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Temperature Dependence of ^{35}Cl Nuclear Quadrupole Resonance Frequencies and Hydrogen Bonding in Some Metal(II) Hexachlorostannate(IV) Hexahydrates

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Synopsis. The temperature dependences of ^{35}Cl NQR frequencies were observed over a fairly wide range of temperature for $MSnCl_6 \cdot 6H_2O$ [M(II)=Mg, Ca, Mn, Co, Ni] forming isomorphous crystals ($R\bar{3}$) at room temperature. These complexes yielded unusual ^{35}Cl NQR temperature dependence curves showing a positive temperature coefficient. This can be attributed to the existence of Cl···H–O type weak hydrogen bonds.

The ^{35}Cl NQR frequencies of $MSnCl_6 \cdot 6H_2O$ [M(II)= Mg, Ca, Zn, Cd, Mn, Co, Ni] were reported by Graybeal et al.[1] and independently by Brill et al.[2] For the Ca(II) and Mg(II) salts, the temperature dependence of ^{35}Cl NQR frequencies was studied and the positive temperature coefficients were found. Although Graybeal et al.[1] attributed the unusual positive temperature coefficient to the π bond character of Sn–Cl bonds,[3] their explanation seems to be implausible because no positive temperature coefficients were observed for several R_2SnCl_6 type complexes.[4] As already suggested by one of the present authors,[5] the observed positive coefficient is attributable to hydrogen bonds formed between chloride ligands and water molecules.

Recently, Kitazume et al.[6] determined the crystal structure of $CaSnCl_6 \cdot 6H_2O$ by single-crystal X-ray diffraction and NQR Zeeman effect measurements. From these studies, they concluded that the anomalous temperature dependence of ^{35}Cl NQR frequencies is due to the hydrogen bonding effect as already pointed out.[5] In order to obtain further information about the suggested mechanism which gives rise to the positive temperature coefficient, the temperature dependence study of ^{35}Cl NQR frequencies was carried out for some hexachlorostannates(IV) crystallized with hexahydrated divalent counter cations.

Experimental

Measurements of ^{35}Cl NQR frequencies were performed above 77 K by use of a modified Dean-type spectrometer described elsewhere.[7] For $NiSnCl_6 \cdot 6H_2O$, the measurements were extended down to 4.2 K by employing a homemade cryostat. Temperatures were determined using a chromel vs. alumel and a chromel vs. gold (0.03% iron) thermocouple above and below 77 K, respectively, within the accuracy of ±1 K.

The all complexes studied were prepared according to the method described in literature.[2] Deuterated compounds, $CaSnCl_6 \cdot 6D_2O$, $CoSnCl_6 \cdot 6D_2O$, and $NiSnCl_6 \cdot 6D_2O$, were synthesized in a dry box using deuterated hydrochloric acid and $SnCl_4$. The extent of deuteration (>95%) was checked by means of Hitachi EPI-G and 345 infrared spectrometers.

Results and Discussion

X-Ray powder patterns recorded for the complexes studied could be well interpreted by use of the reported lattice constants with the space group of $R\bar{3}$.[6,8] Only one ^{35}Cl NQR line was found in each complex studied in agreement with the crystal structure already reported. The frequencies determined at four temperatures are listed in Table 1.

The NQR frequencies observed at room temperature for the present complexes except for the Ni(II) salt agree well with the reported values.[1,2] For the Ni(II) salt, Graybeal et al.[1] reported two very closely spaced ^{35}Cl NQR frequencies. The appearance of multiplet structure for the resonance line of the Mg(II) and Ca(II) salts at lower temperatures was also pointed out by the same authors. However, only a broad single line could be observed for the Ni(II) salt at all temperatures studied and for the Mg(II) and Ca(II) salts even at lower temperatures. Although the existence of phase transitions above room temperature had been reported for the Ca(II) salt,[6] no heat anomaly was observed in the present DTA measurements up to the fade-out temperature of the NQR signal (≈390 K).

