

Structural Elucidation of $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$ and its Hydrogen Bonding in Solution by HMBC Spectroscopy

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Abstract

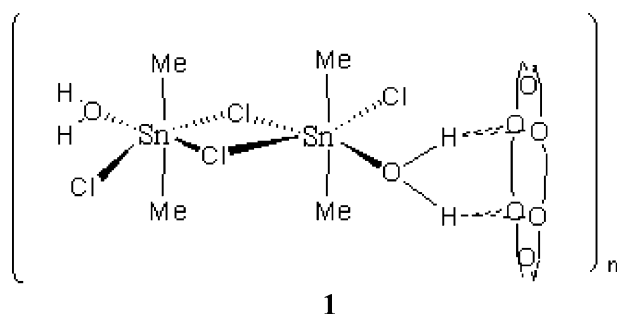
Behavior of $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$ in solution have been investigated by HMBC NMR. The results show that coordination of water to tin containing species and its hydrogen bonding to crown ether remains intact in non-coordinating solvent in contrast to coordinating solvent. H-NMR reveals that the chemical shift of water in complex varies by solvent of crystallization.

Introduction

Aqua complexes of di- and triorganotin compounds are shown to be stable if only extensive hydrogen bonds exist. Single crystal structure determination of several crown ether complexes [1–5], and occasionally with other ligands [6], of di- and triorganotin chloride has demonstrated this. In fact, in all organotin(IV) complexes of crown ethers, hydrogen bonding of crown ether enhance basicity of water and brought it to coordination to tin, in which crown ether is in the second coordination sphere of tin and hold in complex by hydrogen bonds [1]. Apparently, hydrogen bonds have crucial role in the three-dimensional structures of crown ether complexes of organotin halides. Therefore, investigation of coordination status of crown ether complexes of organotin compound in solution and understanding their hydrogen bonding role as a fetal force should be interesting and may bring new insight into self-assembly of molecules and crystal engineering.

Among many crown ether complexes of organotin compound, the X-ray single crystal structure of $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$, **1**, have been determined by two set of data collection and bifurcated hydrogen bonding have been established [1]. However, solution behavior and situation of hydrogen bonding in none of the crown-ether complexes of organotin is known. The $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$ complex slightly is soluble in chloroform and ¹H NMR spectrum of it in chloroform-d₃ at 295 K shows a singlet for water at 2.1 ppm, a singlet for the crown ether protons and a singlet for methyl groups along with ¹¹⁹Sn and ¹¹⁷Sn satellites. The ²J¹¹⁹Sn–¹H markedly increases from 70 Hz in chloroform-d₃ to 90 Hz in CD₃OD and reflects drastic change of structure in solution. Interestingly, the ¹¹⁹Sn NMR shows similar chemical shifts of tin for (CH₃)₂SnCl₂ and $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$, which opens argument for decompose of latter complex in solution. Surprisingly, the ¹¹⁹Sn isomer shifts in Mössbauer spectra for the above mentioned compounds exactly are same in solid state, and no conclusion can be drawn by neither spectroscopy regarding to the coordination status of complex in solution [7].

¹H–¹³C HMBC (Heteronuclear Multiple Bond Correlation) NMR spectroscopy is a well establish technique for the determination of long range ¹H–¹³C connectivity [8] and likewise have been used for the detection of long range coupling of ¹H–¹¹⁹Sn in organotin chemistry [9]. The proton-detected 1D and 2D ¹H–¹¹⁹Sn heteronuclear multiple-bond-correlation experiments successfully have been applied to organotin compounds and disclosed coupling of protons to tin, which is not detectable because of fast exchange or bonding to a quadruple atom,



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O ($I = 5/2$), or small H–Sn couplings in bonds [10]. This technique has become a fascinating tool for the detection of hydrogen bonding in protein chemistry in addition to the identification of metal bound protein [11–14], and there is hope to use magnitude of NMR coupling constant across hydrogen bond for detection of type of hydrogen bond [15]. In the present study, we have employed 2D ^1H – ^{119}Sn HMBC and HNMR spectroscopy with implementation of gradient pulses sequence to investigate the coordination and hydrogen bonding status of the aforementioned complex in solution.

Experimental

All NMR measurements were recorded at 298 K on a Bruker AMX500 MHz spectrometer with concentration of 2–3% (w/vol) in a 5 mm NMR tube. The $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$ complex was prepared according to the reported procedure [1]. Chloroform- d_3 was dried and distilled over phosphorus pentoxide. The HMBC pulse sequence and phase cycling proposed by Bax and Summers have been used to carry the 2D ^1H – ^{119}Sn HMBC experiments [8]. Due to the uncertainty which could arise by calculation of pulse

delay from $\Delta = 1/2 J(\text{H}, \text{Sn})$, as result of wide range of $^nJ^{119}\text{Sn-H}$ values ($n = 2-6$) [16], various pulse delay ranging from 0.700 to 400 ms (0.700, 1.75, 100 and 400 ms) was used to record HMBC spectra. For recording each spectrum the total experiment time was about 18 h. X-ray powder diffraction patterns of **1** that crystallized in various solvent were recorded on a Phillips PW-1730 diffractometer.

