

Temperature Dependence Studies of ^{35}Cl NQR Frequencies in Magnesium and Nickel Hexachlorotellurate(IV) Hexahydrates and Nickel Hexachloroiridate(IV) Hexahydrate *

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The ^{35}Cl NQR frequencies in $\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$, and $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$ have been determined at various temperatures. These compounds form rhombohedral crystals with the space group $R\bar{3}$, showing a single resonance line. The ^{35}Cl NQR frequencies of the Te(IV) complexes exhibit an unusual positive temperature coefficient. The deuterated analogs of the Te(IV) complexes show a small frequency shift at 77 K. These results are interpreted by the presence of $\text{O}-\text{H} \cdots \text{Cl}$ type weak H-bonds. The resonance frequency of the Ir(IV) complex versus temperature curve shows a minimum and a maximum. This unusual temperature dependence is mainly explained by the same type of the H-bond as existing in the Te(IV) complexes. The π -bond formation between Ir and Cl atoms is also partly responsible for the unusual temperature dependence.

Key words: ^{35}Cl NQR frequency, Positive temperature coefficient, H-bond, π -bond, ^1H - ^2H isotope effect.

Introduction

Some of the hexachlorometallate(IV) hexahydrates form rhombohedral crystals belonging to the space group $R\bar{3}$ [1]. Kitazume et al. recently determined the crystal structure of $\text{CaSnCl}_6 \cdot 6\text{H}_2\text{O}$ [2]. The complex ions, $[\text{Ca}(\text{OH}_2)_6]^{2+}$ and $[\text{SnCl}_6]^{2-}$ compose the slightly distorted CsCl-type lattice involving weak $\text{O}-\text{H} \cdots \text{Cl}$ H-bonds. Previously, we reported that the ^{35}Cl NQR frequencies in hexachlorostannate(IV) hexahydrates show unusual positive temperature coefficients [3]. The anomaly was interpreted in terms of the $\text{O}-\text{H} \cdots \text{Cl}$ type H-bond formed, and this was well supported through the ^{35}Cl NQR studies of the deuterated analogs. ^{35}Cl NQR frequencies in hexachloroplatinate(IV) hexahydrates, on the other hand, show normal negative temperature coefficients in the high temperature $R\bar{3}$ phase [4].

The present study has been undertaken to examine the effects responsible of the temperature dependence of the ^{35}Cl NQR frequencies in the hexachlorometallates(IV) hexahydrates having Te(IV) and Ir(IV) as the central metal ions. For $\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$, a ^{35}Cl NQR

frequency at room temperature was already reported by Brill et al. [5].

Experimental

A modified Dean-type superregenerative spectrometer and a chromel-alumel thermocouple with an estimated accuracy of ± 1 K were employed. X-ray powder patterns were recorded with a model RAD-III A diffractometer from Rigaku Denki Co. equipped with a copper anticathode. The thermal stability of the compounds was examined by carrying out thermal gravimetric analysis (TGA) with a thermal balance from Rigaku Denki Co.

$\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$ was prepared in a similar way as in [6]. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and TeCl_4 in the molar ratio 1:3 were dissolved in 3 N hydrochloric acid. When the solution was left to stand over P_2O_5 in a desiccator, yellow rods crystallized. The crystals were hygroscopic, although they easily lost water of crystallization under a dry atmosphere. Samples prepared using hydrochloric acid with concentrations lower than 2 N showed poorer or no signals [7]. $\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$ was obtained by the same method. The crystals have a greenish yellow color. $\text{MgTeCl}_6 \cdot 6\text{D}_2\text{O}$ was prepared in a dry box with anhydrous MgCl_2 and TeCl_4 from a solution of deuterium chloride dissolved in heavy water. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ used for the preparation of MgCl_2 had been thoroughly dehydrated in advance by heating at ca. 200 °C in a vacuum desiccator over

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P_2O_5 [8]. $\text{NiTeCl}_6 \cdot 6\text{D}_2\text{O}$ was synthesized in the same way. For the preparation of $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and IrCl_4 in the molar ratio 1:3 were dissolved in hydrochloric acid by introducing Cl_2 gas. Dark purple and hygroscopic crystals were obtained. TGA measurements indicate the dehydration of 4 waters at ca. 80 °C, 2 waters at ca. 115 °C, and decomposition at ca. 145 °C [4]. Identification of the Te(IV) samples was made by usual elemental analysis.

