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High-resolution solid-state ^{119}Sn NMR spectroscopy of some organotin(IV) oxinates and thiooxinates

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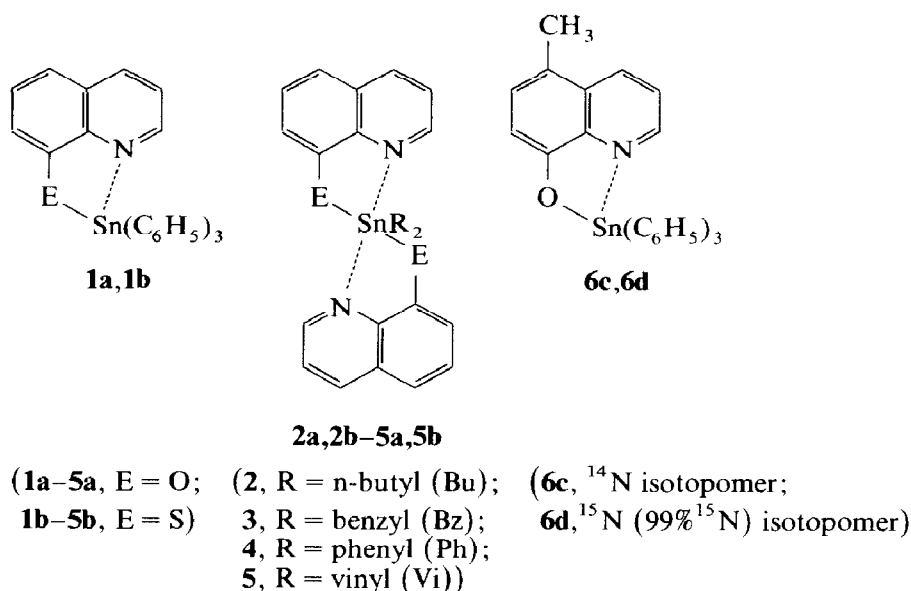
Abstract

Solid-state ^{119}Sn CP/MAS NMR spectra have been recorded for eleven triorganotin(IV) oxinates and thiooxinates and diorganotin(IV) dioxinates and dithiooxinates. The spectra of tri- and diorganotin(IV) oxinates and dioxinates reveal only one centre-band, in accord with their crystal structure determined by X-ray diffraction, whereas those of some analogous thiooxinates show two centre-bands. The ^{119}Sn CP/MAS NMR spectra of the isotopomers, with ^{14}N and ^{15}N , of triphenyltin(IV) 5-methyl-8-chinolinolate show three centre-bands as does the ^{15}N CP/MAS NMR spectrum of the isotopomer containing ^{15}N .

In the ^{119}Sn NMR spectra of triorganotin(IV) oxinates and thiooxinates, the centre- and side-bands which are attributable to the Zeeman effect and to the interaction with the ^{14}N quadrupole nucleus are split unsymmetrically into “doublets” with an approximate integration ratio 1:2. The spectrum of the isotopomer containing ^{15}N , shows splitting into a symmetrical 1:1 doublet attributable only to the Zeeman effect. “Triplet” splittings with a 1:4:4 integration ratio in the spectra of diorganotin(IV) dioxinates and dithiooxinates is probable because of interaction with two equivalent ^{14}N quadrupole nuclei. The triorganotin(IV) oxinates and thiooxinates and diorganotin(IV) dioxinates and dithiooxinates crystallize as molecular chelate complexes, which retain their structure in solutions in non-coordinating solvents.

