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The ^{1}H, ^{13}C and ^{119}Sn NMR spectra of heptacoordinated diorganotin(IV) complexes

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Abstract

The neutral derivatives $R_2Sn(dib)$ (R = Me, n-Bu, Ph and Cl; dib = quinquedentate dianion from diacetylpyridine bis(benzoyl)hydrazone) have been synthesized, and characterized by IR and multinuclear magnetic resonance spectroscopy. The complexes exhibit high-field $\delta(^{119}Sn)$ values owing to the pentagonal bipyramidal environment produced by the planar quinquedentate ligand. In $Me_2Sn(dib)$ the absolute values of $^1J(^{13}C,^{119}Sn)$, 1215.0 Hz, and $^2J(^1H,^{119}Sn)$, 115.8 Hz are among the highest reported for diorganotin(IV) derivatives.

Introduction

Use of NMR spectroscopy in the study of the structures of organotin compounds has increased in the last years [1,2]. Both ^{119}Sn chemical shifts and tin–carbon (or tin–hydrogen) coupling constants provide very useful guides to the structures of such compounds. In particular, it is possible to define semiquantitatively the shape of coordination polyhedra of di- [3,4] and tri-organotin(IV) [5–7] complexes by analysis of their $\delta(^{119}Sn)$ and $^1J(^{13}C,^{119}Sn)$ parameters. The most important feature of the $\delta(^{119}Sn)$ values is that an increase in the coordination number of the tin atom from four to five or six usually produces an increase in shielding, and the δ values define regions with different coordination numbers. Furthermore the values of $^1J(^{13}C,^{119}Sn)$ and $^2J(^1H,^{119}Sn)$ can be used as an indication of the value of the C–Sn–C angle in the coordination polyhedron of individual compounds, both in solution [8–10] and in the solid state [11].

Although all these studies deal with four-, five-, and six-coordinate organotin compounds, it was shown that tin chemical shifts in seven-coordinated species are > 100 ppm upfield from those in six-coordinated analogues [12]. However, very few

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data on tin–carbon and tin–hydrogen coupling constants are available for heptacoordinated organotin complexes.

Recently, we introduced use of the quinquedentate near-planar ligand 2,6-diacetylpyridinebis(benzoyl)hydrazone (H_2dib), for the extraction and chromatographic determination of uranium [13,14]. The same procedure has been successfully applied to a number of di- and tri-organotin derivatives [15], the extracted species being in all cases R_2Sn(dib).

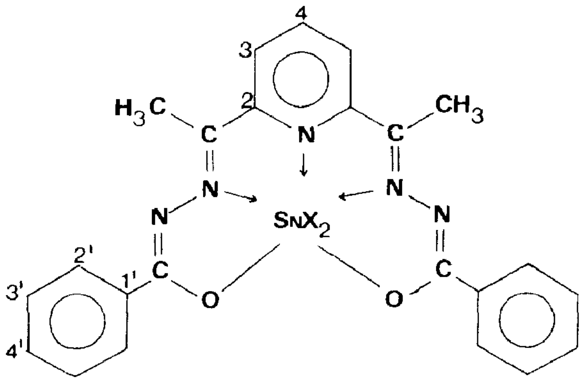
This paper deals with the synthesis and characterization, by IR and multinuclear NMR spectroscopy of such derivatives, in which tin exhibits a well-defined pentagonal bipyramidal environment, as revealed by X-ray structural studies of similar compounds [16,17]. They form a family of compounds suitable for study of the effect of heptacoordination on NMR parameters.

Results and discussion

The reaction of R_3SnOH or $R_{4-n}SnCl_n$ ($n = 1$, 2) with H_2dib in ethanol or chlorinated solvents at room temperature gives yellow, neutral diorganotin complexes of formula R_2Sn(dib). The methyl- and n-butyl-tin derivatives are very soluble in all the common solvents, whereas the phenyl species is rather insoluble, even in dimethyl sulfoxide. Reaction of H_2dib with $SnCl_2$ in the air gives the tin(IV) complex Cl_2Sn(dib) as a light yellow solid, appreciably soluble only in dimethyl sulfoxide.

As noted in the Introduction, these complexes have also been recovered after extraction and subsequent HPLC determination of various di- and tri-organotin derivatives [15]. In the presence of a large excess of tin the complex $(HO)_2Sn$(dib) has been found at the water–chloroform interface.

