Pure Quadrupole Resonance of Halogens in Sodium Tetrahaloaurate(III) Dihydrates and Sodium Tetrachloroiodate(III) Dihydrate[1]

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The pure quadrupole resonance of chlorine in sodium tetrachloroaurate(III) dihydrate was observed between 77 and 400°K using a sample synthesized and identified by means of chemical analysis and X-ray powder technique. We could observe four resonance lines attributable to ^{35}Cl each showing no discontinuity in its temperature dependence. This indicates that four kinds of nonequivalent chlorine atoms exist in a crystal and that no phase transition takes place in this temperature range.

The lowest-frequency line of the quartet shows a positive temperature coefficient ($\Delta\nu/\Delta T=0.4$ and 2.5 kHz/deg at 77 and 400°K, respectively), whereas other lines have normal negative temperature coefficients in the whole range of temperature studied. Moreover, its line width is very broad and its frequency is much lower than that of other lines (25.356, 27.998, 28.867, and 29.466 MHz at 77°K).

Vaciago *et al.*[2] have carried out X-ray analysis on this compound and found that it forms orthorhombic crystals with four formula units in a unit cell and that four chlorine atoms are crystallographically nonequivalent in a distorted square coordination in agreement with our observation of the quartet lines. In this complex ion, one chlorine atom (Cl_1) is separated from the nearest sodium ion by 4.37 Å, whereas three others are closer to sodium ions, the average distance being equal to 3.05 Å. The chlorine atom Cl_1 has four oxygen atoms at the shortest and the second shortest distances (3.36 and 3.42 Å), while other O–Cl distances are longer than 3.45 Å. The four oxygen atoms form a very flat, slightly distorted square pyramid along with the Cl_1 atom at the apex, the Au–Cl_1 axis pointing to the center of the square. Each oxygen atom has two chlorine atoms in its vicinity, *i. e.*, Cl_1 and Cl_1' belonging to different complex anions. The $\angle Cl_1\text{–O–}Cl_1'$ angle (118°) is nearly equal to the valency angle of oxygen in a water molecule. Although hydrogen atoms are not located by the X-ray analysis, it is plausible that weak O–H···Cl_1 hydrogen bonds are formed in the crystal.

The positive temperature coefficient of the lowest-frequency line of the quartet can be interpreted in terms of hydrogen bond formation. To the first approximation, the quadrupole resonance frequency of a halogen is proportional to the number of unbalanced p electrons, $U_p=(N_x+N_y)/2-N_z$, where N_x, N_y, and N_z denote the number of electrons in the p_x, p_y, and p_z orbitals of the halogen atom, respectively. The origin of the coordinate system is taken at the halogen nucleus, the z axis being directed along the metal-ligand bond. When hydrogen bonds are formed, four O–H groups approximately lying on the x and y axes attract electrons from the p_x and p_z orbitals of the chlorine atom, leading to a decrease in the number of unbalanced p electrons. Accordingly, the lowest-frequency line is assigned unequivocally to Cl_1 atoms. As hydrogen bonds are weakened by thermal motion, N_x and N_y increase with increasing temperature and the resonance line shifts to a higher frequency. Because hydrogen atoms are present in the vicinity of Cl_1 atoms, the resonance line is broadened by nuclear spin-spin interaction as was observed experimentally.

We studied also the temperature dependence of the pure quadrupole resonance of ^{79}Br in sodium tetrabromoaurate(III) dihydrate ($\nu=201.70$, 217.66, 224.48, and 229.43 MHz at 77°K; $\Delta\nu/\Delta T=7$ and 18 kHz/deg at 77 and 270°K, respectively, for the lowest-frequency line) and ^{35}Cl in sodium tetrachloroiodate dihydrate[3] ($\Delta\nu/\Delta T=0.5$ and 3.3 kHz/deg at 77 and 300°K, respectively) and found that the resonance pattern of these complexes bears a strong resemblance to that of sodium tetrachloroaurate(III) dihydrate. The crystal structures of these complexes were confirmed to be isomorphous with that of sodium tetrachloroaurate(III) dihydrate, the structural data being $a=13.29$, $b=7.28$, and $c=9.43$ Å for the former and 13.61, 7.14, and 9.24 Å for the latter.

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[2] M. Bonamico, G. Dessy and A. Vaciago, *Atti Accad. Nazl. Lincei, Rend.*, **39**, 504 (1965).

[3] C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957). Resonance frequencies observed at three different temperatures are tabulated therein.