Introduction

In previous papers [1–5] we have elucidated the structure of organotin(IV) oxinates (8-quinolinolates) and thiooxinates (8-quinolinethiolates) in solutions of coordinating and non-coordinating solvents. For an evaluation of the formation and a relative strength of bonding interactions between central tin atom and the N-heteroatom of oxinate or thiooxinate bidentate ligands and for the investigation of structure of these compounds, we used various features their ^1H , ^{13}C , ^{15}N , and ^{119}Sn NMR spectra, i.e. chemical shifts, and the coupling constants, ${}^nJ(^{119}\text{Sn}, ^{13}\text{C})$ ($n = 1-5$), $J(^{119}\text{Sn}, ^{15}\text{N})$ and ${}^2J(^{15}\text{N}, ^1\text{H})$. Our studies [1–5] have shown that in solutions of non-coordinating solvents these compounds exist as molecular chelate complexes. These complexes are characterized by a medium-to-strong Sn–N donor-acceptor bond [2], i.e. oxinate and thiooxinate ligands [3] are bidentate. The strength of the Sn–N bond depends on the nature and the number of organic substituents (bond strength generally increases with decrease in the number of substituents and in the series phenyl \sim vinyl $>$ benzyl $>$ n-butyl) and also on the ligand composition (bonds are stronger in oxinates than in thiooxinates) [3–5]. The coordination polyhedron of the central tin atom in triorganotin(IV) oxinates and thiooxinates is a distorted *cis*-trigonal bipyramid. In diorganotin(IV) dioxinates and dithiooxinates, the carbon, nitrogen, and oxygen or sulfur atoms, directly bonded to central tin atom, are in a strongly distorted octahedral coordination; the C and N atoms are almost *cis* and the O or S atoms, almost *trans*. Similar coordination polyhedra about Sn atoms have been observed in the solid state of these compounds by X-ray diffraction [6–11]. The degree to which the coordination polyhedra, are distorted was determined from the values of the C–Sn–C angles, and was found to be higher for single particles of some of the chelate complexes in solution than in the solid state [3,5].



Scheme 1

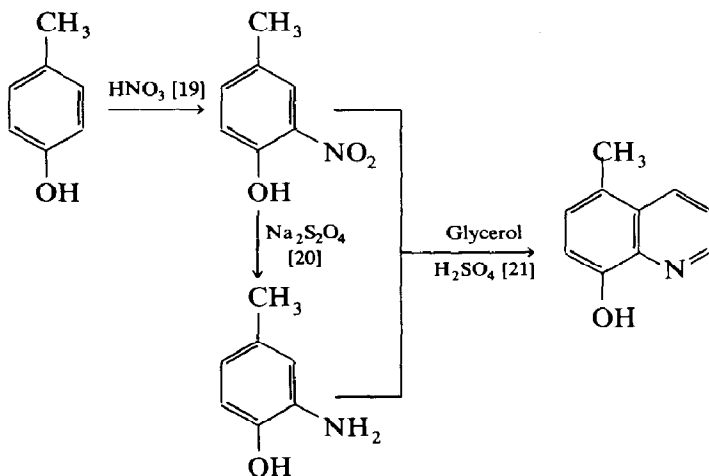
Here we describe the ^{119}Sn CP/MAS NMR spectra of a group of triorganotin(IV) oxinates $\text{R}_3\text{Sn}(\text{oxin})$ and thiooxinates $\text{R}_3\text{Sn}(\text{txin})$ and diorganotin(IV) dioxinates $\text{R}_2\text{Sn}(\text{oxin})_2$ and dithiooxinates $\text{R}_2\text{Sn}(\text{txin})_2$ (see Scheme 1). The data obtained by this very useful technique for the study of the structure of organotin(IV) compounds [12–18] are compared with those obtained by multinuclear NMR spectroscopy in solution and with those obtained from X-ray diffraction studies of their crystal structure.

Experimental

Complexes 1–6 were synthesized by previously published procedures [3,5]. 5-Methyl-8-quinolinol was prepared by the multistep synthesis depicted in Scheme 2; the separate steps were carried out by previously published methods [19–21].

