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^{119}Sn CHEMICAL SHIFTS IN FIVE- AND SIX-COORDINATE ORGANOTIN CHELATES

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Summary

^{119}Sn chemical shifts, $\delta(^{119}Sn)$, relative to Me_4Sn in five- and six-coordinate organotin chelates were measured by means of FT NMR spectroscopy. ^{119}Sn resonances were found to lie between ca. —90 and —330 ppm in the five-coordinate compounds and between ca. —125 and —515 ppm in the six-coordinate derivatives. Thus $\delta(^{119}Sn)$ moves upfield by 60—150 ppm with a change of the coordination number of tin from four to five and by 130—200 ppm from five to six. The $\delta(^{119}Sn)$ values were shifted depending on the nature of chelating ligands and this shift was discussed in terms of the bonding between the ligand and tin. Replacement of methyl groups attached to tin by phenyl groups in five- and six-coordinate compounds induces upfield shifts in $\delta(^{119}Sn)$ parallel to those found in four-coordinate organotin halides.

Introduction

^{119}Sn NMR spectroscopy has proved useful for characterizing organotin compounds in the last decade [1]. A considerable number of ^{119}Sn chemical shifts, $\delta(^{119}Sn)$, have been reported, for which various tentative explanations have been put forth. Yet further systematic accumulation of $\delta(^{119}Sn)$ data and their tentative interpretation seem to be of prime importance, since the theoretical treatment of ^{119}Sn NMR parameters is far from practical use at present [2].

Despite the extensive spectroscopic investigations on the configuration of organotin chelates [3], few studies have been made on the coordination bond itself. The $\delta(^{119}Sn)$ values are qualitatively known to be dependent on the coordination number of tin and accordingly seem to offer an appropriate measure for investigating the coordination about tin. This investigation may be best performed with discrete organotin chelates, because the complexes of other types such as adducts or molecular associates are inevitably at least partially dissociated in solution into their parent components. Several $\delta(^{119}Sn)$

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values for organotin chelates have been reported which, however, have not been studied systematically [1].

As a part of our studies on ^{119}Sn NMR spectroscopy [4], we present here a thorough investigation of $\delta(^{119}\text{Sn})$ in five- and six-coordinate organotin chelates carried out in the hope of obtaining information on the nature of the coordination bond about tin.

Experimental

The preparation of the organotin chelates employed in this study was carried out according to methods in literature cited in the last column of Table 1. Abbreviations for chelating ligands are as follows; acac = acetylacetonate, bzac = benzoylacetonate, dzbm = dibenzoylmethanate, trop = tropolonate, koj = kojate, oxin = oxinate, meox = 2-methyloxinate, mdtc and edtc = *N,N'*-dimethyl- and *N,N'*-diethyldithiocarbamates, benz = benzoate, and SAB = dianion of *N*-(2-hydroxyphenyl)salicylaldimine. All solvents were purified by standard methods.

The ^{119}Sn FT NMR spectra with complete proton noise decoupling were measured using a JEOL FX-100 spectrometer operating at 37.08 MHz at 22°C. Field-frequency control was made with an external D_2O lock. The chemical shifts were determined relative to external tetramethyltin (negative signs indicate upfield shifts from Me_4Sn (δ = 0 ppm)), and were found to be accurate to ±1 ppm by repeated measurements.

Results

The $\delta(^{119}\text{Sn})$ values shown in Table 1 exhibited no concentration dependence within experimental error, as expected from the nonassociative character of organotin chelates, but are evidently dependent on the coordination number of tin. It should also be noted that even in compounds of the same coordination number, these values show large shifts depending on the substituents on tin. ^{119}Sn resonances lie between ca. −90 and −330 ppm in the five-coordinate compounds and between ca. −125 and −515 ppm in the six-coordinate derivatives. The effect of chelating ligands on $\delta(^{119}\text{Sn})$ can be clearly shown in a series of $Me_2Sn(Ch)_2$ (Ch = chelating ligand). Among the chelating ligands with two oxygen donors, β-diketones (**1, 2, 3**) capable of forming a six-membered ring give rise to the greatest upfield shift and a decrease in the ring size to five- and four-membered rings (**4, 5, 10**) induces a downfield shift. The presence of nitrogen in the oxinates (**6, 7**) or of sulfur in the dithiocarbamates (**8, 9**) as a donor atom leads to an increased shielding on tin.