Results and discussion

Figure 1 illustrates the 2D HMBC NMR spectrum of above complex, which recorded in 0.7, 1.7, 100 and 400 ms pulse delay as previously reported pulse sequence [8]. Spectra with 100 and 400 ms do not show coupling of water to tin-119 and only coupling of the methyl protons bonded to tin, $^2J^{119}\text{Sn-C-H} = 70$ Hz, are visible. However, with reduction of pulse delay to 0.700 and 1.7 ms concomitantly coupling of water protons to Sn-119, $^{119}\text{Sn-O-H}$, is disclosed in HMBC spectrum with coupling constant of 70 Hz in addition to $^{119}\text{Sn-C-H}$ coupling. It is clear that the emergence of water protons signals in spectrum and suppression of

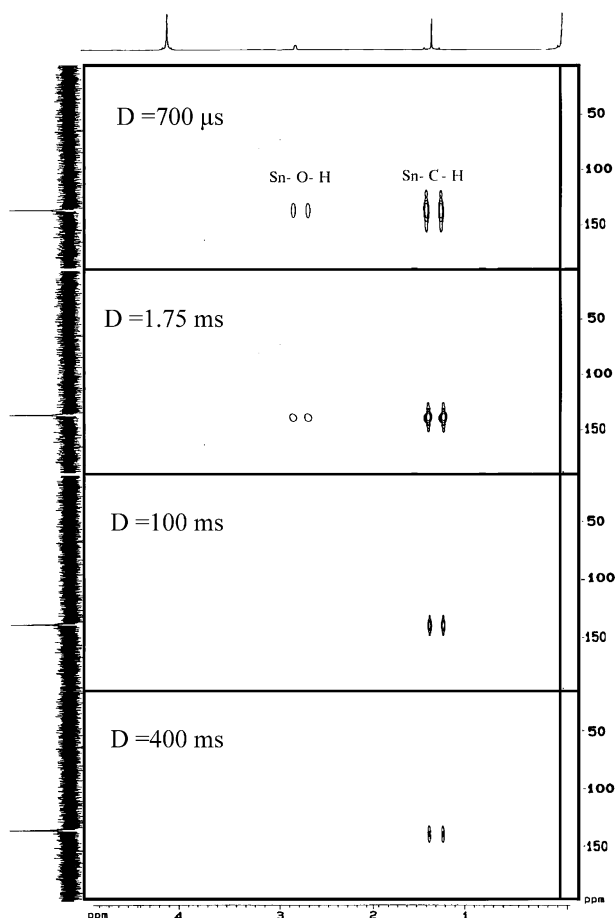


Figure 1. Two-dimensional ^1H – ^{119}Sn heteronuclear multiple bond correlation (HMBC) spectra of **1** recorded with various delay times. One hundred twenty eight scans and a relaxation time of 2.0 s were used.

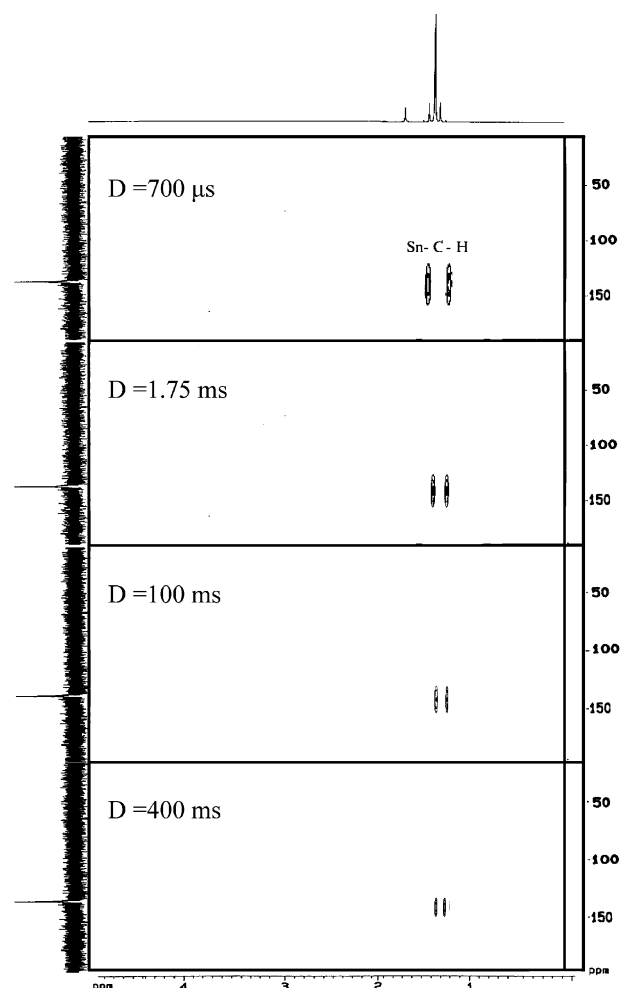


Figure 2. Two-dimensional ^1H – ^{119}Sn heteronuclear multiple bond correlation (HMBC) spectra of $\text{Me}_2\text{SnCl}_2 \cdot \text{H}_2\text{O}$ recorded with various delay times. One hundred twenty eight scans and a relaxation time of 2.0 s were used.