The solid state ^{119}Sn NMR spectra were recorded at 74.62 MHz with a Bruker MSL 200 spectrometer. A combination of cross-polarization, magic-angle spinning and dipolar decoupling, generally known as CP/MAS was used [22–24]. The samples were packed in double bearing polyoxymethylene rotors machined in our laboratory. The magic angle was adjusted by minimization of the line width of the carbonyl carbon of glycine. Typical measurement conditions were as follows: contact time 5 ms, spectral width 50 kHz, acquisition time 20 ms, decoupling field in frequency units 50 kHz, pulse repetition time 20–200 s, number of scans 16–400, MAS frequency 4–5 kHz. The ^{119}Sn chemical shifts were referenced to tetracyclohexyltin by sample replacement with $\delta((\text{C}_6\text{H}_{11})_4\text{Sn}) - 97.35$ ppm [25].

The solid-state ^{15}N NMR spectrum of **6d** (99% ^{15}N) was recorded at 20.218 MHz with the same equipment and by the same techniques. Measurement conditions were as follows: contact time 5 ms, spectral width 20 kHz, acquisition time 77 ms, decoupling field in frequency units 35 kHz, pulse repetition time 60 s, number of scans 88, MAS frequency 4 kHz. The ^{15}N chemical shifts were referenced to solid NH_4Cl by sample replacement and recalibrated to nitromethane from $\delta(\text{NH}_4\text{Cl}) - 341.0$ ppm [26].



Scheme 2

The ^{119}Sn and ^{15}N NMR spectra of compounds **6c**, **6d** in deuteriochloroform were recorded with a JEOL JNM FX-100 instrument at 37.14 MHz and 10.095 MHz, respectively, as described previously [1,2]. Chemical shifts $\delta(^{119}\text{Sn})$ and $\delta(^{15}\text{N})$ were relative to external, neat tetramethylstannane and nitromethane, respectively, (δ 0.0 ppm). Chemical shifts downfield are positive.

Results and discussion

The ^{119}Sn NMR spectrum of each of the compounds studied shows only one resonance signal in deuteriochloroform solutions. In addition, the solid state ^{119}Sn CP/MAS NMR spectra of these complexes show only one centre-band (except for those of **1b**, **3b** and the isotopomers **6c** and **6d**) but the corresponding values of the chemical shifts $\delta(^{119}\text{Sn})$ in the solid state (see also Table 1) are shifted upfield by -0.8 to -25.8 ppm (except for one of the centre-bands of **6c** and **1b** which are shifted downfield by 8.7 and 3.5 ppm respectively) from those measured in deuteriochloroform solutions. Thus a particular ^{119}Sn chemical shift in the NMR spectrum corresponds to the presence of a structure of the complexes studied common to the solid and solution states. This conclusion was confirmed for the diorganotin(IV) dioxinates $\text{R}_2\text{Sn}(\text{oxin})_2$ [7–11] (including compound **2a** [10]) by diffraction studies.

The ^{119}Sn CP/MAS NMR spectrum of triphenyltin(IV) thiooxinate (**1b**) reveal two centre-bands (Table 1) of nearly the same intensity as can be seen in Fig. 1 (vertical arrows denote centre-band positions). A small difference in the values of the corresponding chemical shifts $\delta(^{119}\text{Sn})$ (~ 12 ppm) means that crystalline **1b** contains two crystallographically independent types of molecules which have the same composition but differ slightly in the geometry of the coordination sphere around central tin atom, which was confirmed by X-ray diffraction [6]. The 1:1 ratio of the crystallographically independent molecules in the crystal lattice also corresponds to the 1:1 ratio of the centre-bands. The ^{14}N and ^{15}N isotopomers of **6** give three centre-bands in their ^{119}Sn CP/MAS NMR spectra with $\delta(^{119}\text{Sn})$ chemical shifts of: -183.8 , -215.2 , and -218.3 ppm. In accord with these values, three centre-bands were also observed in the ^{15}N CP/MAS NMR spectra of isotopomers **6d** (Fig. 2) with $\delta(^{15}\text{N})$ chemical shifts of -116.5 , -118.2 and -118.9 ppm. Weak bands at the highest and lowest fields in Fig. 2 are satellite lines attributable to scalar splitting by ^{117}Sn and ^{119}Sn isotopes. The values of the $J(^{119}\text{Sn}, ^{15}\text{N})$ coupling constants obtained from ^{119}Sn and ^{15}N CP/MAS NMR spectra are identical within experimental error. Complex **6d** gives only one line with $\delta(^{15}\text{N}) = -115.5$ ppm with a coupling constant $J(^{119}\text{Sn}, ^{15}\text{N})$ of 96.7 ± 1.0 Hz in deuteriochloroform solution. To the best of our knowledge neither the crystal nor the molecular structure of any of the triorganotin(IV) oxinates and diorganotin(IV) dithiooxinates has yet been determined. The ^{119}Sn - ^{14}N dipolar splitting results in the 1:2 “doublets” in ^{119}Sn CP/MAS NMR spectra of triphenyltin(IV) oxinates and thiooxinates **1a**, **1b**, and **6c**. (see Figs. 1 and 3). Such splitting, between ^{119}Sn and one ^{14}N nucleus, has also been observed in the spectra the other organotin(IV) compounds [27]. A detailed theoretical description of ^{13}C - ^{14}N splitting has appeared [28]. The ^{119}Sn CP/MAS NMR spectra of ^{14}N and ^{15}N isotopomers of **6** unambiguously confirm this effect (Figs. 3 and 4). 5-Methyl-8-quinolinol was used in **6** in

