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The Bond Character of the Sn–Cl Bonds in the Hydrates of Tin(IV) Chloride

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Several hydrates of tin(IV) chloride, *e.g.*, $SnCl_4 \cdot xH_2O$ (x=2, 3, 4 and 5) and $SnCl_4 \cdot yD_2O$ (y=3, 4 and 5), were investigated by means of the nuclear quadrupole resonance (NQR) due to ^{35}Cl and the Mössbauer effect due to ^{119}Sn. The NQR-frequencies were observed at the temperature of liquid nitrogen and room temperature; they were found to range from 17.656 to 21.439 MHz. The Mössbauer effect was investigated only at the temperature of liquid nitrogen; it resulted in isomer shifts ranging from 0.275 to 0.350 mm/sec. The NQR-frequency and the isomer shift decreased with an increase in the number of water molecules in the hydrates, and the relationship between the NQR-frequency and the isomer shift was nearly linear. This relation was interpreted in terms of the transfer of the *s*-electrons of the tin atom to the chlorine atoms. Furthermore, it was revealed that there was a significant difference between the Sn-Cl bond of the hydrates and that of ammonium chlorostannate.

It is well-known that tin(IV) chloride forms various hydrates but their structures have not been determined by any means except the Raman spectra.1) Tin(IV) chloride and its hydrates are suitable for investigating the Sn–Cl bond, since the electronic structures of the tin and chlorine atoms can be investigated by means of the Mössbauer effect due to ^{119}Sn and the nuclear quadrupole resonance due to ^{35}Cl.

The molecular complexes of tin(IV) chloride with organic or inorganic compounds containing oxygen or nitrogen atoms have thus far investigated by means of NQR2,3) and the Mössbauer effect.4—8)

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However, the hydrates of tin(IV) chloride was investigated at the temperature of liquid nitrogen.[2,3,9] Only the pentahydrate $SnCl_4 \cdot 5H_2O$ has been investigated by means of the Mössbauer effect[6,10–16] at both the temperature of liquid nitrogen and room temperature. A variety of values have been reported for the isomer shift of the hydrate, ranging from 0.2 to 0.3 mm/sec with respect to tin(IV) oxide except for the value of 0.09 mm/sec observed by Lees and Flinn.[17] These authors observed a small quadrupole splitting for that hydrate, although others did not. Our value for the isomer shift of the hydrate is 0.275 mm/sec, while the value for $SnCl_4 \cdot 5D_2O$ is 0.300 mm/sec.

Brune and Zeil[1] investigated several hydrates of tin(IV) chloride, $SnCl_4 \cdot xH_2O$ (x=2, 3, 4, 5 and 8) and $SnCl_4 \cdot yD_2O$ (y=5 and 8) by Raman spectroscopy. They concluded from the spectra that chlorine atoms are arranged octahydrally around the central tin atom and that two of the hydrated water molecules occupy the *trans*-position, that is, the hydrate molecules possess the D_{4h} symmetry in the liquid state and in solution. This is consistent with the conclusion drawn from the NQR-frequencies in the solid state.

The molecular configuration described above will be ascertained in this paper. The ionic character of the Sn–Cl bonds increases with the number of water molecules in the hydrates, and the bond character of the Sn–Cl bond in a similar compound, such as ammonium chlorostannate, is different from those of the hydrates.

Experimental

Materials. The hydrate of tin(IV) chloride was prepared by mixing tin(IV) chloride and light or heavy water in a proper molar ratio and in a sealed tube, but attempts to prepare the dihydrate, $SnCl_4 \cdot 2D_2O$, were unsuccessful. Ammonium chlorostannate was prepared by a method reported previously.[18]

Measurements. The NQR-spectrometer used for measuring the ^{35}Cl resonance consisted of a superregerative oscillator, an amplifier, and a detector. The resonance frequencies were determined at both room temperature and the temperature of liquid nitrogen.

The Mössbauer apparatus employed was essentially the same as that described previously.[4] Tin(IV) oxide containing 0.6 mCi of ^{119m}Sn was used as the γ-radiation source; it was kept at room temperature. The hydrate of tin(IV) chloride was mounted as an absorber; for tin it was about 15 mg/cm^2 thick and was cooled with liquid nitrogen.

