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INFRARED STUDY OF WATER IN $Cs_3VCl_6 \cdot 4H_2O$ AND $Rb_3VCl_6 \cdot 4H_2O$

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The appearance of two bands due to the O-D stretching vibrations of isotopically isolated HDO molecules in the spectra of partially deuterated $Cs_3VCl_6 \cdot 4H_2O$ are not consistent with the proposed space group (*Immm*) for this compound and with the alleged existence of only one type of water molecules, the protons of which form equivalent hydrogen bonds.

The two title compounds - cesium dichlorotetraaquavanadate(III) tetrachloride $Cs_3[VCl_2(H_2O)_4]Cl_4$ (a much simpler, although less informative formula $Cs_3VCl_6 \cdot 4H_2O$ will be used hereafter) and its rubidium analogue were prepared and studied by McCarthy et al. [1]. These authors determined the crystal structure of $Cs_3VCl_6 \cdot 4H_2O$ and studied in detail the low-temperature crystal absorption spectra of the two title compounds and, in less detail, their infrared spectra as well.

The crystal structure, however, was refined taking into account only the non-hydrogen atoms and should be considered as moderately reliable (an R value of 9.3% was reported). The space group *Immm* was chosen, although groups with lower symmetry (*Imm2* and *I222*) were also consistent with the observed systematic absences in the Weissenberg photographs. Since the positions of the hydrogen atoms were not determined, the orientation of the water molecules was inferred taking into consideration the possibility of formation of strong hydrogen bonds of the O-H...Cl type. All such bonds were assumed to be identical and the O...Cl distances were reported to be 303.8 pm. $Rb_3VCl_6 \cdot 4H_2O$ was believed [1] to be isomorphous with $Cs_3VCl_6 \cdot 4H_2O$.

As mentioned, some infrared data (a list of wavenumber values for the bands observed in the spectra of the protiated and deuterated samples at room temperature and a tentative assignment) were given in Ref. 1. The infrared spectra were later reported in more detail in Ref. 2, where the Raman spectra were also given.

To complement and extend these studies, we decided to investigate the spectra of the protiated compounds not only at room but also at liquid-nitrogen temperature (RT and LNT hereafter). Also studied were the spectra of samples with low deuterium content at both RT and LNT (no such studies were reported in either Ref. 1 or Ref. 2). Such a choice has been made since the study of the infrared spectra of isotopically isolated HDO molecules is known to provide valuable information about the structural characteristics of the water molecules in crystallohydrates, whereas the comparison of the RT and LNT spectra facilitates the assignment of the water librational bands. The results of such studies are partly reported in the present paper. These studies are, in essence, a continuation of our previous investigations concerning the aqua complexes of metal(III) halogenides [3-5] in which strong hydrogen bonds exist.

EXPERIMENTAL

The crystals of $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ and $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ were prepared following the procedure described in Ref. 1. The partially deuterated compounds were prepared in an analogous manner, using H_2O - D_2O mixtures (containing HCl/DCl) of appropriate composition.

The infrared spectra were recorded at room and liquid-nitrogen temperatures (RT and LNT respectively) on a Perkin-Elmer 580 infrared spectrophotometer. Both CsI pellets and mulls in Nujol were used to obtain the spectra. A VLT-2 cell, cooled with liquid nitrogen was used to record the LNT spectra.

RESULTS AND DISCUSSION

The RT and LNT spectra of $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ are shown in Fig. 1 and those of $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ are given in Fig. 2. As seen, the two sets of spectra are quite similar to each other in agreement with the suspected [1] isomorphism of the two compounds. To be more precise, the isomorphism between the two compounds *can not be ruled out* on this basis alone but further studies are required in order to ascertain the strict isomorphism between $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ on the one hand and $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ on the other.

The frequencies of the majority of the bands found in the RT spectra of the two compounds agree rather well with those reported by Michalska-Fong et al. [2].

