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STUDIES ON ^{119}Sn AND ^{207}Pb NMR SPECTRA OF SEVEN-COORDINATE ORGANO-TIN AND -LEAD CHELATES

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Summary

^{119}Sn chemical shifts, $\delta(^{119}\mathrm{Sn})$, in seven-coordinate organotin chelates, $\mathrm{RSn(Ch)_3}$ and $\mathrm{R_2Sn(pan)(Ch)}$ (Ch = bidentate chelating ligand and pan = 1-(2-pyridylazo)-2-naphtholate), and ^{207}Pb chemical shifts, $\delta(^{207}\mathrm{Pb})$, in $\mathrm{Me_2Pb(pan)(Ch)}$ were measured by means of FT NMR spectroscopy. With a change of the coordination number of tin from six to seven, $\delta(^{119}\mathrm{Sn})$ values moved upfield by 90—300 ppm. In particular, striking upfield shifts (ca. 300 ppm) were observed for $\mathrm{RSn(mdtc)_3}$ (mdtc = *N,N'*-dimethyldithiocarbamate). As for $\mathrm{R_2Sn(pan)(Ch)}$, the magnitude of upfield shifts from corresponding $\mathrm{R_2Sn(Ch)_2}$ was found to range rather widely depending on chelating ligands. On the basis of these upfield shifts, it was suggested that chelating ligands forming a six- or five-membered ring coordinate to tin more weakly in $\mathrm{R_2Sn(pan)(Ch)}$ than in $\mathrm{R_2Sn(Ch)_2}$.

The $\delta(^{207}\mathrm{Pb})$ values in $\mathrm{Me_2Pb(pan)(Ch)}$ exhibited a quite similar trend to $\delta(^{119}\mathrm{Sn})$ values in $\mathrm{Me_2Sn(pan)(Ch)}$. It was, however, found that the coordination of the acetylacetonate ligand in $\mathrm{Me_2Pb(pan)(acac)}$ is not so weakened as in the organotin analog.

Introduction

Many fewer seven-coordinate organotin compounds have been reported than their five- and six-coordinate analogs. The most popular seven-coordinate compounds are monoorganotin tris(chelate), $\mathrm{RSn(Ch)_3}$ (Ch = bidentate chelating ligand). Recently, we have reported a new type of seven-coordinate compounds, $\mathrm{R_2M(pan)(Ch)}$ (I) (M = Sn and Pb, and pan = 1-(2-pyridylazo)-2-naphtholate) [1].

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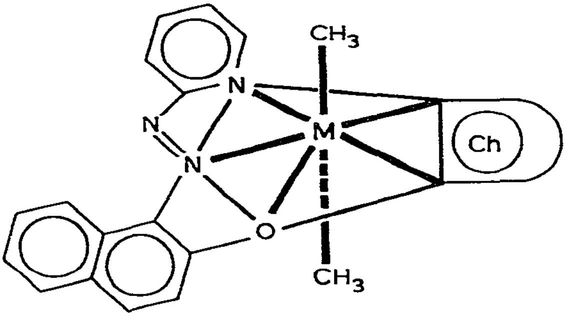
TABLE 1

$\delta(^{119}Sn)$ AND $\delta(^{207}Pb)$ VALUES IN SEVEN-COORDINATE AND CORRESPONDING SIX-COORDINATE ORGANO-TIN AND -LEAD CHELATES

Seven-coordinate	$\delta(^{119}Sn)$ (ppm)	$\delta(^{207}Pb)$ (ppm)	Six-coordinate	$\delta(^{119}Sn)$ (ppm)	$\delta(^{207}Pb)$ (ppm)	Δ_1 [a] (ppm)
1 $BuSn(oxin)_3$	−561		$BuSnCl(oxin)_2$	−395		−166
2 $BuSn(trop)_3$	−525					
3 $MeSn(mdtc)_3$	−786					
4 $PhSn(mdtc)_3$	−659 [b]		$PhSnCl(mdtc)_2$	−361		−298
5 $Me_2Sn(pan)(acac)$	−463		$Me_2Sn(acac)_2$	−365		−98
6 $Me_2Sn(pan)(bzac)$	−459		$Me_2Sn(bzac)_2$	−356		−103
7 $Me_2Sn(pan)(dbzm)$	−456		$Me_2Sn(dbzm)_2$	−348		−108
8 $Me_2Sn(pan)(tfacac)$	−449					
9 $Me_2Sn(pan)(hfacac)$	−409					
10 $Me_2Sn(pan)(oxin)$	−435		$Me_2Sn(oxin)_2$	−237		−198
11 $Me_2Sn(pan)(5\text{-}meox)$	−432					
12 $Me_2Sn(pan)(5\text{-}acox)$	−435					
13 $Me_2Sn(pan)(trop)$	−401		$Me_2Sn(trop)_2$	−197		−204
14 $Me_2Sn(pan)(benz)$	−388		$Me_2Sn(benz)_2$	−125		−263
15 $Me_2Sn(pan)(acet)$	−386					
16 $Me_2Sn(pan)(form)$	−357					
17 $Me_2Sn(pan)(tfacet)$	−341					
18 $Me_2Sn(pan)(mdtc)$	−466		$Me_2Sn(mdtc)_2$	−338		−128
19 $Me_2Sn(pan)(edtc)$	−463		$Me_2Sn(edtc)_2$	−333		−130
20 $Ph_2Sn(pan)(acac) \cdot C_6H_6$	−602		$Ph_2Sn(acac)_2$	−514		−88
21 $Me_2Pb(pan)(acac)$		−1189	$Me_2Pb(acac)_2$		−1051	−138
22 $Me_2Pb(pan)(hfacac)$		−1101				
23 $Me_2Pb(pan)(oxin)$		−1058				
24 $Me_2Pb(pan)(acet)$		−999				

