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NUCLEAR QUADRUPOLE RESONANCE OF CHLORINE IN SOME HEXACHLOROPLATINATE(IV) HEXAHYDRATES

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The nuclear quadrupole resonance of chlorine in $MPtCl_6$-$6H_2O$ (M(II) = Mn, Fe, Co, Ni, Cu, Zn, Cd, Ba) was observed between 77 and 450 K. Copper(II) hexachloroplatinate(IV) hexahydrate shows a phase transition at 137 K. This complex and barium hexachloroplatinate(IV) hexahydrate yield resonance lines showing a positive temperature coefficient capable of being interpreted in terms of hydrogen bond formation.

We have studied the nuclear quadrupole resonance of halogens in various tetrahaloaurate(III) dihydrates and sodium tetrachloroiodate(III) dihydrate,[1-3] and found that these complexes show resonance absorptions having a positive temperature coefficient of resonance frequencies. The anomaly can be interpreted with the aid of X-ray crystal analysis as having its origin in hydrogen bond formation involving halogen atoms. The present investigation has been undertaken as part of a program of nuclear quadrupole resonance studies of chlorine in various hexachloroplatinate(IV) hexahydrates possibly forming hydrogen bonds between chlorine atoms and water molecules.

The nuclear quadrupole resonance of chlorine was observed by means of a modified Dean type spectrometer already described.[4] Resonance frequencies were measured by use of a Model TR-5178 frequency counter from Takeda Riken Company. Hexachloroplatinate(IV) hexahydrates were synthesized by methods described in the literature.[5] Table 1 shows the resonance frequencies of chlorine-35 determined at room, dry ice, and liquid nitrogen temperatures.

Manganese(II), iron(II), cobalt(II), nickel(II), zinc, and cadmium hexachloroplatinate(IV) hexahydrates give rise to a single resonance absorption at all temperatures investigated, indicating that all chlorine atoms are equivalent in the crystals of each complex. The crystal structure of these compounds has not been determined as yet. Therefore we took X-ray powder patterns at room temperature and confirmed that the hexachloroplatinate(IV) hexahydrates are isomorphous with nickel(II) hexachlorostannate(IV) hexahydrate already studied by Pauling.[6] He found that the compound forms rhombohedral crystals belonging to the space group $R\bar{3}$, that the complex anion have the O_h symmetry, and that all chlorine atoms are crystallographically equivalent. The results of nuclear quadrupole resonance agree with those of the X-ray analysis. The resonance frequencies of these complexes decrease almost linearly with increasing temperature. The absolute values of observed temperature coefficient (0.23-0.33 kHz deg^{-1}) are much smaller than the value (0.95 kHz deg^{-1}) of potassium hexachloroplatinate(IV).$^{7,8)}$ This suggests that torsional oscillations of $[PtCl_6]^{2-}$ ions are strongly hindered in the crystals of hexachloroplatinate(IV) hexahydrates. The maximum-slope width of the broad-line PMR signal observed at room temperature amounted to more than 12 G, indicating that water molecules in these crystals have practically no freedom of rotation. Accordingly the very small temperature coefficients might be due to hydrogen bond formation between chlorine atoms and water molecules.

Fig. 1 shows the temperature dependence of quadrupole resonance frequencies of copper(II) hexachloroplatinate(IV) hexahydrate, which was confirmed to be isomorphous with the foregoing complexes. Three resonance lines of almost equal intensity were observed at liquid nitrogen temperature. Two resonance lines on the high-frequency side show a negative temperature coefficient, whereas the lowest-frequency line shows a positive temperature coefficient. The triplet became weak from about 130 K and disappeared at 137 K, above which a very strong single line was observed in agreement with the result of crystal analysis. The appearance of the triplet below 137 K indicates that there are three kinds of nonequivalent chlorine sites in crystals and that a change in crystal structure takes place at this temperature. The abnormal temperature dependence of resonance frequencies below the transition point may be due to a slight rotation of complex anions about respective Cl-Pt-Cl axes as well as to hydrogen bond formation involving chlorine atoms.

Barium hexachloroplatinate(IV) hexahydrate, which is not isomorphous with the foregoing complexes, yielded three resonance frequencies below 309 K as shown in Fig. 2. The curves of two resonance lines on the high-frequency side showing a normal negative temperature coefficient cross each other at about 220 K. The curve of the lowest frequency plotted against temperature shows a very flat minimum at about 160 K. Evidently there are three kinds of nonequivalent chlorine atoms in crystals. Two resonance signals faded out at about 309 K probably owing to the thermal reorientation of water molecules.$^{9)}$ A single resonance line observed above 309 K disappeared at about 340 K presumably because water of crystallization was partially lost. The temperature dependence of resonance lines of this complex bears a strong resemblance to that of sodium tetrachloroaurate(III) dihydrate$^{1-3)}$ in that the resonance frequency of the lowest-frequency line is much lower than those of other lines and that it shows a positive temperature coefficient. Accordingly one can conceive the formation of weak hydrogen bonds between chlorine atoms and water molecules in this complex as well.