Table 1
 ^{119}Sn chemical shifts for **1a**, **1b**–**5a**, **5b**, **6c**, **6d** in deuteriochloroform and in the solid state

Compound	$\delta(^{119}\text{Sn})^a$	$\delta(^{119}\text{Sn})^b$	$\delta(^{119}\text{Sn})^c$	$\Delta\delta(^{119}\text{Sn})^d$	Compound	$\delta(^{119}\text{Sn})^a$	$\delta(^{119}\text{Sn})^b$	$\delta(^{119}\text{Sn})^c$	$\Delta\delta(^{119}\text{Sn})^d$
1a	-190.1 ^e	-213.2	119.1	-23.1	1b	-150.5 ^f	-147.0	129.2	3.5
2a	-260.0 ^g	-277.4	74.4	-17.4	2b	-145.5 ^f	-159.0	123.4	-8.5
3a	-335.2 ^e	-346.9	^g	-11.7	3b	-235.2 ^f	-255.9	188.6	-20.7
4a	-394.2 ^e	-417.2	^g	-23.0	4b	-273.6 ^f	-274.4	102.3	-0.8
5a	-394.1 ^e	-402.8	^g	-8.7	5b	-282.4 ^f	-306.3	134.1	-23.9
6c	-192.5 ^h	-183.8 ^h	132.8	8.7					
		-215.2 ^h	122.7	-22.7					
		-218.3 ^h	134.0	-25.8					

^a In CDCl_3 at 300 K. ^b In the solid state. ^c Distance (in Hz) between lines in multiplets (see text). ^d $\Delta\delta(^{119}\text{Sn}) = \delta(^{119}\text{Sn})(\text{solid}) - \delta(^{119}\text{Sn})(\text{C}^2\text{HCl}_3)$. ^e Ref. [3]. ^f Ref. 5. ^g Not resolved. ^h Practically the same values were observed for **6d**; the differences correspond to the digital resolution.

place of the 8-quinolinol in **1a** because the first step of the synthesis of the isotopomer with the ^{15}N -nuclide (see Scheme 2) becomes more productive.

In accord with expectation, all three centre-bands in the spectra of **6c** (as well as the centre-band for **1a** and the two centrebands for **1b**) show splitting, because of quadrupole interaction and the Zeeman effect, into a 1:2 doublet (Figs. 1 and 3), whereas for isotopomer **6d** (containing ^{15}N -nuclide) all three lines are split into a 1:1 pattern due solely to the Zeeman effect (Fig. 4).