Results and Discussion

Nuclear Quadrupole Resonance. The hydrates, $SnCl_4 \cdot 2H_2O$, $SnCl_4 \cdot 3H_2O$, and $SnCl_4 \cdot 3D_2O$, have a single resonance line due to ^{35}Cl at both room temperature and at the temperature of liquid nitrogen. The pentahydrates, $SnCl_4 \cdot 5H_2O$ and $SnCl_4 \cdot 5D_2O$, have two resonance lines at room temperature. The resonance of the latter hydrates could not be measured at the temperature of liquid nitrogen because of the piezo effect which appeared on cooling. The resonance lines in the tetrahydrates, $SnCl_4 \cdot 4H_2O$ and $SnCl_4 \cdot 4D_2O$, could not be found. The NQR-frequencies and the ionic characteristics found for the rest of the hydrates

TABLE 1. THE NQR-FREQUENCIES DUE TO ^{35}Cl FOR THE HYDRATES OF TIN(IV) CHLORIDE AND THE IONIC CHARACTER

Hydrate	Resonace frequency, MHz		Ionic character[a] %
	77°K	293°K	
$SnCl_4 \cdot 2H_2O$	21.439	21.039	55
$SnCl_4 \cdot 3H_2O$	20.384	20.173	57
$SnCl_4 \cdot 5H_2O$		18.054 17.656	62
$SnCl_4 \cdot 3D_2O$	20.438	20.208	57
$SnCl_4 \cdot 5D_2O$		18.102 17.735	62

a) The percent ionic character was obtained by neglecting the double bond character and the asymmetry parameter.

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are summarized in Table 1. The ionic character is determined by neglecting the double-bond character and by estimating the *s*-electron character of the chlorine atom is 15%. As may be seen in Table 1, the NQR-frequency decreases with an increase in the number of water molecules; that is, the ionic character of the Sn–Cl bonds in the hydrates increases with the number of water molecules. In general, the hydrates of tin(IV) chloride with heavy water show slightly higher frequencies than those with light water. This result, however, shows no appreciable difference in the ionic character between the corresponding hydrates.

The atomic arrangement around the central tin atom in the dihydrates, $SnCl_4 \cdot 2H_2O$ and $SnCl_4 \cdot 2D_2O$, seems to be coordinated octahedrally by sp^3d^2-hybridization. If this is the case, the two water molecules must occupy either the *cis*- or the *trans*-position of an octahedron, as is shown in Fig. 1.

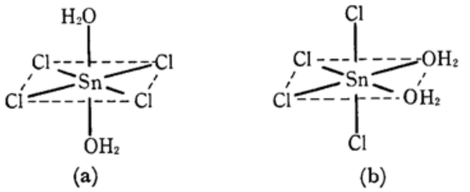

Fig. 1. The configuration of the dihydrate, $SnCl_4 \cdot 2H_2O$.

(a) *trans*-form (b) *cis*-form

From the fact that only a single NQR line was observed in the hydrates, the two water molecules may be considered to occupy the *trans*-position, since all the Sn–Cl bonds must be equivalent. Brune and Zeil suggested that the dihydrate takes the octahedral configuration in the liquid state.[1] Consequently, the D_{4h} symmetry of the dihydrate is preserved in the solid state.

The trihydrates, $SnCl_4 \cdot 3H_2O$ and $SnCl_4 \cdot 3D_2O$, also exhibit a single resonance line. Consequently, it may be assumed that two of the three water molecules are bonded to the central tin atom and occupy the *trans*-positions of the octahedron. The influence of non-coordinated molecules on the Sn–Cl bonds is quite significant, since the resonance frequency of the trihydrate, $SnCl_4 \cdot 3H_2O$, is considerably lower than that of the dihydrate, $SnCl_4 \cdot 2H_2O$, the difference being 1.055 MHz at the temperature of liquid nitrogen. The difference in ionic character between the two hydrates is 2%.

In the pentahydrates, the two resonance lines are situated close together; the difference between them is 0.398 MHz for $SnCl_4 \cdot 5H_2O$ and 0.367 MHz for $SnCl_4 \cdot 5D_2O$. This indicates the existence of two non-equivalent Sn–Cl bonds in the pentahydrates. The findings on the Raman spectra for the hydrates, $SnCl_4 \cdot xH_2O$ and $SnCl_4 \cdot yD_2O$, show that all the hydrates possess the D_{4h} symmetry with regard to the arrangement of the atoms bonded to the central tin atom in the liquid state. If the atomic configuration around the tin atom is the *cis*-form in the pentahydrates, the symmetry class must be C_{2v}. This contradicts the results of the Raman spectra. Consequently, it may be concluded that the small deviation in the resonance frequencies is not caused by the *cis*-form, but is brought about by the crystal field due to the three non-coordinated water molecules as well as the neighboring octahedrons.

