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^{119}Sn NMR Spectra of $SnCl_4 \cdot 5H_2O$ in H_2O/HCl Solutions

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Pentahydrated stannic chloride $SnCl_4 \cdot 5H_2O$ was first reported in 1789 by Adet [1]. Unfortunately, so far its crystal structure data have not been reported. Its structure has been elucidated mainly by Raman [2], Mössbauer and nuclear quadrupole resonance [3] spectroscopy.

In the early investigations, Pfeiffer [4] concluded that $SnCl_4 \cdot 5H_2O$ takes the configuration $SnCl_4(H_2O)_2 \cdot 3H_2O$. This conclusion was confirmed by the later Raman investigation of Brune and Zeil [2], in which they suggested that in $SnCl_4 \cdot 5H_2O$ four chloride atoms and two hydrated water molecules are arranged octahedrally around the central tin atom, and that the two water molecules occupy the *trans*-position only. They also suggested that the D_{4h} symmetry of the hydrate is preserved in the liquid state.

Aqueous solutions of $SnCl_4 \cdot 5H_2O$ containing HCl have been investigated by many authors [5–8]. In extremely concentrated HCl solutions, no doubt $SnCl_4$ forms the $SnCl_6^{2-}$ complex [5]. In lower [HCl] solutions or in pure water solutions, there have been some suggestions that there exist species such as $SnCl_{6-n}(H_2O)_n^{n-2}$ ($n = 1$–6) [1, 6–8]. We here report ^{119}Sn NMR spectra of $SnCl_4 \cdot 5H_2O$ in H_2O/HCl solutions. We are able to assign the resonance lines to species of $SnCl(H_2O)_5^{3+}$, $SnCl_2(H_2O)_4^{2+}$, $SnCl_3(H_2O)_3^{+}$, $SnCl_4(H_2O)_2$, $SnCl_5(H_2O)^{-}$ and $SnCl_6^{2-}$ respectively. This provides direct evidence for these complex species.

Experimental

The $SnCl_4 \cdot 5H_2O$ used in this study was purchased from Shanghai 4th Factory of Chemical Reagents, as analytically pure. Samples were prepared by quantitatively dissolving $SnCl_4 \cdot 5H_2O$ in water or in HCl solutions.

^{119}Sn NMR spectra were recorded on a Varian XL-200 spectrometer with a broad-band probe. The probe was tuned to 74.553 MHz. The acquisition parameters were set as: spectral width = 50 000 Hz, acquisition time = 0.2 s, pulse width = 15 μs (~45°), pulse interval = 0.25 s, data points = 20 000, line broad factor = 50, and transient number = 3000 ~ 8000, depending on the signal-to-noise ratio. The magnetic field was shimmed carefully and then was left alone, *i.e.* D lock was not established during acquisition. No proton decoupling was performed. Neat liquid $SnCl_4$ was used as the external reference with $\delta(SnCl_4) = -150$ ppm, with respect to $\delta(SnMe_4) = 0$ ppm.

Results and Discussion

^{119}Sn NMR spectra were recorded for HCl solutions of $SnCl_4 \cdot 5H_2O$ with HCl concentrations varying from 12 M to 0 M and with the Sn concentration kept constant ($SnCl_4 \cdot 5H_2O$:solvent = 1 g/1 ml, ~2.9 M). Parts of the spectra are shown in Fig. 1. In extremely concentrated HCl solutions, the tin atom must have formed the $SnCl_6^{2-}$ complex species [5] and only a single signal at −700 ppm or so was observed in 12 M, 11 M and 10 M HCl solutions (Fig. 1f). The much wider line-width must be due to the high viscosity of the solution. When the

Fig. 1. ^{119}Sn NMR spectra of aqueous solutions of 2.9 M $SnCl_4 \cdot 5H_2O$ with up to 12 M HCl.

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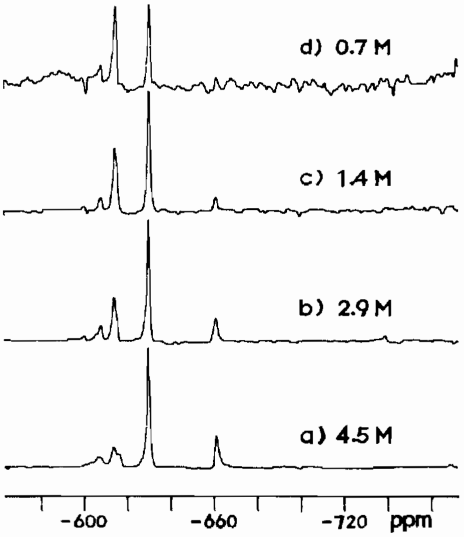

Fig. 2. ^{119}Sn NMR spectra of HCl-free aqueous solutions of $SnCl_4 \cdot 5H_2O$ with various concentrations.

solution was diluted to 9 M HCl, the signal at −660 ppm began to appear. This can be assigned to the $SnCl_5(H_2O)^-$ species. When the solution was further diluted, a signal at −630 ppm appeared and became stronger and stronger. This is the signal from $SnCl_4(H_2O)_2$. The *cis-* and *trans*-species cannot be distinguished, possibly because (i) they might coincide with each other, or (ii) the *trans*-species might dominate the *cis*-one. In 3 M HCl solution, the signal from $SnCl_6^{2-}$ began to disappear and a doublet at −614 and −618 ppm can be seen. They are assigned to $SnCl_3(H_2O)_3^+$ which also has *cis-* and *trans*-forms.

The ^{119}Sn spectra of pure water solutions in which the Sn concentration was varied are shown in Fig. 2. We can see that the doublet of $SnCl_3(H_2O)_3^+$ overlaps in diluted solutions. New signals appeared at −605 and −600 ppm. The former is assigned to $SnCl_2(H_2O)_4^{2+}$ and the latter to $SnCl(H_2O)_5^{3+}$. Under favorable conditions, we could distinguish the doublet of $SnCl_2(H_2O)_4^{2+}$ (Fig. 2b). In rather concentrated solutions the signal of $SnCl_4(H_2O)_2$ is much stronger than the others, which confirms the suggestion of Brune and Zeil [2] that in the liquid state D_{4h} symmetry might still be preserved.

Burke and Lauterbur [9] have reported a $\delta = -590$ ppm value for the ^{119}Sn shift of $Sn(OH)_6^{2-}$, just right in our hydrolytic series. One may find that the chemical shift effect of substitution of Cl^- by H_2O is by no means linear. This is understandable because in high [HCl] solutions, Cl^- is substituted by H_2O on hydrolysis of $SnCl_6^{2-}$, while in lower [HCl], zero [HCl], or basic solutions, Cl^- is in fact substituted by OH^-.

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