For the dipolar interaction and Zeeman effect of the ^{119}Sn nuclide with the two equivalent ^{14}N nuclei in compounds **2a, 2b–5a, 5b**, according to idealized scheme (Fig. 5), modified from [28], splitting of centrebands in ^{119}Sn CP/MAS NMR spectra into “triplets” having a 1:4:4 integral pattern can be expected. Such a pattern was also observed in ^{119}Sn CP/MAS NMR spectra of all the dioxinates **2a–5a** and dithiooxinates **2b–5b** studied. The ^{119}Sn CP/MAS NMR spectrum of compound **4a** is shown in Fig. 6 as an example.

Splitting of three bands in the ^{119}Sn CP/MAS NMR spectrum of isotopomer **6d** into 1:1 doublets is consistent with indirect interaction between the ^{119}Sn and ^{15}N

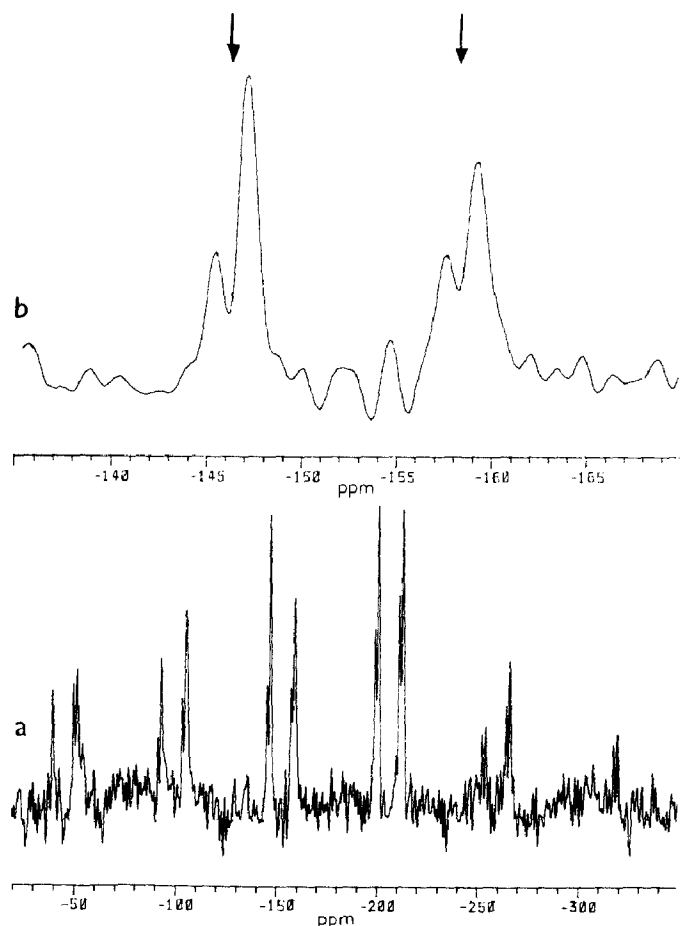


Fig. 1. ^{119}Sn CP/MAS NMR spectrum of **1b** (a) and its expanded part (b). The vertical arrows indicate the centre-bands.

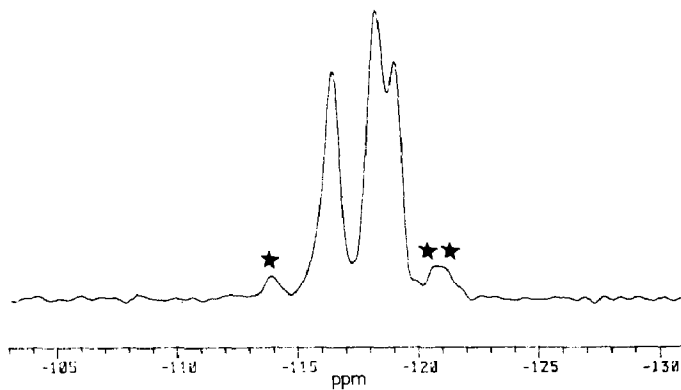


Fig. 2. ^{15}N CP/MAS NMR spectrum of **6d**. Only the centre-bands at expanded scale are shown. Asterisks denote $^{117/119}\text{Sn}$ satellites (see text).

