

VIBRATIONAL SPECTRA OF HEXAAQUA COMPLEXES
III. INTERNAL AND EXTERNAL MOTIONS OF THE WATER MOLECULES IN
THE SPECTRA OF $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

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The infrared spectra of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ as well as those of a series of its partly deuterated analogues were recorded at room and at liquid-nitrogen temperature (RT and LNT respectively). The spectra were analyzed and the bands due to librations of the water molecules were assigned. The order of the librational frequencies was found to be rocking > twisting > wagging. The symmetry of the water molecules is close to C_{2v} .

1. INTRODUCTION

As a part of our systematic studies of various hexaaqua complexes [1,2], the infrared spectra of hexaaquachromium(III) chloride and of its partially deuterated isotopomers were recorded and analyzed. The results are reported here.

The infrared spectrum of the protiated form of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ at RT has already been partly reported [3-6], our RT spectrum being in agreement with the published one. To the best of our knowledge, neither the Raman nor the LNT infrared spectra of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and/or of its partially deuterated analogues have been reported.

The crystal structure of the title compound was determined by Spundflache *et al.* [7]. It was found that this compound crystallizes in the hexagonal system (space group $R\bar{3}c$) with $Z = 6$.

There is only one type of water

molecules which occupy sites of C_1 symmetry. The water molecules are coordinated to Cr, forming practically perfect octahedra. Each water molecule forms very similar and strong hydrogen bonds with $\text{O}_w \cdots \text{Cl}$ distances of 302.8 and 302.6 pm. From the structural point of view, the water molecules are almost symmetric.

2. EXPERIMENTAL

The protiated form of the title compound was prepared using the method described by Spundflache *et al.* [7]. The partially deuterated analogues were obtained from solutions in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures of the appropriate composition. The RT and LNT infrared spectra were recorded from KBr pellets on a Perkin-Elmer 580 spectrophotometer equipped with a RIIC (London) variable temperature cell. The low-frequency part of the spectrum was recorded from Nujol mulls between polyethylene windows.

3. RESULTS AND DISCUSSION

The RT and LNT infrared spectra of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ recorded between 4000 and 350 cm^{-1} are given in Fig. 1. The comparison of these spectra with those of $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ (see [2] and the references therein), shows a remarkable similarity, in agreement with the available structural data [7].

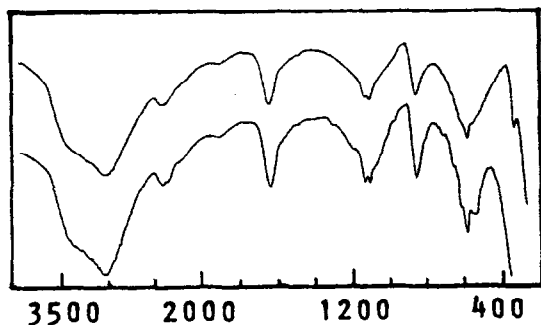


Fig. 1. RT and LNT spectra of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

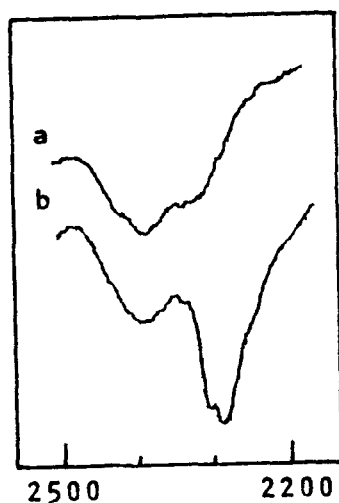


Fig. 2. The OD stretching region in the LNT spectra of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (a) and its partially deuterated ($\approx 5\%$ deuterium) analogue (b)

The existence of two closely lying O-D stretching bands (located at 2309 and 2293 cm^{-1}) in the LNT infrared spectrum of the slightly deuterated $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (cf. Fig. 2) suggests a rather symmetric force field around the water molecules. In line with this is the presence of a *single* H-O-D bending band (it is found at $\approx 1425\text{ cm}^{-1}$, cf. Fig. 3), although *each* of the two protons can be exchanged with deuterium. The $\delta(\text{H-O-H})$ and $\delta(\text{D-O-D})$ modes also give rise to single bands (at 1618 and 1185 cm^{-1} respectively) in the LNT spectra of the protiated and the highly deuterated analogue (see

