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Hydrogen Bonding in Sodium Tetrachloroaurate(III) Dihydrate and Sodium Tetrachloroiodate(III) Dihydrate

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We have discussed the formation of O–H···Cl hydrogen bonds in the crystals of sodium tetrachloroaurate(III) dihydrate in connection to the positive temperature coefficient of nuclear quadrupole resonance frequency of chlorine in this compound.[1,2] An X-ray crystal analysis carried out by Bonamico *et al.*[3] has shown that one of the four chlorine atoms in an $AuCl_4^-$ ion is separated from two oxygen atoms by the shortest O···Cl distance of 3.36 Å and from two other oxygen atoms by the second shortest distance equal to 3.42 Å. Chlorine atoms of this type are responsible for the unusual temperature dependence of quadrupole resonance.[1] Although hydrogen atoms have not been located, it is conceivable that the chlorine atoms in question is involved in weak hydrogen bonds with four water molecules. In fact this is the key point for explaining the positive temperature coefficient mentioned above.

However, the O···Cl distance is appreciably longer than the sum of van der Waals radii, 3.2 Å. This presents a debatable problem in view of the accepted belief that a hydrogen bond, X–H···Y, is surely formed when the X···Y distance is shorter than the sum of van der Waals radii.[4]

The frequency shift of X–H stretching vibration presents another criterion for the formation of hydrogen bonds. Therefore, we have observed the infrared absorption of this compound at room and liquid-nitrogen temperatures. Samples were run as Nujol or hexachlorobutadiene mulls. Measurements were performed in the frequency range from 4000 to 700 cm^{-1}, using a JASCO DS-402G spectrophotometer.

At room temperature, three bands were observed at 3575, 3516, and 1618 cm^{-1}. Undoubtedly they are due to the intramolecular vibrations of water molecules because they show normal frequency shifts on deuteration. At liquid-nitrogen temperature, the frequencies and band shapes were practically unaltered in agreement with the results of our NQR study indicating that no phase transition takes place in the temperature range investigated. Although there are eight water molecules in a unit cell, vibrational coupling among them seems to be inappreciable, because no bands were split even at liquid-nitrogen temperature. Therefore the three bands were assigned to the antisymmetric stretching γ_3, symmetric stretching γ_1, and bending γ_2 of a water molecule, respectively.

Heavily but incompletely deuterated samples yielded a single band at 3545 cm^{-1} in place of the bands, γ_3 and γ_1 of undeuterated samples. The band is attributable to the γ_3 mode of HDO molecules diluted in D_2O molecules. The frequency is very close to the mean value of γ_3 and γ_1 of undeuterated water molecules. Since the vibration is almost free from coupling, the vibrational frequency is used for the following discussion on the O–H stretching frequencies of water molecules in various compounds.

The observed O–H stretching frequency, 3545 cm^{-1}, is significantly higher than those of water molecules, 3275 cm^{-1} in ice[5] and 3450 cm^{-1} in calcium sulfate dihydrate,[6] but is still lower than 3707.5 cm^{-1} of water vapor[7] and 3624 cm^{-1} of water molecules very loosely bound in the crystals of beryl.[8] A frequency shift of about 160 cm^{-1} from the frequency of water vapor provides an evidence in support of the formation of weak hydrogen bonds in the crystals of sodium tetrachloroaurate(III) dihydrate.

Attempts have been made to correlate the frequency shift $\Delta\gamma=\gamma^0{}_{\mathrm{XH}}-\gamma_{\mathrm{XH}}$ with the distance R between heavy atoms in hydrogen-bonded systems, X–H···Y. Here $\gamma^0{}_{\mathrm{XH}}$ refers to X–H stretching free from hydrogen bonding and γ_{XH} stands for the X–H frequency in the hydrogen-bonded systems. Lippincott and Schroeder[9] first succeeded in reproducing an asymptotic approach of $\Delta\gamma$ toward zero for large R by use of a semiempirical potential function proposed by themselves.

$$\frac{\gamma_{\mathrm{XH}}}{\gamma^0_{\mathrm{XH}}}=\Big\{r_0e^{-\alpha}[r_0{}^2-\frac{\alpha}{2}(r+r_0)^2]/r^3 + r_0{}^*\frac{D_0{}^*n^*}{D_0n}e^{-\beta}[r_0{}^{*2}-\frac{\beta}{2}(r^*+r_0{}^*)^2]/r^{*3}\Big\}^{1/2} \qquad (1)$$

$$\alpha=n(r-r_0)^2/2r$$
$$\beta=n^*(r^*-r_0{}^*)/2r^*$$

where r is the X–H distance in a hydrogen-bonded system, r_0 is the corresponding values in an X–H system free from hydrogen bonding, D_0 is the dis-

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sociation energy of the X–H bond, and n is a semi-empirical parameter. Asterisks refer to the H···Y bond. Since the value of r is given as a function of R,[9] the dependence of the frequency shift on R can be obtained.