The Mg(II) and Ca(II) salts gave a very broad signal at 77 K. With increasing temperature, the signals became gradually sharp. A broad and intense ^{35}Cl NQR signal was observed for the remaining complexes at 77 K and for the Ni(II) salt even at 4.2 K. This means that no saturation effect was observed for the Ni(II) salt because of the presence of paramagnetic ions in the crystal. With increasing temperature, the resonance frequencies of these paramagnetic com-

Table 1. ^{35}Cl Nuclear Quadrupole Resonance Frequencies in Some Hexachlorostannates(IV) Crystallized with Hexahydrated Divalent Cations Observed at Several Temperatures

Compound	Frequency(±0.002)/MHz			
	77 K	193 K	293 K	382 K
$MgSnCl_6 \cdot 6H_2O$	15.82_4 b)	15.820 a)	15.834	15.861
$CaSnCl_6 \cdot 6H_2O$	15.94_1 b)	15.902 a)	15.902	15.90_6 b)
$CaSnCl_6 \cdot 6D_2O$	15.906 a)	15.897 a)	15.903	15.90_9 b)
$MnSnCl_6 \cdot 6H_2O$	15.733 a)	15.739	15.770	15.813
$CoSnCl_6 \cdot 6H_2O$	15.694 a)	15.706	15.750	15.808
$CoSnCl_6 \cdot 6D_2O$	15.670 a)	15.697	15.750	15.813
$NiSnCl_6 \cdot 6H_2O$	15.670 a) (15.675 a)) c)	15.681	15.720	15.773
$NiSnCl_6 \cdot 6D_2O$	15.648 a)	15.671	15.718	15.781

a) ±0.005 MHz. b) ±0.010 MHz. c) at 4.2 K.

plexes increased rather rapidly.

For $CoSnCl_6 \cdot 6D_2O$, two ^{35}Cl resonance lines in place of a single line could be observed at first. The complex freshly prepared yielded two broad resonance lines at 15.75 and 15.90 MHz at room temperature. Immediately after the first annealing at ca. 450 K, only the high frequency line could be observed. However, no resonance could be detected with the above same sample after six months. The crystals which gave only the strong and sharp low-frequency line was obtained by the second annealing at ca. 410 K. This crystalline state showing the low-frequency line was stable and the high-frequency line could not be detected any more throughout the measurements of the temperature dependence of NQR frequencies as well as even after six months. For $CoSnCl_6 \cdot 6D_2O$, the data of this crystalline state are indicated in Table 1 and in Fig. 1. No such anomaly due to annealing could be observed for $CoSnCl_6 \cdot 6H_2O$ and the other complexes studied. A similar phenomenon has been also observed for $MnPtCl_6 \cdot 6D_2O$.[7]

It is interesting to note that the resonance frequency observed at 77 K for these complexes decreases in the order of Ca(II), Mg(II), Mn(II), Co(II), and Ni(II), which approximately coincides with the order of increasing electronegativities.[9,10] According to the X-ray analysis of $CaSnCl_6 \cdot 6H_2O$, each chloride ion has three neighboring hydrogens which exist nearly on the plane including the chloride ion and perpendicular to the Sn–Cl bond axis. Let the bond axis be the z axis. Then, the three hydrogens are nearly on the xy plane. Since each hydrogen of water molecules is polarized positively, the hydrogen bearing a fractional positive charge will draw out the $3p_x$ or $3p_y$ electrons of the chloride ligand to the higher orbitals. This means that the $3p_x$ and/or $3p_y$ electron cloud will be expanded and the unbalanced p electrons of the chloride ligand decrease leading to a decrease of the ^{35}Cl NQR frequency. The lone-pair electrons of water molecules attached to a more electronegative divalent cation may be drawn out more strongly to the cation resulting in an increase of a fractional positive charge on the hydrogens. In other words, those water molecules form stronger hydrogen bonds with the chloride ligands at lower temperatures, where the motion of water molecules and/or complex anions can be neglected. This is an explanation of the correlation between the ^{35}Cl NQR frequencies observed at 77 K and the electronegativity of the divalent cations in these complexes.

With increasing the temperature from ca. 100 K, the ^{35}Cl NQR frequency of the all complexes except for the Mg(II) and Ca(II) salts increased and also its temperature coefficient became larger. This effect is remarkable especially for the Mn(II), Co(II), and Ni(II) salts which yield lower NQR frequencies at lower temperatures as can be seen in Fig. 1. The Mg(II) salt showed a maximum of the NQR frequency at ca. 450 K, above which temperature the frequency decreased with increasing temperature. The NQR frequency of the Ca(II) salts decreased with increasing temperature above 77 K. However, $CaSnCl_6 \cdot 6H_2O$ yielded a broad minimum and a maximum at ca. 250 and ca. 380 K, respectively, while $CaSnCl_6 \cdot 6D_2O$ yielded them at ca. 170 and 385 K, respectively. These results can be explained as follows.