Results

According to X-ray diffraction measurements by Angoso et al. [6], $\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$ forms crystals with the space group $R\bar{3}$ and is isomorphous with $\text{CaSnCl}_6 \cdot 6\text{H}_2\text{O}$ [2]. The lattice constants of the hexagonal lattice are $a = 10.86 \text{ \AA}$ and $c = 11.02 \text{ \AA}$. In this structure, all chlorines are crystallographically equivalent. The crystal structure of $\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$ have not been determined as yet. X-ray powder patterns recorded at room temperature indicate that these complexes are isomorphous with $\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$. The lattice constants were determined as $a = 10.69 \text{ \AA}$, $c = 10.88 \text{ \AA}$ for $\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$, and $a = 10.68 \text{ \AA}$, $c = 10.77 \text{ \AA}$ for $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$.

The ^{35}Cl NQR frequencies of $\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$, and $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$ observed at several temperatures are listed in Table 1. The NQR frequencies were determined between 77 K and the fade-out temperature of the signals, yielding a single ^{35}Cl NQR line in agreement with the crystal structure. The temperature dependencies of the ^{35}Cl NQR frequencies for Te(IV) samples are shown in Figure 1. Figure 2 shows the temperature dependence of the ^{35}Cl frequencies for $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$. By annealing the samples, the S/N ratios of NQR lines were improved to a certain extent for the deuterated analogs, especially for $\text{NiTeCl}_6 \cdot 6\text{D}_2\text{O}$.

$\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{MgTeCl}_6 \cdot 6\text{D}_2\text{O}$

$\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$ yielded a sharp ^{35}Cl NQR line at room temperature, and the intensity remained almost unchanged up to 371 K, where the signal weakened rapidly and disappeared at 371.2 K. When the temperature was lowered from room temperature, the line broadened and its intensity decreased gradually. Below ca. 145 K the intensity began to decrease fairly rapidly and the line became broad. The linewidth exceeded 20 kHz and the S/N ratios recorded were ca. 3 below ca. 100 K. For the $\text{MgTeCl}_6 \cdot 6\text{D}_2\text{O}$ ^{35}Cl NQR line above room temperature a clear decrease in

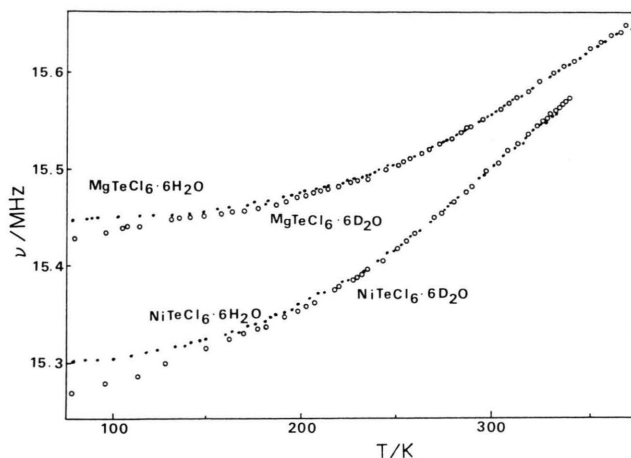


Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies ν observed for $\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$. Dots: frequencies for the protonated complexes; open circles: deuterated analogs.

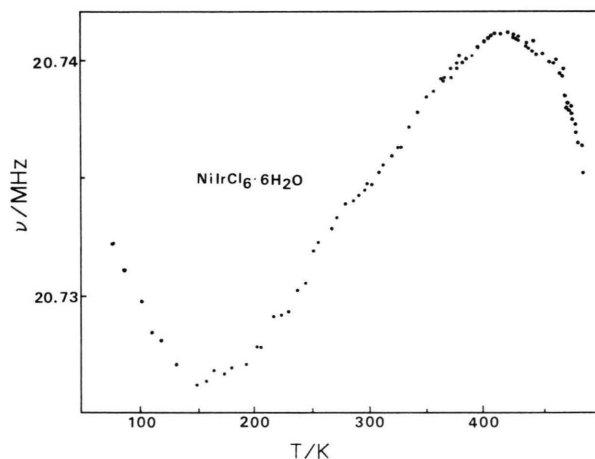


Fig. 2. Temperature dependence of ^{35}Cl NQR frequencies ν observed for $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$.

Table 1. Observed NQR frequencies of ^{35}Cl .

