Motion of Water Molecules and Hydrogen Bonds in Zinc Hexachlorostannate(IV) Hexahydrate as Studied by ^{1}H NMR and ^{35}Cl NQR *

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The ^{1}H NMR spin-lattice relaxation time T_1, ^{35}Cl NQR frequency v_Q, and ^{35}Cl NQR spin-lattice relaxation time T_{1Q} of $[Zn(H_2O)_6][SnCl_6]$ (zinc hexachlorostannate(IV) hexahydrate) have been measured at temperatures between 77 and 350 K. The NQR spin echo signal with $v_Q = 15.689$ MHz at 77 K showed a positive temperature coefficient attributable to O-H−Cl type H-bonds in the crystal. v_Q at 77 K is strongly correlated with the electronegativity χ_M of the metal M in the series of stannates $[M(H_2O)_6][SnCl_6]$ (M = Mg, Ca, Mn, Co, Ni, Zn). A T_1 minimum observed for the Zn salt is ascribed to 180° flips of water molecules with an activation energy of 20 kJ mol^{-1}. The motion is influenced by repulsive forces among the water molecules within a cation rather than by attractive forces between the H-bonded H and Cl atoms. T_{1Q} proved to be mainly governed by lattice vibrations, weakly modulated by the fluctuating electric field gradient caused by the 180° flip motions.

Key words: ^{1}H NMR spin-lattice relaxation, ^{35}Cl NQR frequency, ^{35}Cl NQR spin-lattice relaxation, H-bonding, Electronegativity.

Introduction

Metal hexachlorostannate(IV) hexahydrates $[M(H_2O)_6][SnCl_6]$ (M = Mg, Ca, Mn, Co, Ni) have been extensively studied by NQR. The ^{35}Cl NQR frequencies v_Q in these complexes show positive temperature coefficients [1–4]. The lowering of v_Q at low temperatures has been attributed to the formation of O-H−Cl H-bonds [2, 3]. Recently, the understanding of the dynamic properties of the H-bonds has been deepened through studies on the motions of water molecules, hydrated cations, and complex anions by pulsed NMR and NQR techniques applied to the Ca [5], Mg [6–9], and Ni [7, 8] salts. However, no clear relations have been obtained between the nature of the molecular motions and the H-bonds. In order to further elucidate the nature of the molecular motions related to the H-bonds in this series of stannates we have extended the NMR and NQR works to diamagnetic $[Zn(H_2O)_6][SnCl_6]$ (zinc hexachlorostannate(IV) hexahydrate).

Experimental

A home made pulsed spectrometer [9] was employed for the determination of the ^{1}H NMR spin-lattice relaxation time T_1, the ^{35}Cl NQR frequency v_Q, and the ^{35}Cl NQR spin-lattice relaxation time T_{1Q}. Measurements of T_1 and T_{1Q} were performed with the pulse sequences 180°-τ-90° and 180°-τ-90°-τ_e-180°, respectively, where τ_e was 200 µs throughout the measurements. An exponential decay of the signal amplitude as a function of τ was observed for T_1 and T_{1Q} at all temperatures studied. The second moments M_2 of the ^{1}H NMR absorption spectra were determined by using a JEOL JNM-MW-40S NMR spectrometer operated at 40 MHz. The sample temperatures were estimated to be accurate within ± 1 K. $[Zn(H_2O)_6][SnCl_6]$ was prepared in a similar as in [3, 10]. The NQR signal for the Zn salt had not been observed by a cw spectrometer [3]. In the present study, a polycrystalline sample of the Zn salt was pulverized in a dry atmosphere to avoid spurious signals. The X-ray powder patterns of Zn and Ni salts were recorded on a model 2012 diffractometer from Rigaku Denki Co. equipped with a copper anticathode.