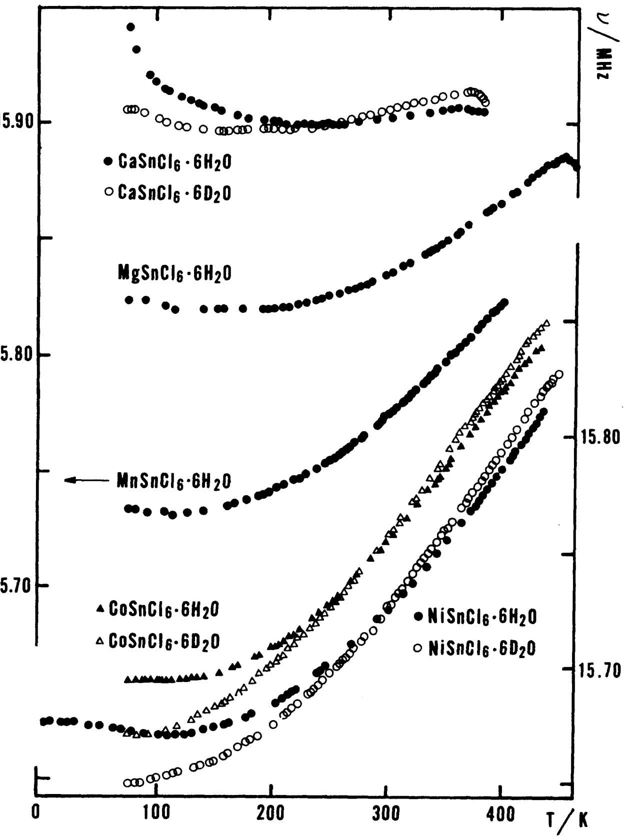

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in the crystals of $MSnCl_6 \cdot 6H_2O$ [M(II): Mg, Ca, Mn, Co, Ni] and $MSnCl_6 \cdot 6D_2O$ [M(II): Ca, Co, Ni] observed above 77 K. For $NiSnCl_6 \cdot 6H_2O$, measurements were extended down to 4.2 K.

At first, we discuss about the above results only on the usual ^1H hydrated complexes. With increasing temperature, the motions of water molecules, which are mainly librational motions are thought to be excited and the hydrogen bonding can be considered to be weakened gradually. This leads to an increase of the NQR frequency for the present type of hydrogen bonding.[5,11] For the Mn(II), Co(II), and Ni(II) complexes, the effect due to the weakening of hydrogen bonding prevails over the normal Bayer effect[12] yielding a positive temperature coefficient up to each fade-out temperature of the NQR frequencies. For the Mg(II) salt, the former effect dominates against the latter below the maximum temperature whereas the latter does above the temperature. The Ca(II) salts probably having the weakest hydrogen bonds among the present complexes show the smallest contribution to the temperature dependence from the hydrogen-bond effect. At high temperatures, the resonance frequencies of these complexes seem to converge upon ca. 15.85 MHz. This is considerably large among various complexes having $[SnCl_6]^{2-}$ ions ever studied at room temperature[2,4] and may be the resonance frequency of the complex anion crystallized with large cations. The cation size effect in complexes was already discussed.[13]

For the deuterated analogs of the Ca(II), Co(II), and Ni(II) complexes, the temperature dependence of ^{35}Cl NQR frequencies was also studied. In these complexes, it was commonly observed that the resonance frequencies determined for each deuterated analog at lower temperatures were smaller than those of the corresponding protonated complex. However, each deuterated analog showed slightly larger NQR frequencies at higher temperatures than the corresponding protonated one. At 77 K, the frequency difference between the deuterated and protonated analogs of each kind is fairly large amounting to 20—30 kHz. The above isotope effect detected on the ^{35}Cl NQR frequencies of these complexes can be understood as described below.

Since the amplitude of the librations and/or the frequency of the reorientational motions of coordinated water molecules can be expected to be reduced by deuteration, the motionally averaged distance $<r_{\mathrm{H\cdots Cl}}>$ may become longer than the $<r_{\mathrm{D\cdots Cl}}>$.[14] Therefore, the ^{35}Cl NQR frequency in crystals having hydrogen bonds of the present type decreases by deuteration at lower temperatures where only low-frequency vibrations such as librations are considered to affect the NQR frequency. At higher temperatures where librations are well excited, however, the anharmonicity of the stretching vibration of water molecules appears as the most important origin of the isotope effect. Owing to the anharmonicity of the interatomic potential, the distance $r_{\mathrm{X\cdots Y}}$ is assumed to be elongated by deuteration in a hydrogen bond system X–H···Y.[15] For this case, the NQR frequency of the present complexes is expected to increase by deuteration as really observed at high temperatures. This isotope effect was already pointed out from the ^{35}Cl NQR study to exist in some compounds involving O–H···Cl type hydrogen bonds.[16]

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