1.1.2 splitting pattern with spacings of approximately $|2J|$ and $|J|$ appears to be fairly common for the Sn–Cl case (see, for instance, Fig. 1 in ref. 11). If we assumed that the interplay of the various

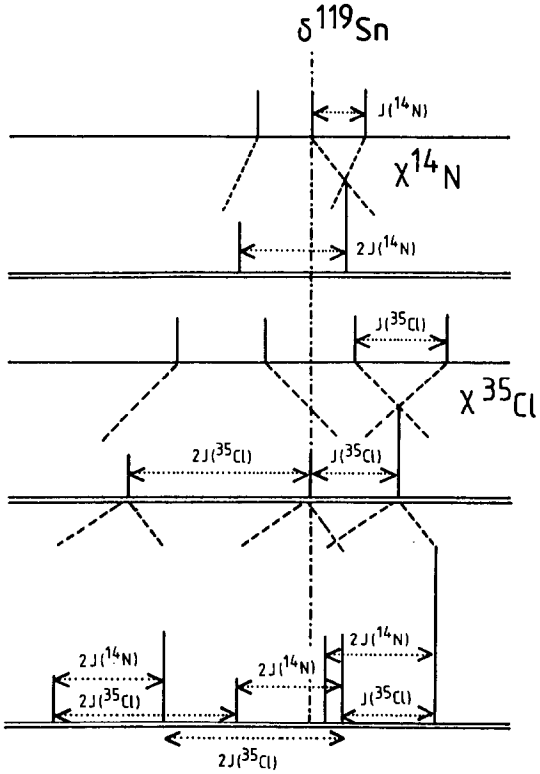


Fig. 2. Schematic drawing of the interplay of the various contributions to the $^{119}Sn-^{14}N-^{35,37}Cl$ splitting pattern.

residual coupling contributions Sn–Cl for the compounds **1–4** is similar to those for compounds R_3SnCl, we can use similar considerations to predict an approximately 1 : 2 splitting pattern with an approximately $|2J|$ splitting for the $Sn-^{14}N$ interaction in agreement with data in ref. 2. If we combine these two coupling patterns, following simple first order rules, a six-line pattern is predicted for the $Sn-^{14}N-^{35}Cl$ case. This pattern resulting from consecutive splittings is illustrated in Fig. 2. Comparing this pattern to the pattern actually observed (see Fig. 1) makes it obvious that ν_4 and ν_5 are not resolved in the experimental spectrum, and this accounts for the relative intensity pattern of 1 : 2 : 1 : 4 : 4 in the experimental spectrum (as compared to the 1 : 2 : 1 : 2 : 2 : 4 pattern from the splitting diagram). Following this qualitative splitting diagram, we can estimate $^1J(^{119}Sn, ^{14}N)$ to 115 Hz, and $^1J(^{119}Sn, ^{35}Cl)$ to 199 Hz for compound **3**. Clearly, these numbers can only represent an estimate, since we have no positive proof whether the assumptions made are perfectly valid. Therefore, in order to obtain exact data, a full simulation of the coupling pattern will have to be carried out. In order to obtain unique solutions for all the equations involved it may be necessary to run the respective ^{119}Sn CP-MAS NMR spectra at more than one magnetic field strength. Such a multi-field strength study would help to separate the field-independent *J*-contributions from the field-dependent quadrupolar coupling contributions [17]. Also, some X-ray crystallographic information on the Sn–Cl and Sn–N bond lengths would be useful for this purpose.

Applying the same procedure as described above to the ^{119}Sn CP-MAS NMR spectra of compounds **1** and **2** yields estimated scalar coupling constants $^{1}J(^{119}Sn, ^{35}Cl) = 236$ and 199 Hz, and $^{1}J(^{119}Sn, ^{14}N) = 118$ and 152 Hz, respectively. The signal-to-noise ratio of the ^{119}Sn CP-MAS NMR spectrum of compound **4** was insufficient for such an analysis.