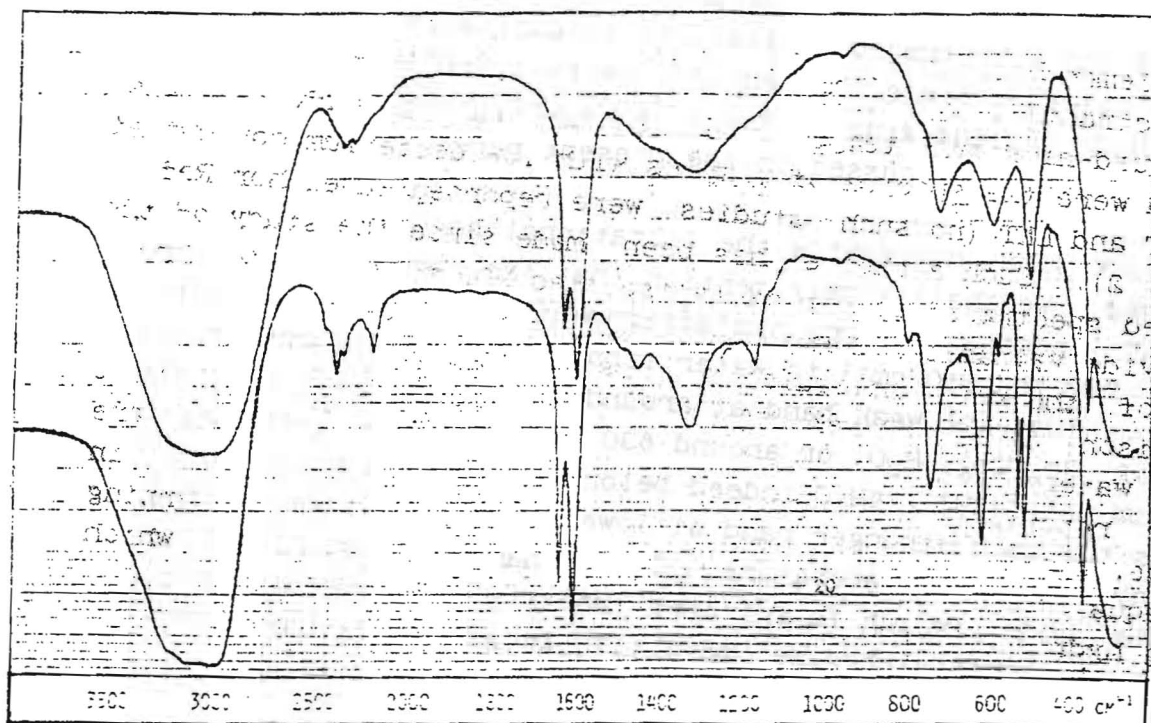


Fig. 1. IR spectra of $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ at RT (a) and LNT (b)

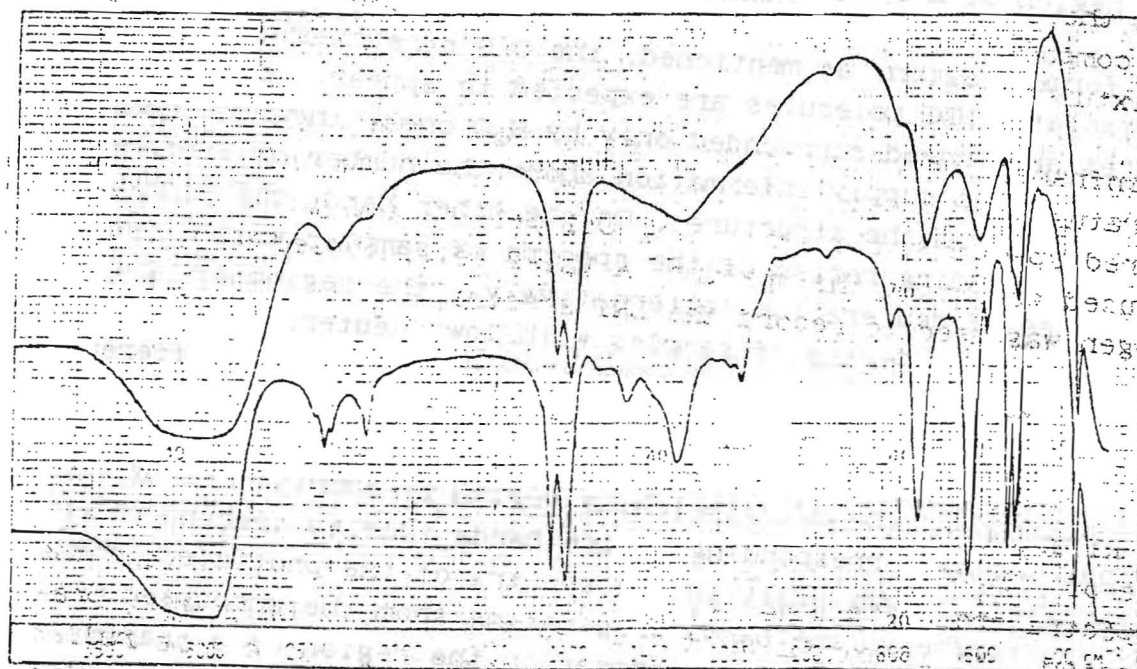


Fig. 2. IR spectra of $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ at RT (a) and LNT (b)

