A Temperature Dependence Study of ^{35}Cl Nuclear Quadrupole Resonance Frequencies in Some Hexachloroplatinate(IV) Hexahydrates

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The temperature dependence of ^{35}Cl NQR frequencies was investigated in various hexachloroplatinate(IV) hexahydrates containing the following divalent ions as counter cations: Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Ba(II). All of the compounds except the Cu(II) and Ba(II) salts yield a single ^{35}Cl NQR line at all temperatures studied. For the Mn(II), Cu(II), and Ba(II) salts, the NQR frequencies are considerably shifted by deuteration. For the deuterated Mn(II) salt, two ^{35}Cl NQR lines were observed whose relative peak-height intensities vary in dependence on the history of the thermal treatment of the sample. The very broad higher frequency line could be observed for a sample which had been at 77 K or below. It could not be observed for a sample which was cooled slowly to room temperature after it had been heated up to ca. 420 K. A structural phase transition was located at $135._6$ and $129._4$ K for the Cu(II) salt and its deuterated analog, respectively. The frequency shift by deuteration is discussed in relation to the strength of O–H ... Cl type hydrogen bonds.

Key words: Magnetic resonance (NQR), hydrogen bonding, phase transition.

Introduction

Preliminary results of ^{35}Cl nuclear quadrupole resonance (NQR) measurements on some platinum(IV) complexes of the type $M(II)PtCl_6 \cdot 6\,H_2O$, where M(II) denotes Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Ba(II) were reported in [1]. These complexes, except the Cu(II) and Ba(II) salts, yielded a single ^{35}Cl NQR line at all temperatures investigated. The Cu(II) salt exhibited a phase transition at about 137 K; above and below this temperature the salt yielded one and three resonance lines, respectively. The Ba(II) salt showed three resonance lines, the lowest-frequency line of which has a positive temperature coefficient.

At room temperature all of the complexes except the Ba(II) salt form isomorphous rhombohedral crystals belonging to the space group $C_{3i}^2-R\bar{3}$ [2]. Kitazume et al. [3] carried out an X-ray structural analysis on $CaSnCl_6 \cdot 6\,H_2O$ which is isomorphous with the present complexes except the Ba(II) salt, and found that weak hydrogen bonds are discernible between chlorines and hydrogens of the water molecules in the crystal. Extensive studies of halogen NQR in various ionic crystals have already been performed focussing on the nature of hydrogen bonds involving halogen atoms [4–10]. The present investigation of ^{35}Cl NQR in the above complexes and the deuterated analogs of the Mn(II), Cu(II), and Ba(II) salts has been undertaken to obtain detailed information about Pt–Cl ... H type hydrogen bond formation and also to clarify the nature of the phase transition revealed for the Cu(II) salt.

Experimental

A modified Dean-type superregenerative spectrometer was constructed by us for the observation of NQR spectra. For NQR measurements, polycrystalline samples were put in a glass ampoule with

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a little amount of exchange gas of N_2 or He and sealed. A chromel vs. alumel and a chromel vs. gold (0.07% iron) thermocouple, calibrated by measuring the ^{35}Cl NQR frequencies of potassium chlorate [11] were used above and below 77 K, respectively. The observed temperature was estimated to be accurate within ± 0.5 K.

The ESR spectra were recorded on a JEOL JES-ME-3X X-band spectrometer. The spectra were calibrated using the spectrum of Mn^{2+} diluted in MgO.

The X-ray powder patterns were obtained with a model D-3F diffractometer from Rigaku Denki Co. equipped with a copper anticathode.

The thermal stability of the complexes was checked by thermal gravimetric analysis (TGA) with a thermal balance from Rigaku Denki Co.

All of the complexes studied were synthesized by dissolving equimolar amounts of hexachloroplatinic(IV) acid hexahydrate and the respective divalent metal chloride in a small amount of water [12]. To obtain the deuterated analogs of the Cu(II), Ba(II), and Mn(II) salts, the respective anhydrous hexachloroplatinate(IV), obtained by heating the hexahydrate, was repeatedly recrystallized from heavy water in a dry box. Examination by IR spectra indicated the absence of the O–H stretching bands for the deuterated Cu(II) and Ba(II) salts. However, very weak bands attributable to the O–H stretching vibration were detected for the Mn(II) salt indicating the presence of traces of hydrogen.