Results

¹H NMR T_1 and M_2

The temperature dependence of ¹H NMR T_1 for [Zn(H₂O)₆] [SnCl₆] yielded the typical BPP curves at the Larmor frequencies 19.5 and 27 MHz as shown in Figure 1. At these frequencies, T_1 minima and T_1 minimum temperatures were determined as follows: 232 ms, 188 K (19.5 MHz); 332 ms, 193 K (27 MHz). T_1 was independent of the Larmor frequency at the higher temperature side of the minima and was dependent on the square of the Larmor frequency at the lower temperature side. The temperature dependence of ¹H NMR M_2 is given in Figure 2. M_2 was nearly constant (21 ± 2 G²) above 200 K and showed a slight increase below 200 K.
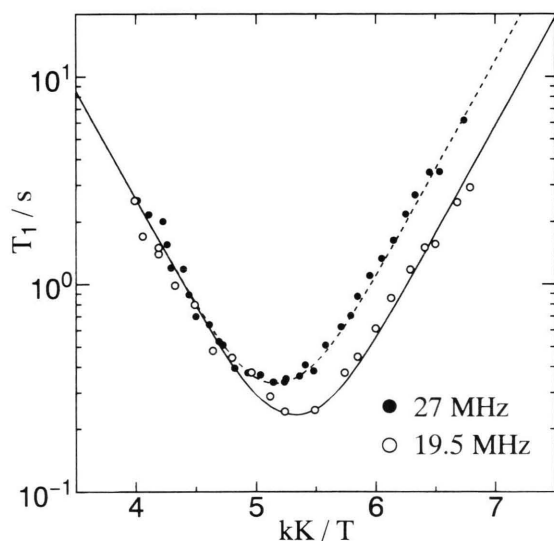
³⁵Cl NQR v_Q and T_{1Q}

At 290 K a single ³⁵Cl NQR spin echo signal arising from the Zn salt was observed at 15.735 MHz, indicating that all chlorine atoms in the crystal are equivalent (A ³⁷Cl NQR signal was observed at 12.402 MHz). This value of v_Q occurs in a narrow frequency range covered by the series of [M(H₂O)₆] [SnCl₆] having isomorphous crystal structure [3]. Graybeal et al. [1] reported the appearance of a doublet NQR line around 15.74 MHz on a superregenerative spectrometer. Our X-ray powder patterns have shown that the Zn salt is isomorphous with Ni salt [11] and belongs to the space group R$\bar{3}$ [2] with the lattice constants $a = 10.65$ and $c = 10.98$ Å as a hexagonal cell. With this crystal symmetry all chlorine atoms are equivalent, supporting the validity of our present NQR experiments.

The ³⁵Cl NQR frequencies v_Q are plotted against temperature in Figure 3. In agreement with very similar temperature dependence of other salts in the series, v_Q occured at frequencies between those of the Co and Ni salts at all temperature studied [3], until the NQR line disappeared at the melting point of ca. 340 K. Open circles in Fig. 4 show the temperature dependence of ³⁵Cl NQR T_{1Q} in the Zn salt. T_{1Q} depends almost linearly on T between 100 and 330 K but is accompanied with a shallow and broad dip around 180 K.

Fig. 1. Temperature dependences of ¹H NMR spin-lattice relaxation time T_1 for [Zn(H₂O)₆] [SnCl₆] at the Larmor frequencies of 19.5 and 27 MHz. The solid and broken lines represent the least squares fitted BPP curves at 19.5 and 27 MHz, respectively.
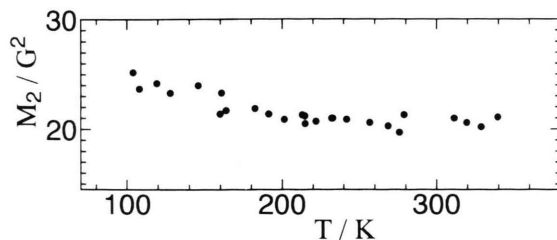