nuclei. The value of coupling constant $J(^{119}\text{Sn}, ^{15}\text{N})$ for this compound in deuteriochloroform solution (96.7 ± 1.0 Hz), agrees well, within experimental error, with the splitting into doublets in the ^{119}Sn CP/MAS NMR spectrum, viz.: 101.4, 94.8 and 104.5 Hz. The small changes in the values of $J(^{119}\text{Sn}, ^{15}\text{N})$ on going from

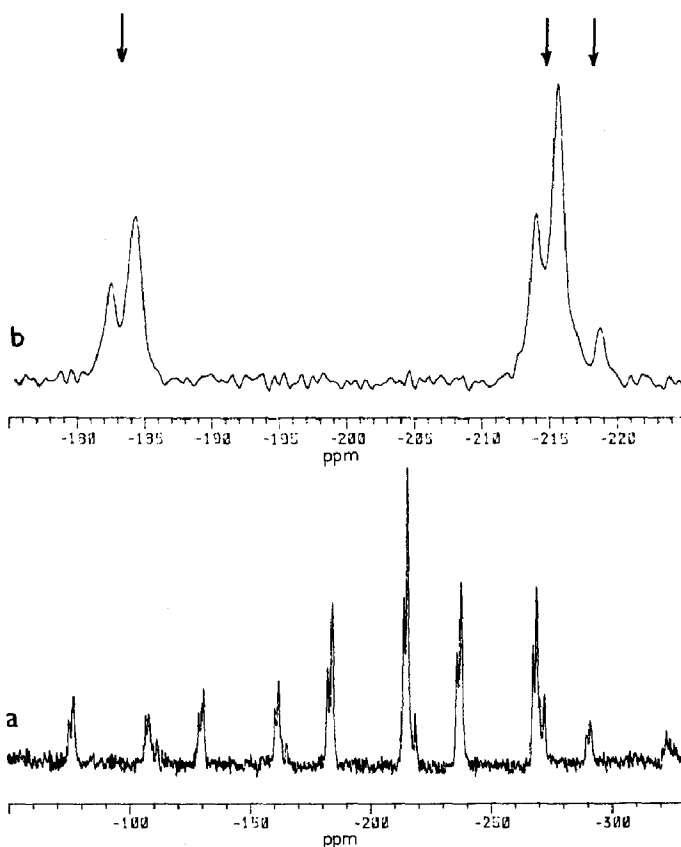


Fig. 3. ^{119}Sn CP/MAS NMR spectrum of **6c** (a) and its expanded part (b). The vertical arrows indicate the centre-bands.