Results and Discussion

In [1] we reported that the X-ray powder patterns of the present nondeuterated salts except for the Ba(II) salt could be interpreted in terms of a hexagonal lattice isomorphous with $CaSnCl_6 \cdot 6H_2O$ [2, 3]. In this structure, all chlorines are crystallographically equivalent.

The experiments of TGA indicated that all the complexes except for the Ni(II) and Ba(II) salts lose weight in two steps corresponding to 4 moles of water at lower temperatures (310–380 K) and 2 moles at higher temperatures (380–470 K). Although the Ni(II) salt also indicated a loss in weight corresponding to 4 moles of water at ca. 410 K, at higher temperatures a partial decomposition of the complex anion took place, chlorine or hydrogen chloride gas being released. The Ba(II) salt loses water in two steps corresponding to 5 moles at 308 K and 1 mole at 453 K.

The ^{35}Cl NQR frequencies of various hexachloroplatinate(IV) hexahydrates determined at several temperatures are listed in Table 1. From the results of TGA, these frequencies can be safely assigned to those of the hexahydrates. The temperature variation of the ^{35}Cl NQR frequencies of the Fe(II), Co(II), and Ni(II) salts could be well interpreted by a simple Bayer equation [9]. The estimated values of a set of parameters ν_0 (MHz), Θ (10^{-37} g cm^2), and ω (10^{11} rad sec^{-1}) were 25.857, 5.06, 84; 25.832, 3.86, 102; and 25.807, 2.44, 121 for the above respective salts. Here ν_0 is the NQR frequency of ^{35}Cl in a fictitious vibrationless lattice, Θ is an effective moment of inertia of the complex anion, and ω is the angular frequency of rotational oscillations of chlorines.

$MnPtCl_6 \cdot 6\,H_2O$ and $MnPtCl_6 \cdot 6\,D_2O$

The Mn(II) salt and its deuterated analog gave rise to a fairly strong resonance signal at room temperature. The latter salt showed a slightly higher resonance frequency than the former (cf. Figure 1). At 4.2 K, however, the frequency of the deuterated salt was lower by ca. 20 kHz. At ca. 220 K the frequencies were equal.

For $MnPtCl_6 \cdot 6\,D_2O$, different thermal treatment gave rise to two different resonance lines at a given temperature, suggesting the existence of two crystalline modifications for this complex. This is very interesting because the protonated salt never showed this anomalous behaviour though the samples were repeatedly prepared and the NQR measurements were carried out under various experimental conditions such as cooling, heating, and annealing. Anomalous NQR results similar to this were also observed for $CoSnCl_6 \cdot 6\,D_2O$ and were already reported [13].

After the measurements on the deuterated sample performed at decreasing temperatures down to 4.2 K the ^{35}Cl NQR of this sample was observed at room temperature. It was quite unexpected that a new resonance line was detected at 26.05 MHz in addition to the foregoing line of 25.80 MHz observed at room temperature. The intensity ratio of these two signals was almost 1:1 at room temperature. The resonance line at higher frequency, however, was broad and broadened very rapidly

Table 1. Nuclear quadrupole resonance frequencies of ^{35}Cl in some hexachloroplatinate(IV) hexahydrates observed at various temperatures.

