On the Hydrolysis of Monoorganotin Trihalides, V**.

Solid State ^{119}Sn -NMR and IR Spectra of the $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ Ion

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Monoorganotin Oxygen Compounds, ^{119}Sn -CPMAS-NMR Spectra, IR Spectra

The ^{119}Sn -CPMAS-NMR spectra of the complex $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ion were recorded for two different salts having twelve and four different tin atoms in the asymmetric unit, respectively. Both spectra agree very well with X-ray crystallographic predictions, and thus demonstrate the great sensitivity of heavy nuclei NMR spectroscopy to subtle structural changes. Infrared spectroscopy is shown to be a suitable routine detection method for the identification of this ion in the solid state.

Introduction

Solid state ^{119}Sn -CPMAS-NMR is a versatile tool for the study of crystalline and amorphous organotin compounds, but a detailed interpretation is often limited to cases, where the spectra are simple or where detailed X-ray diffraction studies are available. If, however, such data are absent or where the spectrum is complicated, showing *e.g.* several different centre bands and/or splitting patterns, it is often impossible to explain the observations either as a result of different crystalline phases being present, or by a single phase with different tin sites in the asymmetric unit.

In order to examine the influence of small changes of bond lengths and angles within a given tin coordination polyhedron on the isotropic ^{119}Sn chemical shifts of the tin atoms, we recorded the solid state ^{119}Sn -CPMAS-NMR spectra of two compounds containing the “football-like” $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ion [1]. This cation consists of six octahedrally and six square-pyramidally coordinated tin atoms bridged by twelve μ_3 -oxygen atoms and six μ_2 -hydroxy groups.

These investigations are supplemented by an IR study of this ion, which turns out to be a good routine method for analysis.

Experimental

The 111.9 MHz ^{119}Sn -CPMAS-NMR spectra were obtained on a Bruker MSL 300 NMR spectrometer, equipped with both 4 mm and 7 mm double bearing probes. The instrumental set-up for ^{119}Sn -CPMAS has been described elsewhere [2]. All ^{119}Sn chemical shifts are given with respect to external Me_4Sn , using the ^{119}Sn resonance of solid Cy_4Sn (−97.35 ppm) as a secondary external reference.

For an unambiguous assignment of the respective centre bands, the spectra were re-run at several sufficiently different spinning speeds, including experiments at MAS rates of 8 and 9 kHz on the 4 mm probe. At such spinning rates, the $^1\text{H} \rightarrow ^{119}\text{Sn}$ cross polarization efficiency was found to decrease dramatically as compared to the more conventional spinning rates of approximately 4–5 kHz. This effect is due to the onset of partial decoupling of dipole–dipole interactions at such high spinning rates. It should be mentioned that at high spinning rates (>5 kHz) the Hartmann–Hahn matching condition for the $^1\text{H} \rightarrow ^{119}\text{Sn}$ cross polarization is modulated by the MAS rate. Accordingly, the Hartmann–Hahn match has to be optimized for each given MAS rate >5 kHz.

In order to confirm the overall 1:1 relative intensity of the two different spinning side band patterns for **2a**, a ^{119}Sn single pulse experiment with a relaxation delay of 30 s and a ^{119}Sn pulse width of 30° was performed. For the CP experiments a contact time of 1 ms was used, the proton 90° pulse length was set to 5 μs , relaxation delays were 5–10 s, and 1100 to 12000 transients were accumulated.

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IR spectra were obtained from K1 discs with a Perkin Elmer 457 instrument in the range 200–4000 cm^{-1} .

Discussion

The syntheses of the $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ion (**1**) and the isolation of its chloride salts $1 \cdot \text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**2a**) and $1 \cdot \text{Cl}_2 \cdot 2\text{DMF}$ (**2b**) have been described in a previous paper [1]. Single crystal X-ray diffraction studies revealed that **2a** contains two centrosymmetric, but crystallographically independent cations, located around (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of the triclinic unit cell (space group: $P\bar{1}$, Nr. 2 [3]). The asymmetric unit, therefore, consists of $2 \times 3 = 6$ octahedrally (Sn_{oct}) and just as many square-pyramidally (Sn_{spy}) coordinated tin atoms. In contrast, **2b** belongs to the tetragonal crystal system (space group: $P4_2/nnm$, Nr. 134 [3]). In addition to the centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$ the $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ion now also possesses a mirror plane parallel to $(x, \bar{x}, z)$. Therefore, the asymmetric unit of **2b** consists of only 2 Sn_{oct} and 2 Sn_{spy} , of which, in both cases, one is in a general position whereas the second occupies a special position, *i.e.* lies on the mirror plane. The different symmetry elements of the cation **1** present in **2a** and **2b** are shown in Fig. 1.

Fig. 1. Perspective view of the tin-oxygen framework of the "football-like" $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ion found in the crystal structure [1] of **2a** and **2b**; organic groups omitted for clarity. The positions of the different symmetry elements (centre of symmetry [i], mirror plane [m]) are shown.

In the ^{119}Sn solid state spectra for **2a**, two different patterns each consisting of six ^{119}Sn resonances (all of equal intensity) for the six crystallographically inequivalent Sn_{oct} and Sn_{spy} , and for **2b** two patterns of two resonances (intensity ratio 1:2) have to be expected.