Table 1. Chemical shifts of water of complex with various crystallization solvent

Complex	Crystallization solvent	NMR recording solvent	δ , H ₂ O ppm
$\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$	CHCl ₃	CDCl ₃	2.1
$\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$	CH ₃ OH	CDCl ₃	1.7
$\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$	CH ₃ CN	CDCl ₃	1.8
$\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$	CHCl ₃	CD ₃ OD	4.9
(CH ₃) ₂ SnCl ₂ + H ₂ O	–	CDCl ₃	1.8
H ₂ O	–	D ₂ O	4.8 ^a
H ₂ O	–	CDCl ₃	1.5 ^a
H ₂ O	–	CD ₃ OD	4.9 ^a

^aFrom reference 26.

unwanted signals, arising from protons which are not coupling to Sn-119, depend on pulse delay and this occurs only under certain circumstances as reported by Willem *et al.* [17]. However, it is interesting to note that it is possible to record magnetic properties of nuclear in HMBC technique only through bonding between them with reduction of delay time and increasing NMR recording time.

Coupling of water protons to tin with coupling constant of 70 Hz unanimously reveals that the coordination of water to tin remains intact, through a strong interaction of oxygen and tin. Interestingly, this value for hydroxyl group coordinated to tin drops to less than 20 Hz [9], which indicates much weaker interaction in comparison with the strong interaction in the studied complex. For further clarification and confirming above claim, the 2D HMBC NMR spectrum of Me₂SnCl₂·H₂O was recorded in various delay times, including 0.700, 1.75, 100 and 400 ms that used to record 2D HMBC NMR spectrum of **1**. Consistently, no coupling of water protons to tin in 2D HMBC NMR spectrum of Me₂SnCl₂·H₂O was observed in various delay times (Figure 2) This further enlighten that the coordination of water to tin in chloroform is not accessible for water without hydrogen bonding to crown ether.

For the elucidation of hydrogen bonding of crown ether to water that coordinated to tin retain in solution or not, $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$ was crystallized in various solvents and their H-NMR chemical shifts in chloroform-d₃ compared with chemical shifts of free water and 1:1 ratio of dimethyltin dichloride and water (Table 1). The significant down field chemical shift of water, in comparison with free water and 1:1 ratio of dimethyltin dichloride and water, attributed to the hydrogen bonding of water to crown ether which remained intact in solution. Apparently, hydrogen bonding between water and crown ether is the main force that holds tin–oxygen bond in crown ether complexes of organotins in solid state and solution. Such a hydrogen bonding emphasize the important of hydrogen bonding in crown ether complexes of organotin in non-coordinating solvents in contrast to several well-defined metal capsule [18]. This hydrogen bonding remains in force in non-coordinating solvents, whereas in protic solvents, e.g. methanol, water

releases from coordinating sphere of tin due to the higher coordination ability of methanol to tin (Table 2). In fact, dispute of capsule host and release of guest by addition of coordinating solvents is not unusual [19]. Interestingly, when $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$ crystallized in methanol and acetonitrile, chemical shift of water protons, in chloroform-d₃, is decreased to 1.7 and 1.8 ppm, respectively. The reason for this effect is not clear at this time, however, it is interesting to note that the melting points of $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$ crystal varies to some extent with crystallizing solvent, chloroform, 132–138 °C [1]; methanol, 119–123 °C [20]; isopropyl ether, 98–101 °C; [21]; acetonitrile, 119–123 °C; but composition remains same accordance to the elemental analysis. Furthermore, the –OH stretching vibration of crystals that obtained from methanol and acetonitrile appears at about 24–30 cm⁻¹ higher than the crystals obtained from chloroform and reveals weaker hydrogen bonding in former.

For argument of isomorphous possibility, we have recorded X-ray powder diffraction of **1** that crystallized in chloroform, methanol, isopropyl ether and acetonitrile. Since **1** in all crystallizing solvents showed identical patterns, formation of isomorphous crystals ruled out. Therefore, it is highly possible that the variation of melting points and chemical shifts arise from type and nature of hydrogen bondings that exist between solute and solvent during crystallization and varies to some extent by the polarity of solvent and extended to the solid state. It seems that hydrogen bonding has strong influence in crystal packing which should be interesting from crystal engineering point of view. As previously noticed, hydrogen bonding is a fetal force in forming the three-dimensional structures and self-assembly of supramolecular structures [22–26], and now we see this fetal force retains in solution and most likely plays significant role in self-assembling of molecules which should be accounted in the engineering of self assembled molecules.

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