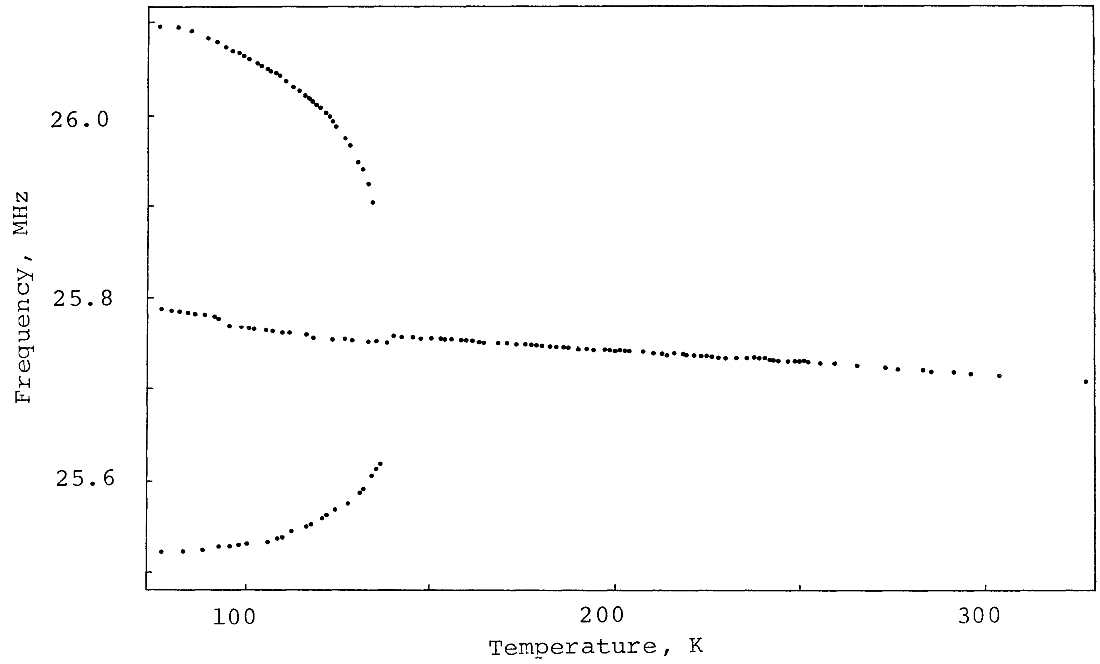

Fig. 1. Temperature dependence of the NQR frequencies of ^{35}Cl in $CuPtCl_6.6H_2O$.

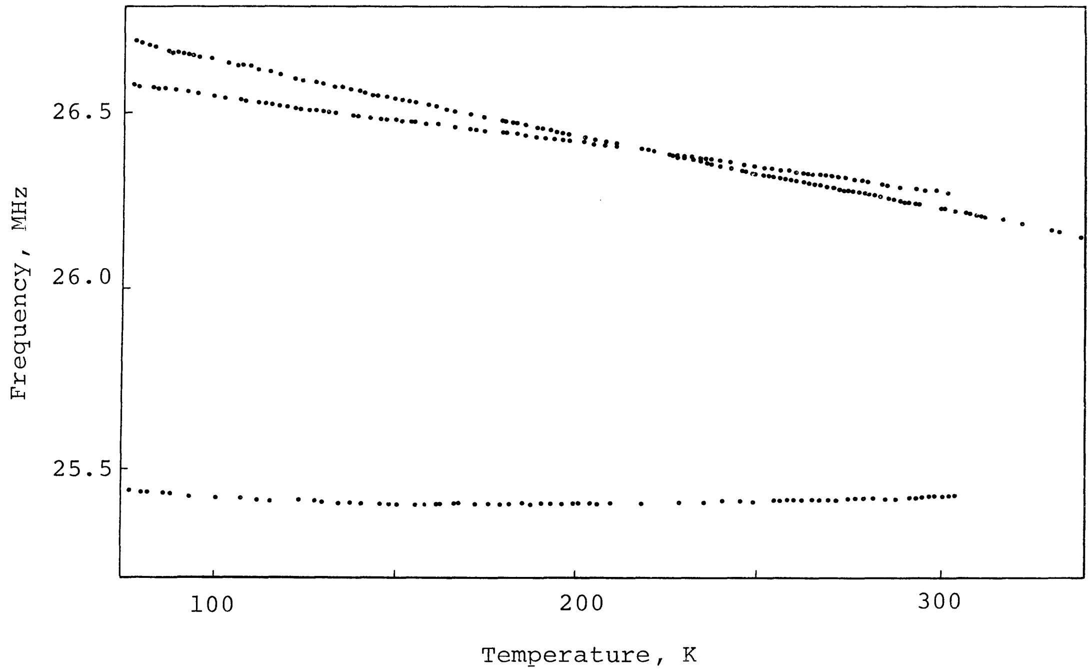

Fig. 2. Temperature dependence of the NQR frequencies of ^{35}Cl in $BaPtCl_6.6H_2O$.

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Table 1

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

	Frequency, MHz (±0.001)		
Compound	77 K	193 K	293 K
$MnPtCl_6.6H_2O$	25.870	25.831	25.798
$FePtCl_6.6H_2O$	25.837	25.805	25.778
$CoPtCl_6.6H_2O$	25.815	25.785	25.762
$NiPtCl_6.6H_2O$	25.789	25.759	25.736
$CuPtCl_6.6H_2O$	25.524	25.748	25.716
	25.788		
	26.097		
$ZnPtCl_6.6H_2O$	25.810	25.778	25.754
$CdPtCl_6.6H_2O$	25.823	25.790	25.763
$BaPtCl_6.6H_2O$	25.442	25.405	25.422
	26.574	26.430	26.288
	26.698	26.452	26.244

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