Compound	Frequency, MHz (± 0.001)			
	77 K	193 K	293 K	
$\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$	15.451*	15.474	15.549	15.641 (368 K)
$\text{MgTeCl}_6 \cdot 6\text{D}_2\text{O}$	15.427*	15.464**	15.547	15.642 (368 K)
$\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$	15.304**	15.358	15.490	15.557 (332 K)
$\text{NiTeCl}_6 \cdot 6\text{D}_2\text{O}$	15.268*	15.344**	15.489	15.558 (332 K)
$\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$	20.732	20.727	20.734	20.735 (484 K)

* ± 0.010 , ** ± 0.005 .

the intensity and an increase in the linewidth were observed at 370 K, and the line faded out at 371.6 K. Below room temperature, the line became broad and strong. Below 230 K, the linewidth became broader than 20 kHz. At ca. 110 K the S/N reached ca. 150, however, it decreased rapidly below 100 K and was reduced to ca. 3 at 77 K. The frequency shift by deuteration became appreciable especially from ca. 230 K and reached 24 kHz at 77 K as shown in Figure 1.

NiTeCl₆ · 6H₂O and NiTeCl₆ · 6D₂O

$\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$ gave rise to a single ^{35}Cl NQR line at all temperatures studied. The line began to weaken rapidly at ca. 330 K and disappeared at 332.4 K. When the temperature was lowered from room temperature, the linewidth gradually increased. For $\text{NiTeCl}_6 \cdot 6\text{D}_2\text{O}$, with increasing temperature the line became suddenly weak at ca. 335 K and faded out at around 339 K. When the temperature decreased to 230 K, the linewidth increased rapidly and it was broader than 20 kHz below 200 K. On the other hand, the S/N ratio showed no remarkable change, keeping the value of ca. 10 at 100 K and even at 77 K. The frequency shift by deuteration became appreciable below ca. 230 K and increased with decreasing the temperature. At 77 K, the frequency shift reached 36 kHz, as shown in Figure 1.

NiIrCl₆ · 6H₂O

$\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$ showed a fairly sharp ^{35}Cl NQR line with an S/N ratio of ca. 30 at room temperature. With increasing the temperature, the line became weak from ca. 390 K, and a line with the S/N ratio ca. 10 was recorded at 440 K. The signal became fairly weak above ca. 470 K and faded out at 485 K. When the temperature was lowered from the room temperature, the intensity and the linewidth increased and reached ca. 40 (S/N) and 9 kHz, respectively, at 77 K. The resonance frequency reached a minimum at ca. 160 K and a maximum at ca. 410 K, as shown in Figure 2.

Discussion

Anomalous Temperature Dependence of NQR Frequencies

Tellurium complexes show an unusual positive temperature coefficient of the resonance frequencies over

the whole range of temperature (see Figure 1). The feature closely resembles that of the ^{35}Cl NQR frequencies in the hexachlorostannate(IV) hexahydrates [3]. Also for the hexachlorotellurates(IV), the π character between the Te(IV)–Cl bonds is negligibly small. Furthermore, positive temperature coefficients have not been observed in anhydrous R_2TeCl_6 type complexes [9–11]. Therefore, this anomaly is attributable to the formation of H-bonds in the crystals.

Both magnesium and nickel salts are isostructural with $\text{CaSnCl}_6 \cdot 6\text{H}_2\text{O}$, which has weak $\text{O} \cdots \text{H} \cdots \text{Cl}$ type H-bonds in the crystal [2]. In the H-bonded system, hydrogen having relatively short distances to chlorines are situated nearly in the plane of chlorine p_π orbitals. Such a H-bond is known to decrease the halogen NQR frequencies [12, 13]. When the temperature increases, the H-bonding is weakened and the NQR frequency will gradually increase. Accordingly, the positive temperature coefficient of the resonance frequencies observed in the present Te(IV) complexes is explained by the positive contribution from H-bonding, predominating the normal negative temperature coefficient [3].