[a] $\Delta_1 = \delta$(seven-coordinate) − δ(six-coordinate). [b] The value (−695 ppm) reported in ref. 3 should read as −659 ppm.

In the previous paper on the ^{119}Sn NMR spectra of five- and six-coordinate organotin chelates, we have shown that the nature of coordination bonds about tin can be characterized to a considerable degree on the basis of ^{119}Sn chemical shifts, $\delta(^{119}\mathrm{Sn})$ [2].



(I)

In the present study, we have measured $\delta(^{119}\mathrm{Sn})$ values in two types of seven-coordinate organotin chelates described above in order to obtain information on the coordination about tin [3]. In connection with these organotin chelates, ^{207}Pb chemical shifts, $\delta(^{207}\mathrm{Pb})$, in $\mathrm{Me_2Pb(pan)(Ch)}$ are also reported.

Experimental

Compounds, **1** [4], **2** [5], **3**, **4** [6], and $\mathrm{R_2M(pan)(Ch)}$ [1] were prepared according to the methods in literature. Abbreviations for chelating ligands are as follows: oxin = oxinate, trop = tropolonate, mdtc and edtc = *N,N'*-dimethyl- and *N,N'*-diethyldithiocarbamates, acac = acetylacetonate, bzac = benzoylacetonate, dbzm = dibenzoylmethanate, tfacac = trifluoroacetylacetonate, hfacac = hexafluoroacetylacetonate, 5-meox and 5-acox = 5-methyl- and 5-acetyloxinates, benz = benzoate, acet = acetate, form = formate, and tfacet = trifluoroacetate.

The ^{119}Sn and ^{207}Pb FT NMR spectra with complete proton noise decoupling were measured using a JEOL FX-100 spectrometer operating at 37.08 and 20.80 MHz at 22°C. Field-frequency control was made with an external $\mathrm{D_2O}$ lock. The chemical shifts (negative signs indicate upfield shifts from the references) were determined relative to external references ($\mathrm{Me_4Sn}$ for $\delta(^{119}\mathrm{Sn})$ and $\mathrm{Me_3PbCl}$ for $\delta(^{207}\mathrm{Pb})$), and were found to be accurate to ±1 ppm by repeated measurements. The $\delta(^{119}\mathrm{Sn})$ and $\delta(^{207}\mathrm{Pb})$ values of all chelates were obtained in chloroform solution (5—30 wt/vol.%) and showed no concentration dependence as expected from a nonassociative character of these compounds.

Results and discussion

The $\delta(^{119}\mathrm{Sn})$ and $\delta(^{207}\mathrm{Pb})$ values in seven-coordinate organo-tin and -lead chelates obtained in this study are listed in Table 1, in which presently available values for corresponding six-coordinate analogs [2] are also given for comparison. Previously we have found upfield shifts of $\delta(^{119}\mathrm{Sn})$ 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 [2]. Among $RSn(Ch)_3$ compounds, the oxinate exhibited a moderate shift (ca. 150 ppm) with a change of the coordination number from six to seven, while striking upfield shifts (ca. 300 ppm) were observed for the *N,N'*-dimethyldithiocarbamates. This presents a marked contrast to the results of Mössbauer spectra. Despite a general trend that an increase in the coordination number of tin(IV) gives smaller isomer shift values, the values for $RSn(dtc)_3$ have been reported to be larger than for corresponding six-coordinate $RSnX(dtc)_2$ [6]. The $\delta(^{119}Sn)$ values, therefore, seem to be preferable for a qualitative estimation of the coordination number. It is interesting to note that the $\delta(^{119}Sn)$ value of $MeSn(mdtc)_3$ (**3**) is comparable with that of $MeSnI_3 \cdot 2\,DMSO$ (−795 ppm) [7] which, to our knowledge, shows the greatest upfield shift reported for organotin compounds so far. Compound **3** is further unique in giving rise to $\delta(^{119}Sn)$ upfield of $PhSn(mdtc)_3$ (**4**), because $\delta(^{119}Sn)$ values in methyltin compounds usually lie downfield of those in phenyltin analogs [8].