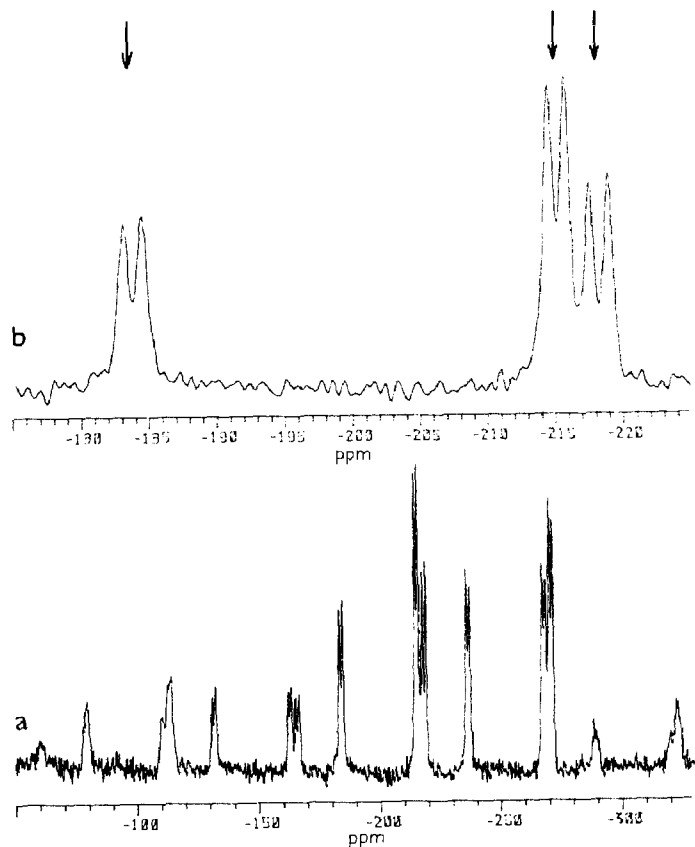


Fig. 4. ^{119}Sn CP/MAS NMR spectrum of **6d** (a) and its expanded part (b). The vertical arrows indicate the centre-bands.

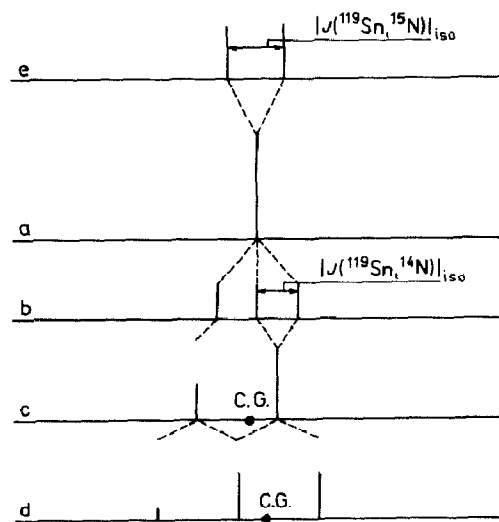


Fig. 5. Stick spectra illustrating the splitting of the tin signal in ^{119}Sn CP/MAS NMR spectrum, (a) without interaction with N, (b) scalar splitting by one ^{14}N nucleus, (c) scalar and dipolar splitting by one ^{14}N nucleus, (d) scalar and dipolar splitting by two equivalent ^{14}N nuclei, (e) scalar splitting by one ^{15}N nucleus. C.G. denotes the centre of gravity.

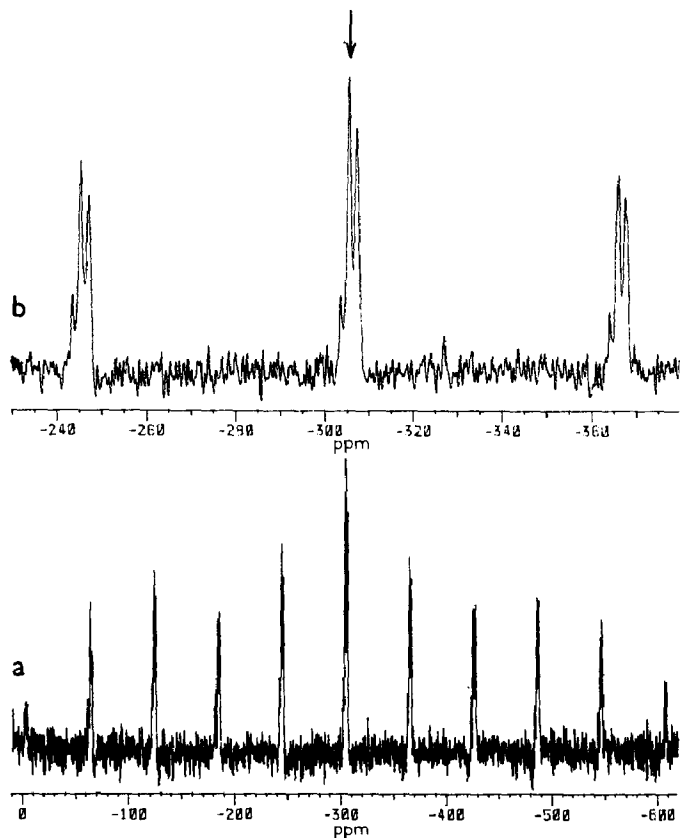


Fig. 6. ^{119}Sn CP/MAS NMR spectrum of **5b** (a) and its expanded part (b). The vertical arrow indicates the centre/band.

solution in a non-coordinating solvent to the solid state corresponds to small upfield shifts in $\delta(^{119}\text{Sn})$ values for the same transition.