All the complexes display pentagonal bipyramidal structures, with the deprotonated and quinquedentate ligand dib spanning the pentagonal plane, as shown in Fig. 1. The caption to this figure lists the ^{119}Sn chemical shifts for three of these compounds. These values agree well with the corresponding values for other seven-coordinated tin complexes [12], and in particular with those for the related pentagonal bipyramidal complex Bu_2Sn(daps) (daps = 2,6-diacetylpyridine bis-



X	δ(ppm)
Me	−437
Bu	−441
Cl	−691

Fig. 1. Sketch of the pentagonal bipyramidal tin-dib complexes projected on the equatorial plane. Tin-119 chemical shifts are also quoted; solvent: chloroform (for X = Me and Bu), dimethyl sulfoxide (for X = Cl).

Table 1

Characteristic IR bands (cm^{-1}) of H_2dib and its tin complexes

Compound	ν(NH)	Amide I [a]	Amide II [a] ν(NC=N-N=C)	Amide III [a]		
				ν(CO),δ(NCO)	ν(SnCl)	ν(OH)
H_2dib	3280ms	1660vs (1580mw) [b]	1520s	1275s –	–	–
Me_2Sn(dib)	–	(1583mw) [b]	1500s	1360vs,1175s	–	–
Bu_2Sn(dib)	–	(1583mw) [b]	1500s	1355vs,1165s	–	–
Ph_2Sn(dib)	–	(1585mw) [b]	1500s	1365vs,1173s	–	–
Cl_2Sn(dib)	–	(1580mw) [b]	1500s	1370vs,1182s	330m	–
$(HO)_2Sn$(dib)	–	(1580mw) [b]	1497s	1380vs,1182s	–	3410m

[a] For the ligand only. [b] Small band probably due to pyridine ring.

(salicyloyl hydrazone) described in ref. 17. It is noteworthy that replacement of the alkyl groups by the chlorine ligands causes a strong upfield shift. The negative value for the dichloride derivative is one of the highest yet observed for tin(IV) complexes, approaching to the value of −695 ppm found for $PhSn(dtc)_3$ (dtc = *N*,*N'*-dimethyldithiocarbamate) [18].

Table 1 lists the main vibrational bands of H_2dib and its tin complexes, along with tentative assignments on the basis of previous reports on *d*- and *f*-transition metal complexes of H_2dib and related species [19,20]. As H_2dib contains the –CO–NH– moiety, its IR spectrum can be considered in the same way of those of the secondary amides, and as can be seen from Table 1, the major bands are derived from the so-called "amide" bands, including the CO stretching and the NH deformation modes. After coordination and deprotonation (disappearence of NH stretching), three major bands are still apparent for the complexes, but at lower frequencies. Their assignments must take into account the "iminol" form for the anionic ligand, i.e. the presence of the $>C{=}N{-}N{=}C<$ system and the $>C{-}O{-}$ coordinating group.

As shown in Table 2, which lists the ^1H chemical shifts for the examined compounds, coordination to tin induces a considerable differentiation of the signals from the aromatic protons, which, in the free ligands, lie within two close multiplets. In the case of the dialkyltin complexes, the protons *ortho* to the amide group (2′) and the proton 4 of the pyridine ring are deshielded, whereas the shifts of the aromatic *meta*- and *para*-protons and the β-pyridine protons (3) are only slightly affected by coordination, as noted in ref. 19. Surprisingly, in the dichloro- and the dihydroxy-tin complexes proton 3 of the β-pyridine is clearly deshielded and the signal from proton 4 moves further to low field. This effect is not attributable to the solvent DMSO, which, on the contrary, appears to increase the shielding of the pyridine protons in Bu_2Sn(dib) relative to those in chloroform.

In Me_2Sn(dib) the satellites around methyltin protons at 0.30 ppm, due to tin-119,117,115 and carbon-13, are readily detectable (see footnote to Table 2). The value of $^2J(^{119}Sn,^1H)$, 115.8 Hz, is higher than those observed for six-coordinated dimethyltin compounds [9], and appears to be typical of seven-coordinated species [12].

Deprotonation and coordination strongly influence the carbon shifts in the tin complexes with respect to those for the free ligand, particularly those of the

Table 2

^{1}H NMR chemical shifts (δ (ppm)) for H_2dib and its tin complexes

Compound	NH(2H)	OH(2H)	CH_3(6H)	3′,4′(6H)	2′(4H)	3(2H)	4(1H)	Me(6H) [c]	CH_3(ω,6H)	CH_2(α,β,γ,12H)
H_2dib [a]	10.96s	–	2.75s	two multiplets at 7.54 and 7.91				–	–	–
Me_2Sn(dib) [b]	–	–	2.73s	7.46m	8.44m	7.77d	8.14t	0.30s	–	–
Bu_2Sn(dib) [b]	–	–	2.75s	7.46m	8.41m	7.81d	8.15t	–	0.55t	0.91m
Cl_2Sn(dib) [a]	–	–	2.92s	7.64m	8.29m	8.60d	8.70t	–	–	–
$(HO)_2Sn$(dib) [a]	–	5.85s	3.01s	7.71m	8.35m	8.62d	8.75t	–	–	–

[a] In dimethyl sulfoxide. [b] In chloroform. s, singlet; d, doublet; t, triplet; m, multiplet. [c] $^2J(^1H,^{119}Sn)$ 115.8 Hz; $^2J(^1H,^{117}Sn)$ 110.7 Hz; $^2J(^1H,^{115}Sn)$ 102. Hz; $^1J(^1H,^{13}C)$ 130.5 Hz.