As an example, the ^{119}Sn -CPMAS spectrum of **2a**, recorded at a spinning rate of 3.6 KHz is shown in Fig. 2. We can distinguish two patterns of centre bands around –310 and –488 ppm, respectively. The assignment of these two centre band regions seems fairly straightforward: the pattern at higher field stems from Sn_{oct} , while the pattern at lower field belongs to Sn_{spy} , $\{\text{R}\text{SnO}_4\}$. There is no data available for direct comparison, but some other isotropic ^{119}Sn chemical shifts for solid organotin-oxygen coordination spheres do support this assignment indirectly. A high shielding for a hexacoordinate environment is represented for $\{\text{SnO}_6\}$ in solid SnO_2 with $\delta^{119}\text{Sn} = -603.3$ ppm [4]. Fivefold, trigonal bipyramidal coordination of the type $\{\text{R}_2\text{SnO}_3\}$, like in solid $[\text{Me}_2\text{SnO}]_n$, yields isotropic ^{119}Sn shifts around –150 ppm [5], and fivefold $\{\text{R}_3\text{SnO}_2\}$ coordination like in solid Me_3SnOH produces shifts of *ca.* –100 ppm [6]. The well-established ligand effects on $\delta^{119}\text{Sn}$ [7], and the well-documented increase of the ^{119}Sn shielding by 150–250 ppm associated with an increase of the coordination number by one unit [8], strongly support this assignment.

The insets of Fig. 2 show, however, that these centre bands have a fine structure, which consists of 5 (Sn_{spy}) and 6 (Sn_{oct}) more or less well resolved single resonances, respectively. With the exception of the one resonance missing for the sixth Sn_{spy} -atom, this spectrum agrees very well with the results based on the crystallographic predictions. This resolution is somewhat surprising as the changes of bond angles and bond lengths in each set of the differently coordinated tin atoms are very small [1]. However, the result shows the high sensitivity of solid state ^{119}Sn -NMR to such small variations.

Due to the complex structure of the centre bands (and of their associated spinning sidebands) no attempt has been made to quantify the tensorial properties of the ^{119}Sn shielding for **2a** and **2b**. Inspection of Fig. 2, however, clearly shows that – as one might predict – the anisotropy for the hexa-

Fig. 2. ^{119}Sn -CPMAS NMR spectrum of compound **2a**. Centre bands are indicated by arrows, the expanded insets show the two different centre band regions. Experimental conditions: spinning rate 3.6 kHz, 1 ms contact time, 1 s recycle delay, 12000 transient; no line broadening function has been used prior to Fourier transformation.

coordinated tin atoms is somewhat less pronounced than for the five-coordinated tin atoms.

The ^{119}Sn -CPMAS spectra of **2b** also fulfil the predictions based on the crystallographic results. Two different patterns of two resonances are observed with an intensity ratio near 1:2 and isotropic chemical shifts similar to those found for Sn_{Okt} and Sn_{spy} in **2a**.

The solid state ^{119}Sn -NMR studies of the $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ion were complemented by infrared spectroscopic investigations. The spectra are shown in Fig. 3. To help with the evaluation of the main bands of the tin-oxygen framework, the IR spectrum of $i\text{-PrSnCl}_3$ has also been included.

The hydroxyl groups of the cation form strong hydrogen bridges in the solid state, as indicated by the strong and broad $\nu(\text{O}-\text{H})$ bands around 3220 (**2a**) and 3240 (**2b**) cm^{-1} , respectively. X-ray diffraction studies have shown that in both com-

Fig. 3. IR spectra of compounds **2a** and **2b** in the region 200–4000 cm^{-1} with the assignment of the fingerprint bands of the tin-oxygen framework. For comparison the IR spectrum of isopropyltin trichloride is also included.

pounds all six hydroxyl groups are involved in such hydrogen bonds, either to oxygen (short bonds, 262–277 pm) or to chlorine (long bonds, 299–321 pm) atoms. In case of **2a**, the $\nu(\text{O–H})$ band is broader than in **2b** and has two additional maxima at lower wavelengths. This results from the additional hydrogen bridges of the water molecules which are present in the crystal structure of **2a**. By contrast, the band of the oxygen-to-hydrogen vibrational mode of an hydroxy group bridging two tin atoms normally is sharp but weak, and lies in the range 3574–3638 cm^{-1} when not participating in hydrogen bonds, as it is the case in the structures of polymeric triorganotin hydroxides [9]. Its position does not change if the triorganotin hydroxide has a monomeric crystal structure, as *e.g.* Mesityl₃SnOH [10].

The $\nu(\text{Sn–O})$ modes **2a, b** form two more or less well resolved patterns of three peaks at 675, 610,

542 cm^{-1} and 438, 410, 332 cm^{-1} , respectively. As indicated in Fig. 3, we tentatively assign these bands to the asymmetric and the symmetric tin-oxygen vibrational modes, respectively. For hexaorganodistannoxanes, $(\text{R}_3\text{Sn})_2\text{O}$, the bands of these vibrations are found in the range 856–740 cm^{-1} [$\nu_{\text{asym}}(\text{Sn–O})$], strongly depending on the tin-oxygen-tin angle, and in the range 412–370 cm^{-1} [$\nu_{\text{sym}}(\text{Sn–O})$], respectively [9]. The peak at 332 cm^{-1} may represent a $\delta(\text{Sn–OH})$ vibration, because its position is very similar to that of the same vibration observed in the IR spectra of polymeric triorganotin hydroxides [9].

The $\nu(\text{Sn–O})$ pattern of six bands is generally very useful to detect $[(\text{RSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ ions in mixtures of other organotin oxygen compounds.

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