Expected values of the coupling constants $J(^{119}\text{Sn}, ^{14}\text{N})$ of isotopomer **6c** in the solid state, calculated from the expression $|J(^{119}\text{Sn}, ^{15}\text{N})| = 1.4027 |J(^{119}\text{Sn}, ^{14}\text{N})|$ [29] are 72.3, 67.6 and 74.5 Hz. The observed dipolar splittings under a given field (J 130.6, 123, 8 and 134.0 Hz) are somewhat smaller (coefficient 0.9) than the double value of the above mentioned scalar coupling constants (see Fig. 5). In spite of inaccuracies because of experimental conditions (digitization of ca. 2 Hz/point) the simplified scheme (Fig. 5) is a good reflection of the real situation. Thus the multiplet patterns in ^{119}Sn CP/MAS NMR spectra recorded at ca. 4.7 T for the compounds studied can be assigned both to indirect (scalar) and direct (dipolar) interactions between the ^{119}Sn and the ^{14}N or ^{15}N nuclei. Similarly, interactions of the ^{119}Sn nucleus with ^{35}Cl or ^{37}Cl have been reported recently by Harris and Sebald [15].

The problem arises of how to determine the most correct values of $\delta(^{119}\text{Sn})$. If, as in ref. 15, we take the most real value of $\delta(^{119}\text{Sn})$ to be the centre of gravity of the “multiplet” in Fig. 5, it is evident that this point is lying one third of the distance between the 1 : 2 “doublet” lines downfield from the intense line for the interaction of ^{119}Sn nucleus with one ^{14}N nucleus. For the interaction of the ^{119}Sn nucleus with

two nuclei of ^{14}N , this point is lying in one third of the distance between the 1 : 4 : 4 pattern lines upfield from the central line. The values corrected in this way are given in Table 1.

The chemical shifts $\delta(^{119}\text{Sn})$ for compounds **1–6** in the solid state and in deuteriochloroform solutions and their difference $\Delta\delta(^{119}\text{Sn}) = \delta(^{119}\text{Sn})$ (solid state) $- \delta(^{119}\text{Sn})$ (CDCl_3 solution) are given in Table 1. The values of $\delta(^{119}\text{Sn})$ for the oxinates and thiooxinates **1a**, **1b**, **6c** and **6d** are typical of five-coordinate triphenyltin(IV) compounds [30], those of dioxinates **2a–5a** and dithiooxinates **2b–5b** correspond to diorganotin(IV) compounds with a six-coordinate central tin atom [31–33] both in the solid state and in solutions of non-coordinating solvents. Small differences in $\delta(^{119}\text{Sn})$ values (and also the direction of its shift on going from the solution to the solid state) cannot be ascribed to changes in the coordination of the central tin atom. We assume that these differences are due to small changes in the coordination geometry (see the $\Delta\delta(^{119}\text{Sn})$ values for **1b**) or to the Sn–N bond strength. This effect has been observed several times previously, such as $(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{POC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}]_2$ [15] which has a $\Delta\delta(^{119}\text{Sn})$ of -47 ppm without showing a change in coordination number.

Conclusion

The ^{119}Sn CP/MAS NMR spectra of triorganotin(IV) oxinates and thiooxinates and diorganotin(IV) dioxinates and dithiooxinates show that both in the solid state and in solutions in non-coordinating solvents **1–6** are monomeric chelates. The differences in the structures of complexes **1–6** are negligible on going from deuteriochloroform solution to the solid state. The characteristic pattern of multiplets in the ^{119}Sn CP/MAS NMR spectra recorded at ca. 4.7 T for **1–6** can be attributed to the dipolar interaction of the ^{119}Sn nucleus with one or two ^{14}N quadrupole nuclei, which confirms an Sn–N bonding interaction.

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