In addition, the resonance frequencies of the pentahydrates, $SnCl_4 \cdot 5H_2O$ and $SnCl_4 \cdot 5D_2O$, are considerably lower than those of the dihydrate and trihydrates. Taking into account this lowing and the appearance of the two lines in the pentahydrate, the influence of the non-coordinated water molecules on the Sn–Cl bonds seems to be significant. On the other hand, the resonance frequencies of all the hydrates are much lower than those of pure tin(IV) chloride, 24.294, 24.226, 24.140, and 23.179 MHz at 77°K. The four chlorine atoms are spatially directed to the corners of a distorted tetrahedron in the crystal state, forming sp^3-hybrid orbitals, although Sn–Cl bonds have an ionic character of 48% if the double-bond character is disregarded. According to Haas[3] and Schawlow,[19] the ionic character is estimated to be 41 and 38% respectively. When tin(IV) chloride is hydrated, the atoms around the tin atom are arranged almost octahedrally, forming sp^3d^2-hybrid orbitals quite ionic in character. The *d*-electrons necessary for this hybridization are brought from the lone-pair electrons of the oxygen atoms of water molecules. The Sn–Cl bonds in the hydrates are more ionic than those of pure tin(IV) chloride, since the resonance frequencies of the former are lower than those of the latter.

Mössbauer Effect. The results of the Mössbauer effect are summarized in Table 2. The values of the isomer shift at the temperature of liquid nitrogen are shown with respect to tin(IV) oxide. These values fall in a range from 0.275 to 0.350 mm/sec and decrease with an increase in the number of water molecules in the same way as do the NQR-

TABLE 2. THE MÖSSBAUER EFFECT DUE TO ^{119}Sn OF THE HYDRATES OF TIN(IV) CHLORIDE

Hydrate	δ,[a] mm/sec	Hydrate	δ,[a] mm/sec
$SnCl_4 \cdot 2H_2O$	0.350		
$SnCl_4 \cdot 3H_2O$	0.325	$SnCl_4 . 3D_2O$	0.350
$SnCl_4 \cdot 4H_2O$	0.300	$SnCl_4 \cdot 4D_2O$	0.330
$SnCl_4 \cdot 5H_2O$	0.275	$SnCl_4 \cdot 5D_2O$	0.300

a) δ is the isomer shift at liquid nitrogen temperature relative to the source of SnO_2 crystal. The accuracy is ±5% in the measurement.

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frequencies. It may be noted again that the values for the hydrates of light water are slightly smaller than those of the hydrates of heavy water, but this fact will not be taken into account. From the tendency of the isomer shift, it is evident that the *s*-electron density at a tin nucleus decreases with an increase in the number of water molecules. The decrease in the *s*-electron density is caused by either losing *s*-electrons directly to other atoms or by receiving *p*- and/or *d*-electrons, the shielding effect of which decreases the *s*-electron density indirectly. The latter theory would mean an increase in the covalent character, and this is in conflict with the NQR results. Therefore, the tin atom is becoming a complete stannic ion with an increase in the number of water molecules. The increase in the ionic character results in a decrease in the covalent character and bring about a variation in the shielding effect.

According to the NQR results, the increase in the number of water molecules causes an increase in the electron density around the chlorine nucleus. Supposing that the *s*-electrons in the tin atom move to the chlorine atoms, the *s*-electron density at the tin nucleus should decrease, and hence the isomer shift should be diminished. This interpretation fits well with the findings on the Mössbauer effect.

The $(x-2)$ non-coordinated water molecules in the hydrates, $SnCl_4 \cdot xH_2O$, affect the nature of the Sn–Cl bonds significantly. However, these molecules do not take part directly in the decrease in the electron density at the tin nucleus, since they are located outside the octahedron centered about the tin nucleus. They seem to affect the tin atom through the coordinated chlorine atoms and/or water molecules, which may form hydrogen bonds with one another.

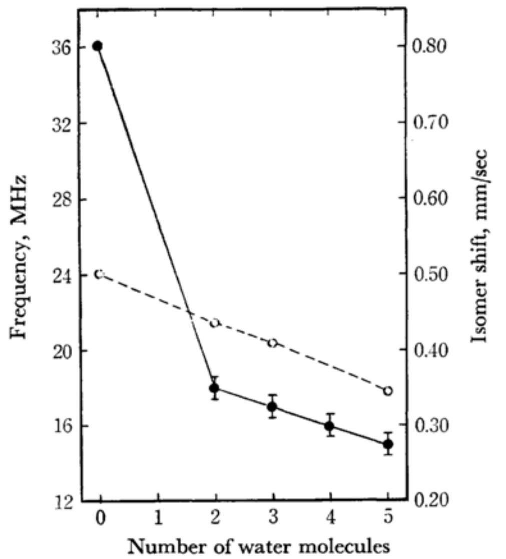

Fig. 2. The relation between the number of water molecules and the NQR-frequency or the isomer shift for the hydrate $SnCl_4 \cdot xH_2O$ at 77°K.