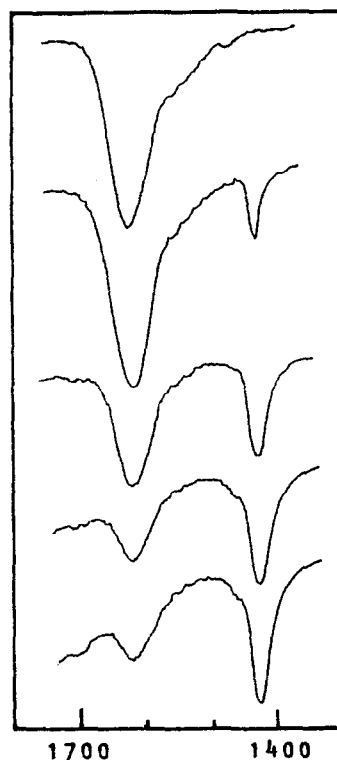


Fig. 3. The H-O-H bending region in the LNT spectra of a series of partially deuterated $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ analogues (the deuterium content increases from the top towards the bottom curve)

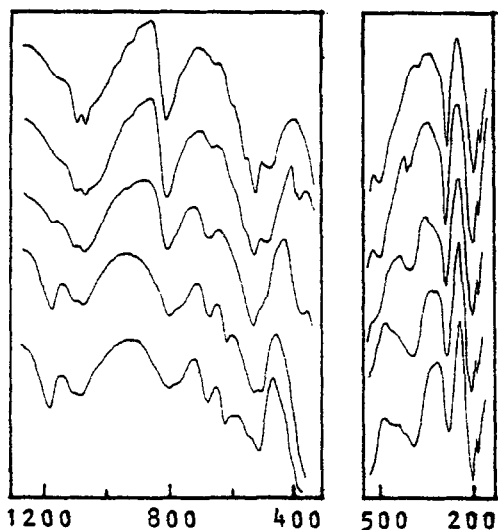


Fig. 4. The LNT spectra of a series of partially deuterated analogues of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ in the $1300\text{--}180\text{ cm}^{-1}$ region

Figs. 3 and 4), in a good agreement with the existence of only one type of water molecules in the structure.

The OD stretchings of the isotopically isolated HDO molecules have quite low frequencies, indicating a rather strong hydrogen bonding as is, indeed, found in the structure [7]. In fact, the OD frequencies can be lowered through a synergetic effect between the hydrogen bonding and metal-water interactions [8].

Three H_2O librational bands are found in the LNT infrared spectra, their frequencies and assignment being given in Fig. 5.

Because of the appearance of a band at intermediate frequency between 825 and 629 cm^{-1} (these being the wavenumber values where bands due to H_2O and D_2O librations are found), the 825 cm^{-1} band was attributed to the H_2O rocking mode. This assign-

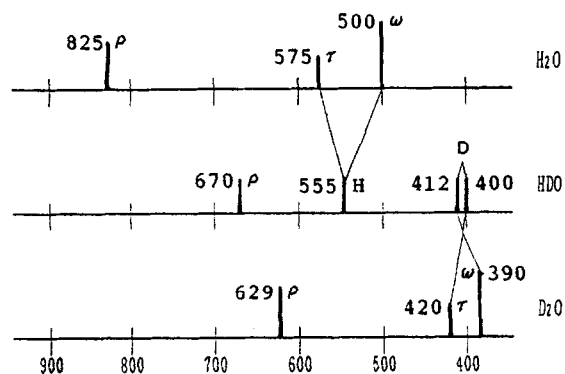


Fig. 5. Schematic representation of the position and intensity of the H_2O , HDO and D_2O librational bands

ment is in agreement with the results of our recent study of the vibrational spectra of the analogous aluminium compound [2]. The band at 575 cm^{-1} was assigned to the H_2O twisting mode on the basis of its low intensity so that the 500 cm^{-1} one could only be attributed to the H_2O wagging mode. Thus, the order of the water librational frequencies is rocking > twisting > wagging.

The results of the analysis are summarized in the schematic representation (cf. Fig. 5), the abbreviations H and D designating the out-of-plane modes of the HDO molecules resulting from the vibrational coupling of the twisting and wagging motions. It has already been shown (see [9] and the references given therein), namely, that one of the HDO modes resulting from the coupling of the wagging and twisting motions may be best described as an out-of-plane motion of the proton and the other as an out-of-plane motion of the deuteron.

The strong and irregularly shaped band, centered at around 1100 cm^{-1} , in the spectra of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

(Fig. 1) was assigned to second-order transitions involving the H₂O twisting and wagging librations, possibly with some contribution from the antisymmetric Cr-OH₂ stretching. The band originating from the Cr-OH₂ stretching fundamental is located at 546 cm⁻¹ its Cr-OD₂ analogue being found at 520 cm⁻¹.

The band at ≈ 290 cm⁻¹ was assigned to the skeletal bending vibration in which water molecules are predominantly moving whereas the bands at around 210 and 190 cm⁻¹ were attributed to lattice modes which are essentially hindered translations of the chlorine anions.

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