Substituents other than chelating ligands also shift $\delta(^{119}\text{Sn})$ to a considerable extent. Replacement of methyl groups in $Me_2Sn(Ch)_2$ (**1, 6, 9**) and $Me_2SnCl(oxin)$ (**19**) by phenyl groups (**12, 13, 14, 24**), in general, results in an upfield shift of $\delta(^{119}\text{Sn})$ by ca. 150—170 ppm, which is comparable with the shift observed between Me_2SnCl_2 and Ph_2SnCl_2 [1]. The $\delta(^{119}\text{Sn})$ value in $Ph_3Sn(edtc)$ (**27**) lies upfield of $Me_3Sn(edtc)$ (**25**) by 216 ppm. This is also consistent with the difference between $\delta(^{119}\text{Sn})$ values in Me_3SnCl and Ph_3SnCl [1].

TABLE 1

^{119}Sn CHEMICAL SHIFTS IN FIVE- AND SIX-COORDINATE ORGANOTIN CHELATES

Compound	Solution in wt/vol concentration	$\delta(^{119}Sn)$ (ppm)
Six-coordinate		
1, $Me_2Sn(acac)_2$	15% in $CHCl_3$	−365 [5]
2, $Me_2Sn(bzac)_2$	30% in CH_2Cl_2	−356 [5]
3, $Me_2Sn(dbzm)_2$	20% in CH_2Cl_2	−348 [5]
4, $Me_2Sn(trop)_2$	20% in CH_2Cl_2	−197 [6]
5, $Me_2Sn(koj)_2$	20% in DMSO	−174 [7]
6, $Me_2Sn(oxin)_2$	20% in $CHCl_3$	−237 [8]
7, $Me_2Sn(meox)_2$	8% in CH_2Cl_2	−228 [9]
8, $Me_2Sn(mdtc)_2$	30% in $CHCl_3$	−338 [10]
9, $Me_2Sn(edtc)_2$	30% in $CHCl_3$	−333 [10]
10, $Me_2Sn(benz)_2$	25% in $CHCl_3$	−125 [11]
11, $Bu_2Sn(oxin)_2$	30% in $CHCl_3$	−262 [8]
12, $Ph_2Sn(acac)_2$	30% in $CHCl_3$	−514 [5]
13, $Ph_2Sn(oxin)_2$	15% in $CHCl_3$	−397 [8]
14, $Ph_2Sn(edtc)_2$	30% in $CHCl_3$	−501 [10]
15, $BuSnCl(oxin)_2$	30% in $CHCl_3$	−395 [8]
16, $[BuSn(oxin)_2]_2S$	15% in $CHCl_3$	−333 [12]
17, $PhSnCl(mdtc)_2$	10% in $CHCl_3$	−361 [10]
Five-coordinate		
18, $Me_2Sn(SAB)$	25% in CH_2Cl_2	−150 [13]
19, $Me_2SnCl(oxin)$	30% in $CHCl_3$	−92 [8]
20, $Me_2SnCl(mdtc)$	30% in $CHCl_3$	−204 [10]
21, $Me_2SnCl(edtc)$	30% in $CHCl_3$	−201 [10]
22, $Bu_2SnCl(oxin)$	30% in $CHCl_3$	−112 [14]
23, $Ph_2Sn(SAB)$	20% in $CHCl_3$	−329 [15]
24, $Ph_2SnCl(oxin)$	20% in $CHCl_3$	−245 [14]
25, $Me_2Sn(mdtc)_2$	20% in $CHCl_3$	+25 [10]
26, $Ph_3Sn(oxin)$	30% in $CHCl_3$	−192 [8]
27, $Ph_3Sn(edtc)$	30% in $CHCl_3$	−191 [16]

Evaluation of the shift caused by chlorine is important for five-coordinate compounds, since $R_2SnCl(Ch)$ is the most common species in this category. The effect of a halogen substitution, however, has not been fully interpreted, even for $R_{4-n}SnCl_n$ [1], and it seems impossible to evaluate this effect in organotin chelates unambiguously with the presently available data. In order to rule out this uncertainty, we have measured the $\delta(^{119}Sn)$ values of $R_2Sn(SAB)$, where SAB is a tridentate ligand involving two oxygen and one nitrogen atoms.