Fig. 2. Temperature dependence of ¹H NMR second moment M_2 for [Zn(H₂O)₆] [SnCl₆].
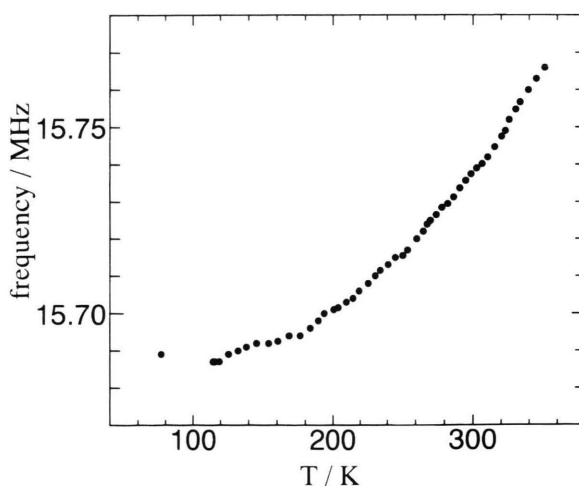
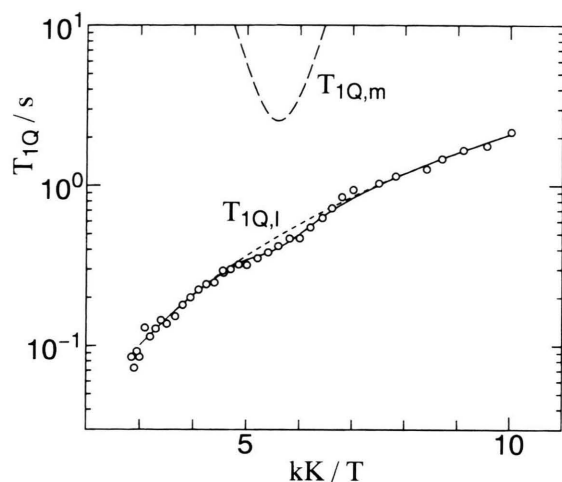Fig. 3. Temperature dependence of ³⁵Cl NQR frequency v_Q for [Zn(H₂O)₆] [SnCl₆].

Fig. 4. Temperature dependence of ^{35}Cl NQR spin-lattice relaxation time T_{1Q}. The observed T_{1Q} values are indicated by the open circles. The broken lines $T_{1Q,l}$ and $T_{1Q,m}$ show the contributions to T_{1Q} from the lattice vibration and from the EFG modulation by the 180° flips of water molecules, respectively. The solid line represents the calculated overall T_{1Q}. These lines are expressed in (3–5).

Discussion

Motion of the Water Molecules

The observed ^{1}H NMR M_2 and T_1 for the Zn salt are similar to those for [Mg(H$_2$O)$_6$] [SnCl$_6$] [9]. The intramolecular contribution to the proton dipole-dipole interaction $M_2 = 21 \pm 1$ G^2 is calculated on an assumption of 160 ± 1 pm as the interprotonic distance within a water molecule in agreement with the observed value above 200 K (Figure 2). The interprotonic distance in a water molecule ranges from 156 to 161 pm in several hydrated crystals [12]. The observed $M_2 \sim 25$ G^2 at 100 K, therefore, may contain the intermolecular contribution as well. When the water molecules begin the 180° flips, the intermolecular interactions average out to zero, so that only the intramolecular contribution remains as observed at present above 150 K. Since the 180° flips fluctuate the intermolecular dipole interactions, the motions are also responsible for the spin-lattice relaxation. The observed T_1 curves (Fig. 1), assignable to the 180° flips, are expressed by the equations [13]

$$1/T_1 = C[\tau/(1 + \omega^2 \tau^2) + 4\tau/(1 + 4\omega^2 \tau^2)] \quad (1)$$

and

$$\tau = \tau_0 \exp(E_a/RT), \quad (2)$$

where C, ω, and τ represent the motional constant, the angular Larmor frequency of the proton, and the correlation time, respectively. It is assumed that τ obeys the Arrhenius relation (2). The broken and the solid lines in Fig. 1 are the best fits of the data with (1) and (2) by using the parameters τ_0 and E_a listed in Table 1 and $C = 3.59 \times 10^8$ s^{-2}. The observed E_a for the 180° flips of water molecules in the Zn salt is nearly the same as in the Mg salt, while E_a for Ca salt is lower (Table 1). Figure 5 shows the relationship between E_a of the 180° flips and the ionic radius (Pauling scale) of the metal M^{2+} ion [14]. The smaller the M^{2+} ion, the higher is E_a for the 180° flips. With decreasing ionic

Table 1. Motional modes and parameters for [M(H$_2$O)$_6$] [SnCl$_6$] (M = Mg, Ca, Ni, and Zn).