As for $R_2Sn(pan)(Ch)$, the $\delta(^{119}Sn)$ values were observed in a rather narrow range and moved downfield in the following order; the β-diketonates ≃ the dithiocarbamates > the oxinates > the tropolonate > the carboxylates. On the other hand, the difference between the corresponding seven- and six-coordinate compounds, Δ_1, ranges widely (from −88 to −263 ppm) depending on chelating ligands, suggesting that a replacement of one of chelating ligands in $R_2Sn(Ch)_2$ by pan does not necessarily induce a similar effect on $\delta(^{119}Sn)$ for all compounds.

Let us suppose that a contribution of each chelating ligand to a $\delta(^{119}Sn)$ value is a half of the $\delta(^{119}Sn)$ values in $Me_2Sn(Ch)_2$, and that the contribution of the pan ligand (Cp) is adjusted to −325 ppm according to the following equation:

$$\delta(Me_2Sn(pan)(benz)) = Cp + \tfrac{1}{2}\delta(Me_2Sn(benz)_2)$$

The Cp value thus obtained would be reasonable if the contribution of the benz ligand is invariant in both six- and seven-coordinate complexes. IR spectra suggest a fair appropriateness of this assumption since $\nu_{asym}(C{=}O)$ band in solution appears at 1607 cm^{-1} in $Me_2Sn(benz)_2$ and 1603 cm^{-1} in $Me_2Sn(pan)(benz)$, indicative of little change in a coordination mode of the benz ligand in both compounds. Then, the estimated $\delta(^{119}Sn)$ values in mixed chelate compounds are obtained by summation of contributions from each fragment as given in Table 2. In the last column of this table is shown a difference of the observed and the estimated values (Δ_2), which increases with an increasing ring size of bidentate ligands. Since any substantial difference in coordination of the pan ligand in $Me_2Sn(pan)(Ch)$ has not been detected on the basis of visible spectra [1], an increase in Δ_2 can be attributed mostly to a change of coordination mode of bidentate ligands. We have revealed that $\delta(^{119}Sn)$ values in organotin chelates move downfield when bidentate ligands become less symmetric [2]. The downfield deviation of the observed values from the estimated values, therefore, may be induced by a symmetry reduction of bidentate ligands in $Me_2Sn(pan)(Ch)$. The asymmetric chelation has been postulated for $Me_2Sn(pan)(acac)$ (**5**) on the basis of ^1H NMR and IR spectra [1]. Although the acac ligands coordinate to tin symmetrically in $Me_2Sn(acac)_2$ as depicted in structure II, two Sn—O bonds are not equivalent in **5** so that a considerable

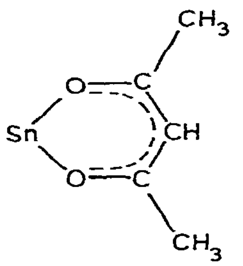
TABLE 2

ESTIMATED $\delta(^{119}Sn)$ VALUES

Ligand	Contribution of ligand (ppm)	δ(estimated) (ppm)	δ(observed) (ppm)	(Δ_2) [a] (ppm)
pan	−325			
benz	−63	−388	−388	0
trop	−99	−424	−401	+23
oxin	−119	−444	−435	+9
dbzm	−174	−499	−456	+43
bzac	−178	−503	−459	+44
acac	−183	−508	−463	+45

[a] $\Delta_2 = \delta(\text{observed}) - \delta(\text{estimated})$.

contribution of the structure III is involved. The reduction of symmetry in the trop ligand in **13** is also suggested by IR spectra. That the Sn—O stretching vibration of this compound (562 cm^{-1}) appears at higher wave number than that of $Me_2Sn(trop)_2$ (543 cm^{-1}) indicates a lowered symmetry; that is, the covalently linked Sn—O bond which is responsible for a ν(Sn—O) band around 550 cm^{-1} enhances its covalency and the coordination bond between tin and carbonyl oxygen is weakened in **13**. The Δ_2 values decreases in the following order, the β-diketonates > the tropolonate > the oxinate, parallel with the decreasing order of ligand symmetry. Apparently, a symmetric character of bidentate ligands is perturbed in $Me_2Sn(pan)(Ch)$ to a higher degree for a more essentially symmetric ligand.



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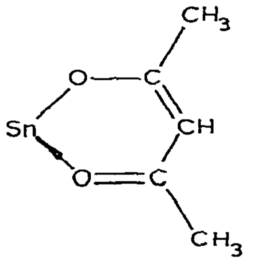

(III)

The $\delta(^{207}Pb)$ values in $Me_2Pb(pan)(Ch)$ exhibited a quite similar trend to $\delta(^{119}Sn)$ values in $Me_2Sn(pan)(Ch)$ and moved downfield in the order of the β-diketonates > the oxinate > the acetate. However, the Δ_1 value for the acetylacetonate **22** is somewhat larger than that for the organotin analog **5**, suggesting that the coordination of the acac ligand in **22** is not so much weakened as in **5**. This is consistent with the results of ^{1}H NMR and IR spectra which have disclosed more symmetric chelation of the acac ligand in **22** as compared with **5** [1].

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