Discussion

For an estimation of the effect of the coordination number on $\delta(^{119}Sn)$, the influence of substituents should be minimized as much as possible. However, it is difficult to satisfy this condition in all cases, since compounds which involve similar substituents in different coordination states are not always available. In Table 2 is shown a comparison of $\delta(^{119}Sn)$ values in some compounds of different coordination number. In general, the $\delta(^{119}Sn)$ values in the five-coordinate compounds appear at ca. 60—150 ppm upfield of the corresponding four-coordinate analogs. However, for $Me_2SnCl(mdtc)$, an unusual Δ_1 value was obtained, the reason for which is not clear. Six-coordination gives rise to an addi-

TABLE 2

COMPARISON OF $\delta(^{119}Sn)$ VALUES IN ORGANOTIN COMPOUNDS WITH DIFFERENT COORDINATION NUMBERS

Four-coordinate		Five-coordinate			Six-coordinate		
Compound	δ (ppm)	Compound	δ (ppm)	Δ_1 [a] (ppm)	Compound	δ (ppm)	Δ_2 [b] (ppm)
$Ph_3SnOOBu^t$	—95 [17]	$Ph_3Sn(oxin)$	—192	—97			
Ph_3SnSMe	—47 [18]	$Ph_3Sn(edtc)$	—191	—144			
Me_3SnSMe	+85.1 [19]	$Me_3Sn(mdtc)$	+25	—60			
$Me_2Sn(OBu^t)_2$	—1.8 [20]	$Me_2Sn(SAB)$	—150	—148	$Me_2Sn(acac)_2$	—365	—215
		$Me_2SnCl(oxin)$	—92		$Me_2Sn(oxin)_2$	—237	—145
		$Ph_2Sn(SAB)$	—329		$Ph_2Sn(acac)_2$	—514	—185
$Me_2Sn(SMe)_2$	+144 [19]	$Me_2SnCl(mdtc)$	—204	—348	$Me_2Sn(mdtc)_2$	—338	—134

[a] $\Delta_1 = \delta$(five-coordinate) — δ(four-coordinate). [b] $\Delta_2 = \delta$(six-coordinate) — δ(five-coordinate).

tional upfield shift of ca. 130—200 ppm. From these observations, it is apparent that an increase in the coordination number induces a stepwise upfield shift of $\delta(^{119}Sn)$.

As has been confirmed already by an X-ray diffraction study [21], compound 1 has a *trans*-octahedral configuration in which two oxygen atoms are symmetric and equal in coordinating ability. Some ionicity in the Sn—O bonds has been postulated from the bond distance. The Raman spectrum has supported the same configuration in solution [5], with which the large $^2J(^{119}Sn—CH_3)$ value (99.3 Hz) is consistent. The ^{119}Sn and ^1H NMR spectra suggest the analogous configurations for other β-diketone derivatives [4]. On the other hand, an octahedral configuration with a bent C—Sn—C moiety has been proposed for 4 [6] and 5 [7] on the basis of ν(Sn—C) and $^2J(^{119}Sn—CH_3)$. This configuration is different from that of 1 in that two oxygen atoms are not symmetric anymore and one Sn—O bond is essentially covalent while the other is considered as a coordination bond from the carbonyl oxygen atom. The ionic character of the Sn—O bond in 1 may be caused by sharing of covalency in two Sn—O bonds. These explanations are confirmed by IR spectra; that is, the ν(Sn—O) band in 1 (406 cm^{-1}) appears at much lower frequency than those in 4 and 5 (543 and 552 cm^{-1}, respectively). Evidently, the chelating ability of the tropolonate and kojate ligands is less than that of the acetylacetonate, resulting in decreased shielding on tin. A further downfield shift of $\delta(^{119}Sn)$ in the benzoate 10 is interpreted in terms of the reduced covalency of the Sn—O bond as indicated by a low ν(Sn—O) frequency (283 cm^{-1}) as well as the fact that the four-membered ring is unfavorable for chelation. These results illustrate well the sensitivity of $\delta(^{119}Sn)$ to the coordination bonds. Previously we have shown that the $^2J(^{119}Sn—CH_3)$ value in $Me_2Sn(Ch)_2$ is linearly correlated with the C—Sn—C angle, but not necessarily associated with the strength of the chelation [4]. Interestingly, this postulation is supported by comparing the NMR parameters of 6 and 7 with one another. The latter compound exhibits the larger $^2J(^{119}Sn—CH_3)$ value (89.0 Hz) and the $\delta(^{119}Sn)$ resonance is more downfield as compared with the former ($^2J(^{119}Sn—CH_3)$ = 71.2 Hz). Introduction of a methyl group into the α-position of the quinoline ring evidently results in a change of the configuration from *cis* in **6** to *trans* in **7**, but leads to a reduction of coordinating ability of nitrogen due to a steric repulsion.

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