Recently, Bellamy and Owen[10] proposed a simple empirical relationship between $\Delta\gamma$ and R on the basis of the Lennard-Jones 6-12 potential function.

$$\Delta\gamma\ (\mathrm{cm}^{-1}) = 50[(d/R)^{12}-(d/R)^{6}] \qquad (2)$$

where d is the distance at which the potential energy curve intersects the abscissa.

The validity of Eqs. (1) and (2) has been checked especially for O–H···O systems, for which a large number of available data cover a wide range of R. For O–H···Cl systems, only hydroxylamine hydrochloride (R=2.99 Å) and chloral hydrate (3.15 Å) are cited in the original papers.[9,10] No evidence has been obtained for confirming that these equations are valid also for hydrogen bonding in inorganic chloride hydrates having a relatively large value of R.

Figure 1 shows the O–H stretching frequencies of $CuCl_2\cdot 2H_2O$,[11] $CoCl_2\cdot 2H_2O$, $FeCl_2\cdot 2H_2O$, and $MnCl_2\cdot 2H_2O$[12] as observed for HDO species plotted against the O···Cl distance.[13,14] These crystals are particularly suitable to the present purpose, because each of them contains only one kind of water molecules and also beacuse they are isomorphous with one another except for the copper compound. Figure 1 shows two theoretical curves for the O–H···Cl systems quoted from the original papers also.[9,10] Both curves are drawn with γ^0_{OH} equal to 3700 cm^{-1}. Agreement between theoretical and experimental data is excellent, indicating that relations (1) and (2) can be used for discussing hydrogen bonding in inorganic chloride hydrates having a relatively large value of R.

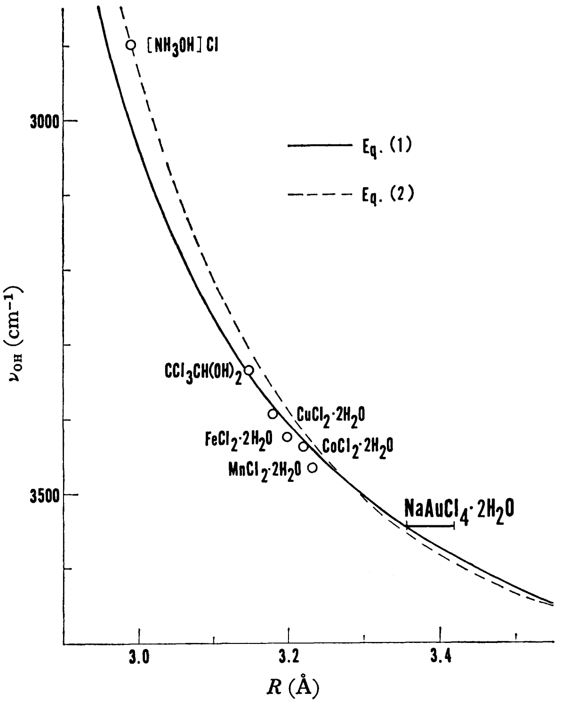

Fig. 1. O–H stretching frequency of hydrogen-bonded water molecules in various inorganic chloride hydrates plotted against the O···Cl hydrogen-bonded distance.

The O–H stretching frequency of sodium tetrachloroaurate(III) dihydrate is shown by a horizontal line in the figure in order to take into account two observed O···Cl distances possibly involved in hydrogen bonding. Since its deviation from the theoretical curves is rather trivial, it is concluded that although the hydrogen bonding is weak, the nature of the hydrogen bonds is essentially the same as those in other compounds mentioned above. The O···Cl distances are longer than the sum of van der Waals radii, but are considerably shorter than d (=3.85 Å) defined by Bellamy and Owen, which is very close to the sum of collision radii, 3.81 Å, of gas molecules. This implies that water molecules are bonded to $AuCl_4^-$ ions in this compound mainly by electrostatic and van der Waals forces.

Sodium tetrachloroiodate(III) dihydrate has been known to form crystals isomorphous with sodium tetrachloroaurate(III) dihydrate.[1] However, the crystal structure has not been determined in detail as yet. We have recorded the infrared spectra of this compound at liquid-nitrogen temperature, and observed bands at 3577, 3515, and 1611 cm^{-1} attributable to γ_3, γ_1, and γ_2 of water molecules, respectively. These values agree almost perfectly with those of water in sodium tetrachloroaurate(III) dihydrate. This fact indicates that weak O–H···Cl hydrogen bonds are formed in the crystals as in the case of sodium tetrachloroaurate(III) dihydrate and that the O···Cl distances are practically the same in these two compounds.

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