| Compound	$E_a/$ kJ mol^{-1}	$\tau_0/$s	Motional mode	References
Mg	21	1.2×10^{-14}	H$_2$O 180° flips	[9]
	95	6.4×10^{-20}	Cation (C_3 or C_4)	[6]
	116	1.6×10^{-21}	Cation (isotropic)	[6]
	115	3.5×10^{-18}	Anion (reorientation)	[6]
Ca	13.7	1.5×10^{-13}	H$_2$O 180° flips	[5]
	38.1	1.8×10^{-13}	Cation (C_3 or C_4)	[5]
	48	2.0×10^{-14}	Cation (isotropic)	[5]
	29.5	$\sim 10^{-7}$	Anion (reorientation)	[5]
Ni	44	8.6×10^{-17}	Cation (C_3 or C_4)	[8]
	52	9.9×10^{-17}	Cation (isotropic)	[8]
	86	7.5×10^{-14}	Anion (reorientation)	[8]
Zn	20 ± 1	1.4×10^{-14}	H$_2$O 180° flips	
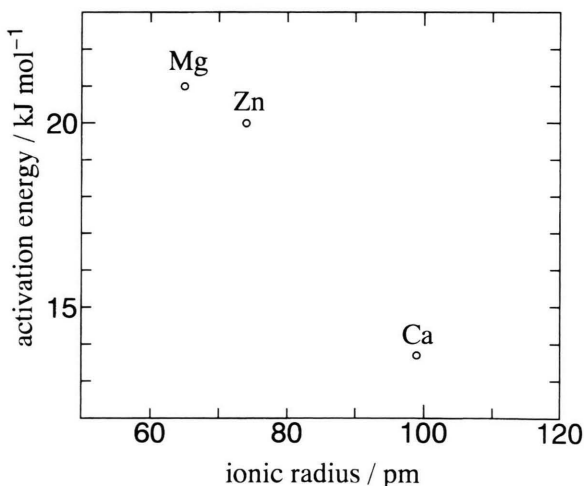
Fig. 5. Relation between the ionic radius of M^{2+} ions and the activation energy E_a for the 180° flips of the water molecules coordinated to M^{2+}.

radius, the distance between the neighboring water molecules within a hydrated cation is reduced. The observed linear relationship between E_a and the ionic radius, therefore, suggests that E_a is mainly influenced by the repulsive forces among the water molecules within a hydrated cation.

Strength of the Hydrogen Bonds

The ^{35}Cl NQR frequencies v_Q for [Zn(H$_2$O)$_6$][SnCl$_6$] yielded a positive temperature coefficient. Such positive temperature coefficients of v_Q in various compounds containing NH$_4^+$ ions have been interpreted in terms of breaking of H-bonds caused by the motion of NH$_4^+$ ions [15–19]. It has been suggested that in the case of [M(H$_2$O)$_6$][SnCl$_6$], the positive temperature coefficients of v_Q are attributable to the weakening of the O–H–Cl H-bonds caused by molecular motions of water molecules [2–5, 17]. The present Zn salt shows a similar temperature dependence of v_Q with that for other [M(H$_2$O)$_6$][SnCl$_6$] (M = Mg, Ca, Mn, Co, Ni) [3]. At low temperatures, the influence of the molecular motion on v_Q is relatively small (τ^{-1} for the 180° flips is smaller than v_Q) so that the contribution to the EFG at the chlorine from the H-bonded hydrogen is important. The hydrogen interacts electrostatically with the lone pair electrons of the chlorine atom causing polarization of the chlorine atoms to lower v_Q at low temperatures as observed for [M(H$_2$O)$_6$][SnCl$_6$] [3]. Estimates of τ for the 180° flips by using the parameters listed in Table 1 show that τ^{-1} becomes comparable to v_Q at ca. 160 K, above which temperature a sharp increase of v_Q is observed (Figure 3). The positive temperature coefficient observed for the present Zn salt is, therefore, attributable to the breaking of the H-bonds caused by the 180° flips of water molecules.