There is, however, a very important omission in both Ref. 1 and Ref. 2 - no mention was made of the broad bands apparently centered (at RT) around 1350 cm^{-1} in the spectra of the two titled compounds. As seen in Fig. 1 and Fig. 2, a series of quite well-

resolved bands having considerable intensity appears at LNT instead of the ill-structured features present at RT. Similar bands but at somewhat lower frequencies, were found in the spectra of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ [3] and also in those of $\text{Cs}_2\text{CrCl}_5 \cdot 4\text{H}_2\text{O}$ [5]. This region will not be discussed in the present paper.

The discussion concerning the librational bands will also be postponed. We shall simply mention that the comparison of the RT and LNT spectra confirms the assignment [1,2] of the bands at around 740 and 810 cm^{-1} to water librations. It is not certain, however, that the weak band at around 810 cm^{-1} in the LNT spectrum of $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ or around 830 cm^{-1} in the corresponding spectrum of $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ indeed belong to the same librational mode as the much stronger band at lower frequency, as claimed by McCarthy and his collaborators. It is, namely, possible that the twisting mode (which is infrared inactive for a water molecule with C_{2v} symmetry) has become active because of the symmetry lowering.

We shall instead concentrate our attention to the O-D stretching region of the spectra of samples with a low deuterium content and to the region of H-O-H bending vibrations.

In the former region, as mentioned, the O-D stretches of isotopically isolated HDO molecules are expected to appear. If the HDO molecules are indeed surrounded only by H_2O ones, then the number of O-D bands can supply information about the number of different hydrogen atoms in the structure. On the other hand, the study of the H-O-H bending region of the spectra of samples with a very high degree of deuteration (alternatively, the region of D-O-D bendings in the spectra of samples with low deuterium content) can give indications about the number of structurally different water molecules in the structure.

The situation in the O-D stretching region is complicated by the fact that in the corresponding region bands (due to second-order transitions) already exist in the spectra of the protiated compounds. Fortunately, the bands originating from the uncoupled O-D stretches of the HDO molecules appear in the region of a transmission window and are, as a consequence, visible even when the samples contain not more than 5 % deuterium (Fig. 3 and Fig. 4).

As mentioned above, according to the structural data [1], only one type of water molecules (located on a mirror plane) forming equivalent hydrogen bonds is expected to be present in the

structure. The application of group theory shows that if this is true, then in the spectra of partially deuterated (1-5 % D) analogues only one band due to the O-D stretchings of isotopically isolated HDO molecules should appear (around or below 2500 cm^{-1} , depending on the hydrogen-bond strength).

The expectations are not born out, however. As seen in Figure 3 in the LNT spectra of $\text{Cs}_3\text{VCl}_6 \cdot 4(\text{H},\text{D})_2\text{O}$ and $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ two O-D stretching bands (instead of one) are found. The frequencies of the components of the doublets are 2288 and 2278 cm^{-1} in the case of the cesium compound and 2288 and 2258 cm^{-1} for the rubidium one (the values are taken from spectra recorded from Nujol at LNT). Whereas the splitting in the former case is clearly visible only at LNT, the much larger separation of the two components in the spectrum of partially deuterated $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ makes it possible to discern the existence of two O-D stretching bands at much higher temperatures (the consecutive spectral curves are, namely, recorded as the temperature is lowered from RT to LNT).