Compound	Frequency/MHz (± 0.003)							
	4.2 K	77 K	150 K	193 K	250 K	293 K	350 K	400 K
$MnPtCl_6 \cdot 6\,H_2O$	25.882	25.869	25.845	25.831	25.812	25.797	25.773	25.745
$MnPtCl_6 \cdot 6\,D_2O$	26.20**	26.16**		26.10**(196 K)		26.05**(290 K)		
	25.863*	25.853	25.837	25.827	25.815	25.804	25.782	25.755
$FePtCl_6 \cdot 6\,H_2O$	25.852	25.837	25.816	25.803	25.790	25.775	25.762	–
$CoPtCl_6 \cdot 6\,H_2O$	25.827	25.815	25.793	25.785	25.772	25.759	25.748	25.730
$NiPtCl_6 \cdot 6\,H_2O$	25.800	25.789	25.773	25.755	25.748	25.734	25.721	25.710
$CuPtCl_6 \cdot 6\,H_2O$	25.525*	25.525*	25.752	25.742	25.728	25.717	25.697	–
	25.801*	25.785*						
	26.152*	26.125*						
$CuPtCl_6 \cdot 6\,D_2O$	25.523*	25.521*	25.745	25.740	25.731	25.723	25.707	25.686
	25.797*	25.779*						
	26.120*	26.095*						
$ZnPtCl_6 \cdot 6\,H_2O$		25.810	25.792	25.778	25.766	25.754	25.740	25.723
$CdPtCl_6 \cdot 6\,H_2O$		25.823	25.801	25.790	25.775	25.763	25.742	–
$BaPtCl_6 \cdot 6\,H_2O$		25.442	25.403	25.405	25.411	25.422	–	–
		26.574	26.480	26.430	26.352	26.288	–	–
		26.698	26.542	26.452	26.332	26.244	–	–
$BaPtCl_6 \cdot 6\,D_2O$		25.448	25.402	25.400	25.410	25.419	–	–
		26.480	26.448	26.415	26.350	26.282	–	–
		26.661	26.530	26.440	26.330	26.246	–	–

* ± 0.005 MHz; ** ± 0.01 MHz. – Not observed.

with decreasing temperature. The linewidths observed at 77 K were ca. 25 kHz and 7 kHz for the higher and lower frequency lines, respectively. Below 77 K, the higher frequency line could barely be detected with our spectrometer even when using an unusually large modulation amplitude. The temperature dependence curves for the two lines were almost parallel to each other from 4.2 K to room temperature as shown in Figure 1.

It was confirmed from the experiments repeatedly carried out that the complex always gave a single resonance line at room temperature just after recrystallization was made from heavy water. Although only the single line was observed during the first cooling run down to 77 K, the two lines could be observed after the sample was warmed to room temperature. However, it was not possible to obtain the crystal with almost equal intensities of the two resonance lines as in the experiment described above. The higher frequency line was always weaker and the intensity ratios varied around ca. 1:5. The higher frequency line disappeared when the sample sealed in a glass tube was heated to ca. 420 K and slowly cooled down to room temperature.

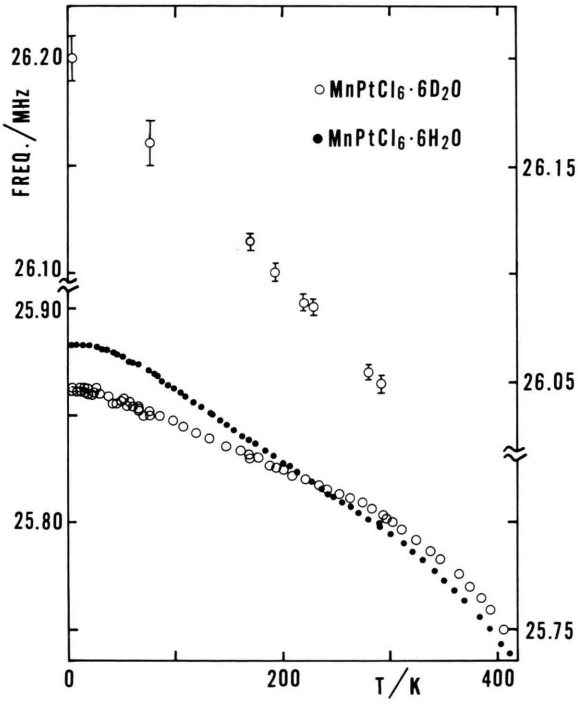

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequencies of $MnPtCl_6 \cdot 6\,H_2O$ and $MnPtCl_6 \cdot 6\,D_2O$.