In the series of [M(H$_2$O)$_6$][SnCl$_6$], v_Q shows a tendency to converge around 15.85 MHz near 400 K [3]. Therefore we assume that v_Q at 77 K has a close relation to the relative strength of the H-bonds in these complexes. A plot of the reported [3] and newly determined v_Q at 77 K for [M(H$_2$O)$_6$][SnCl$_6$] against the electronegativity (Allred-Rochow scale) χ_M of M [20] gives rise to a good correlation, as shown in Figure 6. Smaller values of χ_M will induce larger positive charges on the hydrogens because the total charge +2 on a whole hydrated cation will be preserved irrespective of the kind of M in these complexes. A larger positive charge on hydrogens will have the stronger effect on the polarization of chlorine and will lower v_Q to a larger extent. In the present type of the crystals, v_Q at 77 K offers a good measure for the strength of the H-bonds. For the 180° flips of the water molecules, E_a has been determined on the diamagnetic Mg and Ca salts (Table 1). Including E_a of the Zn salt and E_a of the various complexes for other motional modes listed in Table 1, no clear correlation can be observed between E_a and the strength of the H-bond. The magnitude of E_a for the 180° flips is not concerned with the breaking of the H-bonds, instead it is strongly related to the rotational hindrance among the water molecules within a cation.
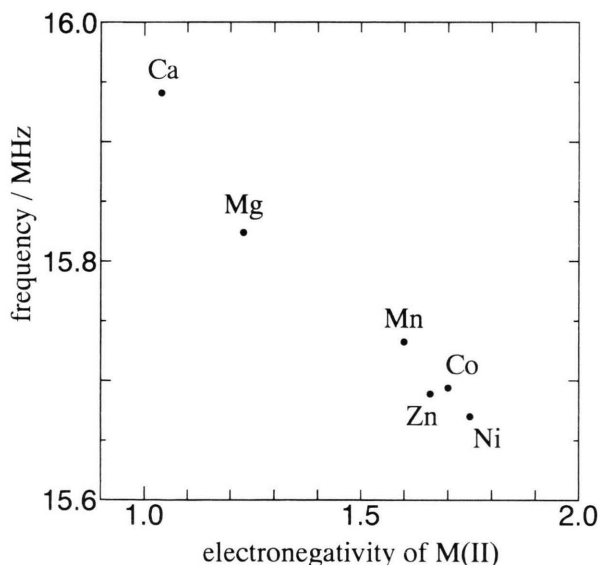
The Symmetry of the Axis of the 180° Flips of Water Molecules

The temperature dependence of T_{1Q} for the Zn salt (Fig. 4) is attributable to the EFG fluctuation caused by the lattice vibration involving the chlorine nuclei ($T_{1Q,1}$), and by the 180° flips of water molecules ($T_{1Q,m}$) [7]:

$$T_{1Q}^{-1} = T_{1Q,1}^{-1} + T_{1Q,m}^{-1}. \tag{3}$$

The first term is given as

$$T_{1Q,1}^{-1} = a\,T^n, \tag{4}$$

Fig. 6. Relation between the electronegativity χ_M of the metal M and ^{35}Cl NQR frequency v_Q at 77 K for [M(H$_2$O)$_6$][SnCl$_6$] (M = Mg, Ca, Mn, Co, Ni, and Zn).

where, a represents a constant and usually $n \sim 2$. The second term has the effect of modulating EFG and has the following form for a nucleus with $I = 3/2$ and asymmetry parameter $\eta = 0$:

$$T_{1Q,m}^{-1} = (1/3)(q'/q)^2 [4\pi^2 v_Q^2 \tau/(1 + 4\pi^2 v_Q^2 \tau^2)], \quad (5)$$

where q'/q is a fluctuating fraction of EFG caused by the 180° flips and τ is the correlation time as defined in (2). If we employ τ as specified by E_a and τ_0 in Table 1, the observed T_{1Q} dip around 180 K is explained satisfactorily, as shown with the solid line (3) in Figure 4. The parameters have been determined as follows: $a = 2.30 \times 10^5$, $n = 2.52$, $q'/q = 1.1 \times 10^{-4}$, $v_Q = 15.6870 \times 10^6$. These parameters are close to those reported for the Mg salt [7]. The small but nonzero magnitude of the fluctuation in EFG, arising from the 180° flips, suggests that the water molecules flip about the pseudo C_2 and not the C_2 axes [8].

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