The ^{35}Cl NQR frequency of $\text{NiTeCl}_6 \cdot 6\text{H}_2\text{O}$ is lower than that of $\text{MgTeCl}_6 \cdot 6\text{H}_2\text{O}$ at 77 K, and the frequency difference decreases with increasing temperature. This suggests that the Ni(II) salt forms stronger H-bonds in crystals than the Mg(II) salt. Similar results have been obtained in the hexachlorostannate(IV) hexahydrates [3]. In the series of $\text{M(II)SnCl}_6 \cdot 6\text{H}_2\text{O}$, the ^{35}Cl NQR frequencies at 77 K decrease in the order Ca(II), Mg(II), Mn(II), Co(II), and Ni(II), which accords with the order of increasing electronegativities [14, 15]. Brill *et al.* [16] estimated the charge distribution in the aqua cation of stannates(IV) using a point charge model calculation. They allowed delocalization of the charges within the complex cation and found that the fractional charges on the hydrogens increase with increasing electronegativity of the divalent metal. Greater fractional charges on the hydrogens lead to stronger H-bonds between the chlorines and the hydrogens of water molecules in crystals, and this explains well the foregoing lower resonance frequencies of the Ni(II) salt.

The temperature coefficients of the ^{35}Cl NQR frequencies in various anhydrous hexachloroplatinates(IV) are ca. $-0.8 \text{ kHz deg}^{-1}$ [10, 11, 13], whereas the corresponding coefficient of K_2IrCl_6 , having Ir–Cl π -bonding, is only $-0.54 \text{ kHz deg}^{-1}$ [10, 12, 13, 17, 18]. On the other hand, various $\text{M(II)PtCl}_6 \cdot 6\text{H}_2\text{O}$

yield a much gentler gradient of ca. $-0.3 \text{ kHz deg}^{-1}$ [4, 13, 19], suggesting that the rotational oscillation of the anion is considerably hindered in crystals through the formation of H-bonds.

The NQR frequency of $\text{NiIrCl}_6 \cdot 6\text{H}_2\text{O}$ is nearly constant in the whole temperature range studied, as shown in Figure 2. This results from the compensation of the normal negative temperature coefficient with the positive temperature coefficient due to the effects of H-bonding and to the π -bonding effect of Ir–Cl bonds. Below 150 K, the normal effect slightly predominates the unusual one. With increasing the temperature, the unusual effects become superior to the normal one. Above 420 K, the molecular motion in the crystal is well excited and the H- and π -bond effects will become smaller, so that the normal negative temperature dependence again predominates.

^1H – ^2H Isotope Effect on the ^{35}Cl NQR Frequency

The ^{35}Cl NQR line of the Te(IV) complexes shifts to lower frequencies by deuteration. The observed frequency shifts are 24 and 36 kHz for the Mg(II) and Ni(II) salts at 77 K, respectively. The shifts gradually decreased with increasing temperature and tended to almost zero at room temperature. Although similar frequency shifts of the ^{35}Cl NQR frequencies have been observed in hexachloroplatinate(IV) hexahydrates [4] and hexachlorostannate(IV) hexahydrates [3], their frequency shifts and temperature coefficients differ considerably from those of the present tellurates (IV). In the plantinates (IV) and stannates (IV), the sign

of the frequency shifts changed at ca. 200 K and below 300 K, respectively. However, for the tellurates(IV) a clear inversion of the sign does not occur below the fade-out temperatures of the resonance lines.

The frequency shift in the tellurates(IV) is relatively small. Large frequency shifts beyond 100 kHz are usually explained by the anharmonicity of the O–H vibrations [20]. When the shift does not exceed the order of 10 kHz, the torsional motion of the water molecules is considered as the origin for the shift [21]. Contrary to the effect of the anharmonic vibrations, this makes the $\text{D} \cdots \text{Cl}$ distances shorter than the $\text{H} \cdots \text{Cl}$ ones in the present type of H-bonds because of the larger amplitude of the O–H₂ molecular motions [21].

The electric field gradient (EFG) arises from the charge distributions within the $[\text{TeCl}_6]^{2-}$ anion, has the positive sign and gives the main contribution to the resultant EFG at the site of ^{35}Cl nucleus. The principal axis coincides with the Te–Cl bond axis. On the other hand, the EFG coming from the neighboring ions is much smaller. Among them, the EFG produced by the H or D atoms should be negative in the present type of H-bonds. Accordingly, the shorter distance of $\text{D} \cdots \text{Cl}$ reduces the magnitude of the resultant EFG to a greater extent, which explains well the lower NQR frequency of the deuterated analogs at lower temperatures. When the reorientational motion of water molecules is excited at higher temperatures, the isotope differences in the amplitudes of the torsional oscillations will be no more important. This reduces the isotope frequency shifts as observed in the present tellurates (IV).

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