X-ray powder patterns of $MnPtCl_6 \cdot 6\,H_2O$ indicate a $CaSnCl_6 \cdot 6\,H_2O$ type structure with the hexagonal lattice constants $a = 10.50$ and $c = 11.02$ Å. The single ^{35}Cl NQR line at various temperatures is consistent with this structure.

In order to clarify the structure of the deuterated crystals, X-ray powder patterns were recorded for both crystals which gave two resonance lines (with intensity ratio of 1:7 at room temperature) and a single resonance line. The latter crystals were obtained by annealing crystals showing two lines at ca. 410 K followed by slow cooling to room temperature. Unexpectedly, both deuterated crystals yielded the same diffraction patterns. However, two strong reflections which were not observed in the protonated salt appeared at $2\Theta = 21.50°$ and $23.90°$ as shown in Figure 2. These reflections could not be explained by assuming the space group $R\bar{3}$, although the other reflections were completely the same as those of the protonated salt. The freshly prepared crystals of $MnPtCl_6 \cdot 6\,D_2O$ yielded the same diffraction patterns as those of the samples treated thermally as described above.

Possibly the deuterated salt forms a superlattice with almost the same local structure as the protonated one. Some disorder may exist in the superlattice. The degree of this disorder may change on heat treatment as follows: Ordered parts of the superlattice are developed when cooling the sample to extremely low temperature. By heating the sample to ca. 420 K this order is broken. The long range disorder of the superlattice is frozen in by cooling down the heated sample to room temperature. The freshly prepared crystal has the same kind of disorder as the annealed sample.

In the deuterated salt the line at higher frequency is much broader than the other one and disappears in some cases. The frequency of the unusual line is by ca. 200 kHz higher than that of the protonated salt. These facts suggest that the surroundings of the chlorines which give the higher frequency line differ much from those of the chlorines in the protonated salt, i.e. there exist two chemically non-equivalent chlorines in the deuterated crystals. The lower line in the deuterated salt is to be compared with that of the protonated one.

$CuPtCl_6 \cdot 6\,H_2O$ and $CuPtCl_6 \cdot 6\,D_2O$

The temperature dependence of NQR frequencies of the Cu(II) salt and its deuterated analog is shown

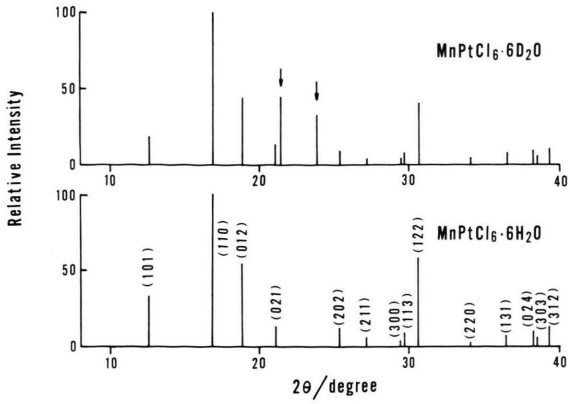

Fig. 2. X-ray powder patterns of $MnPtCl_6 \cdot 6\,H_2O$ and $MnPtCl_6 \cdot 6\,D_2O$ recorded at room temperature using CuKα radiation. The pattern of $MnPtCl_6 \cdot 6\,H_2O$ could be well explained with the crystal parameters reported in the literature. The deuterated salt showed additionally the two strong reflections indicated by arrows. These reflections disappear rather rapidly when the sample is exposed to air.

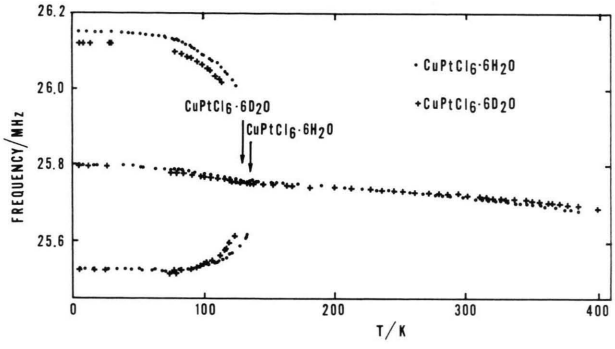

Fig. 3. Temperature dependence of the ^{35}Cl NQR frequencies of $CuPtCl_6 \cdot 6\,H_2O$ and $CuPtCl_6 \cdot 6\,D_2O$.

