Nuclear Quadrupole Resonance of Chlorine in Hexachloroplatinic(IV) Acid Hexahydrate and Sodium Hexachloroplatinate(IV) Hexahydrate

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The pure quadrupole resonance of ^{35}Cl in hexachloroplatinic(IV) acid hexahydrate $H_2PtCl_6\cdot6H_2O$ and sodium hexachloroplatinate(IV) hexahydrate $Na_2PtCl_6\cdot6H_2O$ was observed at room temperature using a spectrometer previously described[1]. The observed frequencies are shown in Table I. in which that of potassium hexachloroplatinate(IV)[1] at room temperature is included for comparison.

TABLE I. PURE QUADRUPOLE RESONANCE FREQUENCIES OF ^{35}Cl IN HEXACHLOROPLATINIC(IV) ACID HEXAHYDRATE AND RELATED COMPOUNDS

Compound	Temp. °C	Frequency Mc./sec.
$H_2PtCl_6\cdot6H_2O$	25.0	26.55 ±0.05
$Na_2PtCl_6\cdot6H_2O$	23.5	25.730±0.005 26.470±0.005 27.040±0.005
K_2PtCl_6	23.5	25.813±0.001

At dry ice and liquid nitrogen temperatures, these compounds gave rise to a number of weak signals appearing in the frequency range of 28~35 Mc. and 20~30 Mc., respectively. These signals were attributable to piezoelectricity arising from lattice deformations formed in crystals on cooling[2]. The pure quadrupole resonance lines escaped detection either because they were masked by the piezoelectric signals or because the signal-to-noise ratio was small.

The single resonance line observed for hexachloroplatinic(IV) acid might suggest that all chlorine atoms in the crystals are mutually equivalent. However, it is probable that additional resonance lines escaped observation owing to their small signal-to-noise ratios. In fact, the single line was barely detectable. Sodium hexachloroplatinate(IV) yielded three resonance lines of approximately the same signal-to-noise ratio equal to about 3, indicating the presence of at least three kinds of crystallographically nonequivalent chlorine atoms in the crystals.

No X-ray analysis has ever been performed on the crystals of these two compounds. It is reported[3] that sodium hexachloroplatinate(IV) hexahydrate forms triclinic pinacoidal crystals. In order to obtain some information on the crystal structure of these compounds, powder patterns were taken by means of a Norelco X-ray diffractometer. Since the crystals were deliquescent, high-speed scanning was carried out. The recorded powder patterns of these two compounds were quite different from each other. Unlike potassium hexachloroplatinate(IV), which forms cubic crystals, two compounds under investigation gave powder patterns suggesting lower symmetry than the tetragonal symmetry. Evidently, the crystal structures of these three compounds are of quite different type. It is noteworthy that despite the difference in crystal structures, the observed resonance frequencies of these three compounds are nearly the same, the deviations being within several percent. This indicates that the pure quadrupole resonance frequency of chlorine in $[PtCl_6]^{2-}$ is determined primarily by the electronic distribution in the complex ion without being affected greatly by neighboring cations and complex ions[4].

The present authors have already determined the pure quadrupole resonance of halogens in a number of metal complexes[5,6]. The results have been analyzed through the Townes-Dailey procedure[7] to discuss the covalent character of metal-ligand bonds in complex ions, ignoring the effect of neighboring ions on the pure quadrupole resonance frequencies. The present results confirm the adequacy of the analysis.

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