We would like to emphasize that our estimated $^{1}J(^{119}Sn, ^{35}Cl)$ data for compounds **1–3** are fairly close to such data in organotin(IV) compounds reported in the literature [10]. Coupling constants $^{1}J(^{119}Sn, ^{14}N)$ 152 and 115 Hz, as estimated from the ^{119}Sn CP-MAS NMR spectrum of compounds **2** and **3** are very similar to the value of this scalar coupling constants obtained in $CDCl_3$-solution (Table 1, $J(^{119}Sn, ^{15}N) = 164.2$ Hz, corresponding to $J(^{119}Sn, ^{14}N) = 117.2$ Hz and $J(^{119}Sn, ^{15}N) = 198.2$ Hz corresponding to $J(^{119}Sn, ^{14}N) = 141.3$ Hz, using the coefficient $J(^{119}Sn, ^{15}N) : J(^{119}Sn, ^{14}N) = 1.4027$ [18]).

Not only is this qualitative analysis of the splitting pattern strong evidence for the existence of the postulated Sn · · · N bonding interaction in the solid state, it also rules out the existence of further intermolecular chlorine bridges in the solid state: the interaction with yet another quadrupolar ^{35,37}Cl nucleus would almost certainly yield even more complicated splitting patterns.

Conclusions

The structures of compounds **1–4** are the same, or very similar in the solid state and in $CDCl_3$ solution. The crystals of compounds **1–4** are formed by only one type of chelate complex which exists in a distorted *cis*-trigonal bipyramidal arrangement. There is no evidence from the NMR data for a significant association of these compounds in the solid state through intermolecular chlorine bridges.

Experimental

Equimolar mixtures of the sodium salts of 8-hydroxyquinoline or 8-quinolinethiol (Reakhim, USSR) were mixed with the appropriate diorganotin(IV) chlorides in methanol to give compounds **1–4**. After 30 min, methanol was distilled from the reaction mixture *in vacuo* and the residue was extracted with chloroform. After partial evaporation of solvent the compounds were crystallized from the chloroform–methanol solutions [2,19].

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 a 5 mm dual probe as described in ref. 1. The ^{1}H and ^{13}C chemical shifts were referred to internal tetramethylsilane ($\delta = 0.0$). Approximately 10% solutions or saturated solutions (in case of poor solubility of a compound) in deuteriochloroform were used for the measurement at 300 K.

The ^{15}N NMR spectra were taken at the natural abundance level at 30.43 MHz on a Bruker AM 300 in 10 mm tubes at 300 K. The selective INEPT technique with polarization transfer and selective decoupling of H(3) ($\gamma B = 25$ Hz) from H(2) was used. For details see ref. 2. The ^{15}N chemical shifts were referred to external neat nitromethane ($\delta = 0.0$).

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

Table 5

Analytical and physical data for compounds **2–4**

Compound [a]	Elemental analysis (found (calc.)) (%)						M.p. (°C)
	C	H	Sn	S	N	Cl	
2	55.85 (55.63)	3.98 (4.06)	24.05 (23.90)	6.38 (6.46)	2.70 (2.82)	7.08 (7.14)	130–131
3	53.52 (53.83)	3.57 (3.44)	25.30 (25.33)	6.69 (6.84)	3.04 (2.98)	7.78 (7.57)	199–200
4	42.14 (42.38)	3.35 (3.28)	32.24 (32.21)	8.59 (8.70)	3.71 (3.80)	9.82 (9.62)	173–175

[a] See Table 1.

In all cases positive values of chemical shifts denote down-field shifts with respect to a standard.

All ^{119}Sn CP-MAS spectra were obtained on a Bruker MSL 300 NMR spectrometer using double bearing probes. The set-up procedure for ^{119}Sn CP-MAS has been described elsewhere [15]. All chemical shifts are given with respect to external Me_4Sn, whereby the ^{119}Sn resonance of solid $Sn(C_6H_{11})_4$ served as a secondary external reference (−97.35 ppm). Recycle delays of 15-20 s were necessary, and the contact time for the $^1H \rightarrow {}^{119}Sn$ cross polarization experiments was 1 ms throughout. The proton 90°-pulse length was set to 5 μs. Between 100 and 5000 transients were accumulated. All spectra were repeated at a second spinning speed, sufficiently different to warrant the assignment of the centre-band. Spinning speeds of 3400–5000 Hz were used.

Analytical and physical data of compounds **2–4** are presented (Table 5).

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