in Figure 3. Both salts yield a fairly strong line at room temperature. On lowering the temperature, the frequency of both salts increased almost linearly, the line became gradually broad and disappeared in the noise level at $135._6$ and $129._4$ K for the protonated and deuterated salts, respectively. Below these temperatures, the salts yielded three resonance lines having each about 1/3 of the intensity of the single line above the transition temperature (T_{tr}). With increasing temperature from 77 K, the reverse process could be exactly followed.

From these experimental results it is concluded that the protonated Cu(II) salt undergoes a structural phase transition, possibly of the second order, at $135._6$ K and has a structure of a lower symmetry below T_{tr}. This T_{tr} shifts to the lower side by 6 K on

deuteration. This isotope effect on the phase transition is fairly large and, then, strongly suggests that the structural phase transition involves a slight rearrangement of hydrogen bonding formed around resonant chlorines.

In order to obtain information about the structure of the $[Cu(H_2O)_6]^{2+}$ ion in the Cu(II) salt, ESR measurements were performed on a powder sample at various temperatures. The spectra recorded above and below T_{tr} are shown in Figure 4. The spectra above T_{tr} are nearly symmetric. This indicates that the site symmetry of the position of the Cu(II) ions is only slightly lower than cubic. However, considerably deformed spectra suggesting the existence of a large anisotropy in the g values were obtained below T_{tr}. Evidently the water molecules coordinated nearly octahedrally around the cation above T_{tr} are distorted considerably below T_{tr}, possibly due to the Jahn-Teller effect of the Cu(II) ion [14]. The distortion of the $[Cu(H_2O)_6]^{2+}$ ion causes the appearance of three kinds of chlorines due to the formation of different kinds of O−H ... Cl hydrogen bonds, although all chlorines are surrounded by hydrogens in the same way as in the high-temperature R $\bar{3}$ crystal.

$BaPtCl_6 \cdot 6\,H_2O$ and $BaPtCl_6 \cdot 6\,D_2O$

Figure 5 shows the temperature dependence of the ^{35}Cl NQR frequencies of the Ba(II) salt and its deuterated analog. At room temperature the protonated salt yielded three resonance lines, among which the lowest-frequency line was slightly broader than the other lines. With increasing temperature the highest- and lowest-frequency lines became gradually weak from ca. 290 K and disappeared around 305 K, whereas the remaining line could be observed up to ca. 340 K and faded out above this temperature. The lowest-frequency line showed a flat temperature dependence and gave a very broad minimum around 160 K. This line became gradually broad as the temperature decreased. As for the remaining higher frequency lines, the frequency decreased almost linearly with increasing temperature.

The temperature dependence of the resonance frequencies for the deuterated analog bears a strong resemblance to that of the foregoing protonated salt. It is interesting to note that the resonance frequencies of the deuterated analog almost exactly coincided with those of the protonated salt over a wide range of temperature studied.

$^1H-^2H$ Isotope Effect on the ^{35}Cl NQR Frequency Through H-Bonding

The shift of the ^{35}Cl NQR frequencies by deuteration of weakly coordinated water molecules was investigated for the Mn(II), Cu(II), and Ba(II) salts. A frequency shift of the order of 10 kHz at the

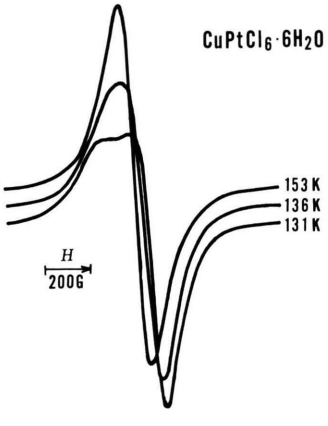

Fig. 4. X-band ESR spectra recorded for a powder sample of $CuPtCl_6 \cdot 6\,H_2O$ at various temperatures above and below T_{tr} (= 135.6 K). Symmetric spectra having $g = 2.23$ were obtained at 153 K, whereas anisotropic spectra were obtained below T_{tr}.