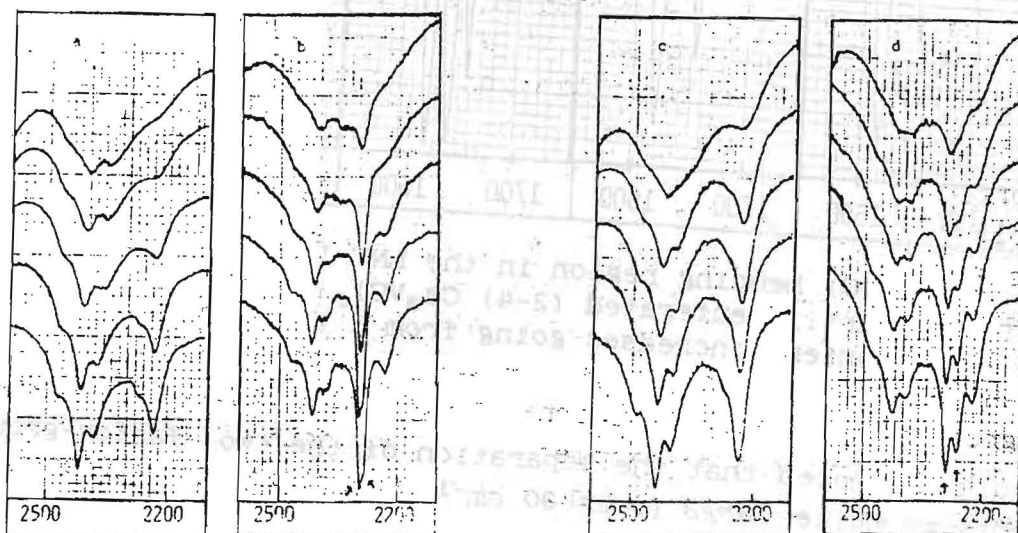


Fig. 3. Changes on cooling in the IR spectra of $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ (a,b) and $\text{Rb}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ (c,d); spectra of the protiated (a,c) and partly deuterated (b,d) species are shown. The OD stretchings are marked with arrows

It is thus certain that not all protons in either of the two compounds are equivalent, at least at low temperatures.

The study of the H-O-H bending region, on the other hand, shows that there is indeed one single type of water molecules. In the case of the protiated compounds a doublet of bands exists in each

of the spectra shown in Fig. 1 and Fig. 2. As the deuterium content in the samples is increased, however (Fig. 4), a third band appears in the transmission window between the components of the doublet. The intensity of this third band gradually increases and only a single band (flanked by two very weak satellites) is found in the spectra of the almost completely deuterated compounds instead.