Table 3

^{13}C NMR chemical shifts (δ (ppm)) for H_2dib and its dialkyltin complexes

Compound	C=O	C=N	CH_3	2	3	4	1′	2′	3′	4′	Me [c]	C_α	C_β	C_γ	C_ω
H_2dib [a]	164.4	151.5	12.8	154.2	120.7	137.3	133.9	128.4	128.4	131.8	–	–	–	–	–
Me_2Sn(dib) [b]	173.1	144.8	12.8	149.3	121.4	141.1	135.8	129.0	127.8	130.9	12.1	–	–	–	–
Bu_2Sn(dib) [b]	173.2	144.7	12.8	149.4	121.2	141.0	135.9	129.0	127.9	130.8	–	26.2	30.6	27.4	13.4

[a] In dimethyl sulfoxide. [b] In chloroform. [c] $^1J(^{13}C,^{119}Sn)$ 1215.0 Hz.

hydrazide chains and of the pyridine ring, as shown in Table 3. In the dialkyltin dib complexes the signals from the carbonyl carbons have undergone a significant downfield shift, whereas those from the hydrazone C=N carbons undergo an upfield shift, as previously observed for d^{10} metal complexes of an aroylhydrazone of 2-formylpyridine [21]. In the pyridine ring, the resonances due to carbons 3 and 4 shift downfield relative to those of the free ligand, whereas those of carbons 2 exhibit an upfield shift. Such behaviour seems to be characteristic of coordinated pyridine rings [21]. In the phenyl rings, the *ipso* and *ortho* carbons become more deshielded, whereas the *metal* and *para* positions become slightly more shielded.

In the case of the dimethyltin derivative, the coupling constant $^1J(^{119}Sn,^{13}C)$ is readily determined. This constant has been shown to be linearly related to the Me–Sn–Me angle by analysis of CP-MAS solid-state ^{13}C NMR data on four-, five- and six-coordinated di- and tri-methyltin compounds [11]. A similar relationship has been developed for n-butyltin(IV) compounds by use of solution NMR data [10]. When the angle reaches 180°, for the six-coordinated complex $Me_2Sn(acac)_2$ the observed value of $|J|$ attains its highest value of 1175 Hz. This value is exceeded, however, by the value found for $Me_2Sn(dib)$, 1215.0 Hz, which to our knowledge is the highest yet observed for methyltin derivatives. As the Fermi contact term is assumed to make the largest contribution to $|J|$, for group 14 nuclei the apical tin orbitals bonded to the methyl groups in the pentagonal bipyramidal compounds must possess larger *s*-character compared with those in the octahedral complexes.

Experimental

All reagents and solvents were reagent grade. The solvents (Carlo Erba) were dried by standard techniques. The organotin compounds R_3SnOH, R_3SnCl and R_2SnCl_2 (R = Me, n-Bu, Ph) and $SnCl_2$ (Strem, Merck, Alfa) were used as supplied commercially. 2,6-Diacetylpyridine bis(benzoylhydrazone) (H_2dib) was prepared as described previously [20]. The diorganotin complexes were synthesized by slow evaporation of chloroform (or ethanol) solutions, initially containing equimolar amounts of the ligand and the organotin compound, after a few hours, stirring at room temperature. The rates of these reactions were higher at the reflux temperature. The dichlorotin(IV) dib-complex was obtained from $SnCl_2$ by the same procedure, whereas the dihydroxytin complex was recovered at the water/chloroform interface during some extraction experiments in the presence of large molar excess of tin. In all cases the yellow microcrystalline solids were filtered, washed with cold ethanol and ether, and dried in vacuo. The chemical analyses were in agreement with the formulae given in the tables. No NMR data are available for the diphenyl derivative owing to its poor solubility in all common solvents.

Elemental C, H and N analyses were carried out with a Perkin–Elmer model 240 automatic equipment. Infrared spectra (4000–200 cm^{-1}), for KBr discs, were recorded on a Perkin–Elmer model 283B spectrophotometer. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker CXP 200 instrument using ^2H solvent lock (chloroform-*d* or dimethyl sulfoxide-d_6). Chemical shifts are relative to internal tetramethylsilane (proton and carbon) or external neat tetramethylstannane (tin).

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