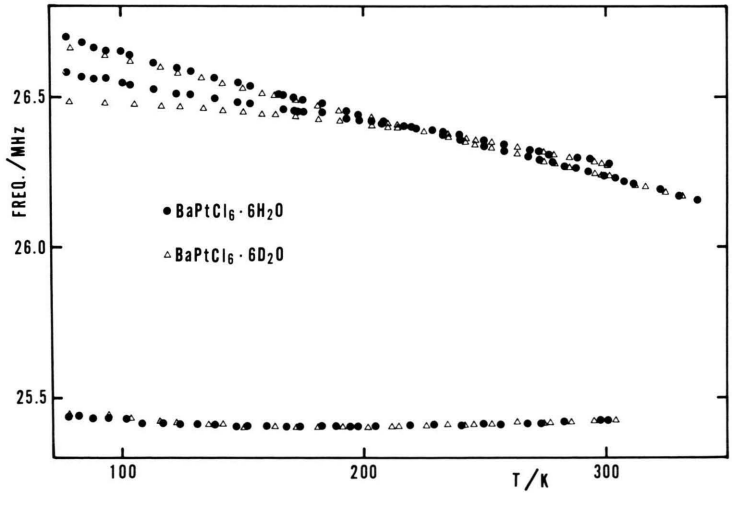

Fig. 5. Temperature dependence of the ^{35}Cl NQR frequencies of $BaPtCl_6 \cdot 6\,H_2O$ and $BaPtCl_6 \cdot 6\,D_2O$.

largest was observed (see Table 1). This value is rather small, indicating that H-bonding involved in these complexes is weak. In fact, for $CsHCl_2$ [15], in which chlorines are known to form very strong hydrogen bonds in the crystal, upon deuteration a large frequency shift of several hundred kHz has been observed. The conclusion of weak H-bonding in the present complexes agrees with the expectation from the crystal analysis of $CaSnCl_6 \cdot 6\,H_2O$ [3].

According to the structural analysis of $CaSnCl_6 \cdot 6\,H_2O$, three hydrogens are located near one chlorine, which is nearly on a plane formed by the hydrogens. The plane is approximately perpendicular to the metal-ligand bond axis of the chlorine [3]. This means that hydrogens are located approximately in the direction of the $3p_x$ and $3p_y$ orbitals of the chlorine when the z axis is defined as along the Sn–Cl bond. Therefore the formation of hydrogen bonds will reduce the absolute value of the field gradient at the chlorine and hence decrease the NQR frequencies [9].

The frequency shift due to an isotope effect on the NQR of chlorines forming strong or moderate O–H ... Cl type hydrogen bonds is attributed to the anharmonicity of O–H(D) stretching vibrations [6]. It is expected that the O–D distance becomes slightly shorter than the O–H distance due to the anharmonicity of the potential well [16]. The elongation of the distance $R_{O \ldots Cl}$ by deuteration is also expected from an analogy with the case of short or intermediate asymmetric O–H ... O hydrogen bonds [17, 18]. Owing to these effects it is expected for the present complexes that the hydrogen will be placed farther away from the chlorine on deuteration. This results in a decrease of the electrostatic interactions operative between the hydrogens and chlorines forming weak hydrogen bonds. Thus, the NQR frequency will increase by deuteration. This is one mechanism to be considered for the isotope effect of the present complexes.

From the experimental results, however, we can conclude that librational and/or reorientational motions of the water molecules [19, 20] dominate the isotope effect on ^{35}Cl NQR frequencies in the present weak O–H(D) ... Cl hydrogen bond system at lower temperatures. This is because the present deuterated complexes yielded, at lower temperatures, ^{35}Cl NQR frequencies lower than or approximately equal to those of the corresponding line of the protonated complexes. However, the anharmonicity of O–H(D) stretching vibrations is considered to become an influential origin for the isotope effect at higher temperatures where the rotational motions are well excited.

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