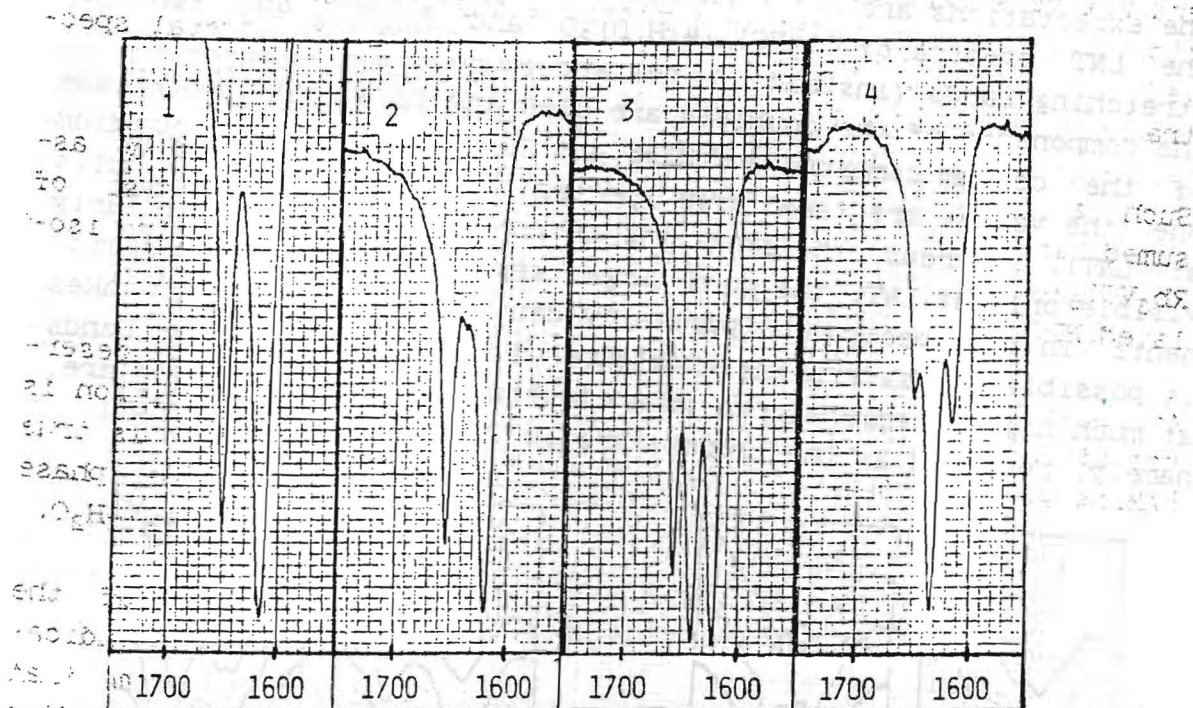


Fig. 4b. The $\delta(\text{HOH})$ bending region in the LNT IR spectra of protiated (1) and partly deuterated (2-4) $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ (the deuterium content increases going from 2 to 4)

It should be noted that the separation of the two factor-group components is quite large (over 30 cm^{-1}).

Another point worth mentioning is the fact that not all axes of the thermal ellipsoid of the oxygen atom (calculated on the basis of the published temperature factors) are real. This may be taken as another indication of incorrectly determined crystal structure. A similar situation was encountered [5] in the case of $\text{Cs}_2\text{CrCl}_6 \cdot 4\text{H}_2\text{O}$.

Taken altogether, our experimental data are not in a complete agreement with the conclusions drawn on crystallographic grounds.

Various reasons may lie behind the observed discrepancies. The one which is easiest to take into consideration is the incorrect choice of the space group. As mentioned above, two other space groups are possible and it is possible that one with lower sym-

metry should have been chosen instead. Thus, if the space group $I222$ is the correct one, then there can be no mirror plane present in the structure and the two $O \cdots Cl$ hydrogen bonds formed by the water protons need not be equivalent.

The possibility of symmetry lower than assumed, has been briefly and not very explicitly mentioned in Ref. 1 where a small rhombic distortion was taken as a possible explanation of the observed inequality of the intensities in the polarized crystal spectra recorded at two polarizations.

Such a notion (that the actual symmetry is lower than that assumed in Ref. 1) seems especially attractive for the case of $Rb_3VCl_6 \cdot 4H_2O$ where the O-D stretching bands of isotopically isolated HDO molecules are split even at room temperature.

At least for $Cs_3VCl_6 \cdot 4H_2O$, an alternative explanation also deserves attention. It is, namely, possible that a phase transition is taking place in the interval between RT and LNT. If this is true for $Rb_3VCl_6 \cdot 4H_2O$ as well, then the temperature of the phase transition must be much higher than in the case of $Cs_3VCl_6 \cdot 4H_2O$.

As seen, the two O-D stretching bands in the spectrum of the slightly deuterated $Cs_3VCl_6 \cdot 4H_2O$ are almost coincident, indicating a structure which may not be grossly different from that described in [1]. The large separation between the corresponding bands in the spectrum of $Rb_3VCl_6 \cdot 4H_2O$, on the other hand, is indicative of more drastical differences in the hydrogen bond strengths so that the two compounds may not, after all, be strictly isomorphous.

Another point worth mentioning is the very low frequency of the O-D stretching bands. Using the correlation curve published by Mikenda [6], frequencies lower than 2300 cm^{-1} would correspond to $O \cdots Cl$ distances shorter than 300 pm, i.e. much shorter than reported in [1], although even the reported $O \cdots Cl$ distances are indicative of quite strong hydrogen bonds.

It would be interesting to have the structure of $Cs_3VCl_6 \cdot 4H_2O$ rerefined and then compare the crystallographic and spectroscopic data in order to determine the reliability of the spectra-structure correlations and/or make them more reliable. Before this is done, it does not seem advisable to estimate the $O \cdots Cl$ distances in $Rb_3VCl_6 \cdot 4H_2O$ on the basis of the observed O-D frequencies. It is safe to assume, however, that one of them is shorter than in $Cs_3VCl_6 \cdot 4H_2O$.

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POVZETEK

V infrardečem spektru delno devteriranega $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ se pojavita dva trakova, ki izvirata iz valenčnih vibracij molekule HDO. Ta ugotovitev ni skladna s kristalografskimi podatki, po katerih spojina kristalizira v prostorski skupini Immm, molekule vode pa bi v njej tvorile ekvivalentne vodikove vezi.

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