○: NQR-frequency ●: isomer shift

Figure 2 shows how the isomer shift and the NQR-frequency vary with the number of water molecules in the hydrate; the literature values of the pure tin(IV) chloride, 0.7,[6] 0.78,[20] 0.8,[7] 0.85,[13] and 0.9[15] mm/sec, have been averaged. It is apparent that there is a sudden decrease in the isomer shift from $x=0$ to $x=2$. This seems to be attributable to the shielding due to the *d*-electrons and to the increased ionic character of the tin atom. The gradient of the curve of the NQR-frequency *versus* the number of water molecules from $x=0$ to $x=2$ is almost the same as that from $x=2$ to $x=5$. The NQR-frequency of pentahydrates at the temperature of liquid nitrogen was roughly estimated from the value at room temperature. Taking the gradual decrease in the NQR-frequency into consideration, the sudden decrease of the isomer shift from $x=0$ to $x=2$ can be attributed to the shielding effect due to the *d*-electrons.

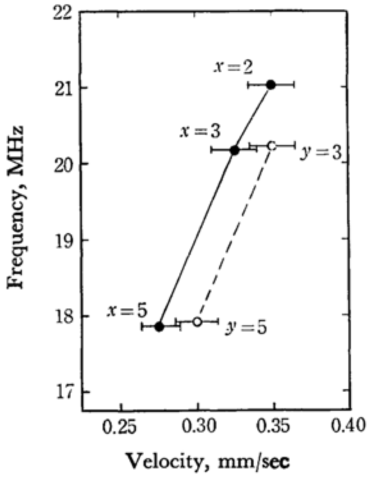

Fig. 3. The isomer shift at 77°K *versus* the NQR-frequency at 293°K for the hydrates, $SnCl_4 \cdot xH_2O$ and $SnCl_4 \cdot yD_2O$.

Figure 3 shows that the NQR-frequency increases almost linearly with the isomer shift in the two series of hydrates, $SnCl_4 \cdot xH_2O$ and $SnCl_4 \cdot yD_2O$. From this relation it may be concluded that the *s*-electrons of the tin atom move to the chlorine atoms. In other words, the less the isomer shift due to ^{119}Sn, the more ionic is the Sn–Cl bond. The resonance frequencies of the tetrahydrates, $SnCl_4 \cdot 4H_2O$ and $SnCl_4 \cdot 4D_2O$, which could not be observed in the present investigation are assumed

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to be as follows: The frequency for $SnCl_4 \cdot 4H_2O$ lies in the immediate neighborhood of 19 MHz, while that for $SnCl_4 \cdot 4D_2O$ is about 0.05 MHz higher than this value.

Ammonium hexachlorostannate, $(NH_4)_2SnCl_6$, shows two resonance lines at the temperature of liquid nitrogen, *i.e.*, 15.61 and 15.65 MHz. The value of the isomer shift for this compound is 0.475 mm/sec with respect to tin(IV) oxide in our experiment, although its literature values are 0.3,[15] 0.40,[14] 0.42,[16] 0.49,[21] and 0.50.[13] The crystal structure was analyzed by X-ray diffraction.[22] The tin atom is surrounded octahedrally by six equivalent chlorine atoms, but the NQR results show that two groups of slightly different bonds exist. The atomic arrangement around the tin atom in the hydrates can be obtained by substituting water molecules for chlorine in the hexachlorostannate ion. The NQR-frequencies reveal that the chlorine atoms in the ammonium hexachlorostannate are more ionic than that in the dihydrate. On the other hand, the Mössbauer effect reveals that the *s*-electron density at the tin nucleus in the chlorostannate is greater than in the dihydrate. Consequently, the tin atom is not as ionic as we had expected, although anions are coordinated to the tin atom. In other words, the Sn–Cl bonds in the chlorostannate are quite covalent. The conclusion that the more ionic the chlorine atoms, the more ionic is the tin atom does not apply to ammonium hexachlorostannate. $[SnCl_6]^{2-}$ ion has two minus charges distributed among the six chlorine atoms almost uniformly, while each chlorine atom has a charge of $-1/3$. Assuming that most of these charges participate in the ionic bond with an ammonium ion, the charges do not have a great influence upon the tin atom. This assumption is consistent with the NQR results and the Mössbauer effect.

The Sn–O bond is expected to be more ionic than the Sn–Cl bond in the dihydrate since the oxygen atom is more electronegative than the chlorine atom, and the isomer shift due to the ^{119}Sn of the dihydrate is smaller than those of $M^I_2SnCl_6$ or $M^{II}SnCl_6$ (M^I=H, K, NH_4; M^{II}=Mg, Ca, Ni), which are reported to be 0.42—0.49 mm/sec.[10,20]

The authors wish to express their thanks to Miss T. Shimazu for her help in checking some of the results.

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[22] R. G. Dickinson, *J. Am. Chem. Soc.*, **44**, 276 (1922). Ammonium chlorostannate is the crystal of the cubic system with the space group O_h^5 and the lattice constant a_0=10.05 Å. The unit cell contains four molecules and the bond length of the Sn–Cl bond is 2.46 Å.