

INFRARED INVESTIGATION OF THE WATER MOLECULES IN
trans-Cs₂[CrCl₂(H₂O)₄]Cl₃

Viktor Stefov, Bojan Šoptrajanov and Vladimir Petruševski

Institute of Chemistry, Faculty of Science, Arhimedova 5,
 91000 Skopje

The infrared spectra of the title compound were investigated at both room and liquid-nitrogen temperature. The spectra of the partly deuterated analogue are not in agreement with the structure of the compound [1], indicating that either a disorder of the water molecules is present or the structure (space group) is incorrectly determined.

INTRODUCTION

The infrared spectra of various M^{III}Cl₃·xH₂O compounds have been very extensively studied in our laboratory. The general feature of such compounds, when the cation is a *p* or *d* element (e.g. AlCl₃·6H₂O or CrCl₃·6H₂O, VCl₃·6H₂O etc.), is the existence of strong hydrogen bonds between water molecules and chlorine atoms. Multiple bands in the stretching and/or bending region of the IR spectra of such compounds are often found, indicating that the water vibrations are highly anharmonic. The present investigation represents a continuation of our study of aqua complexes of trivalent cations.

EXPERIMENTAL

The crystals of Cs₂[CrCl₂(H₂O)₄]Cl₃ were obtained following the procedure described in [1]. The results of the elemental and thermal analysis were in agreement with the formula Cs₂CrCl₅·4H₂O. The IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer as KBr pellets and mulls in *Nujol*. The LNT spectra were recorded using a VLT-2 cell. Deuterated samples were obtained by recrystallization of the compound from HCl (*c* = 6 mol·dm⁻³) containing ~ 5% D.

RESULTS AND DISCUSSION

The RT and LNT spectra of $\text{Cs}_2[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$ are shown in Fig. 1.

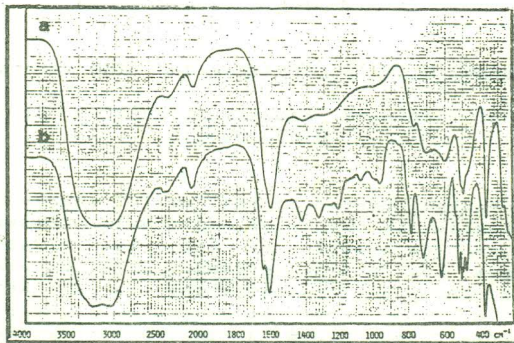


Fig. 1 : IR spectra of $\text{Cs}_2[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$ at RT (a) and LNT (b)

The crystals of the title compound are monoclinic, space group $C2/m$ ($C2h^3$) with $Z = 2$. The water molecules and two of the chlorine atoms are coordinated to Cr, the complex cation having an almost ideal D_{2h} symmetry. All water molecules are crystallographically equivalent and lie on sites with symmetry 1. The hydrogen bonds are of the $\text{O}-\text{H}\cdots\text{Cl}$ type, the donor-acceptor distances being : $R(\text{O}\cdots\text{Cl}_1) = 300.6$ pm and $R(\text{O}\cdots\text{Cl}_2) = 306.2$ pm (indicating rather strong hydrogen bonding).

The general appearance of the spectra (broad and low-lying bands due to the H_2O stretching vibrations) suggesting that the hydrogen bonds are rather strong is in agreement with the crystallographic results [1]. However, instead of *two* bands originating from OD stretchings, *three* bands are found in the spectra of samples with low deuterium content, the one with highest frequency being the most intense (cf. Fig. 2). This clearly shows that there is *more than one* type of water molecules in the crystal and may point either to the presence of disorder or to an incorrectly determined crystal structure. In order to decide which of the above possibilities is more probable, we calculated, using the published [1] anisotropic displacement factors, the r.m.s. amplitudes of all atoms in the structure (cf. Table I).

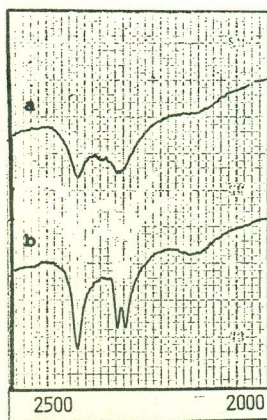


Fig. 2 : The isolated OD stretching bands in the RT (a) and LNT (b) IR spectra of partly deuterated $\text{Cs}_2[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$

Table I : R.m.s. amplitudes of the atoms in $\text{Cs}_2[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ (*i* - imaginary value)

Atom	(r.m.s. amplitude along the principal axes of the thermal ellipsoid)/pm		
Cs	18.8	17.6	12.9
Cr	16.0	11.6	4.7
Cl ₁	19.1	18.0	8.1
Cl ₂	21.5	17.0	<i>i</i>
Cl ₃	20.8	18.6	<i>i</i>
O	90.9	<i>i</i>	<i>i</i>

As seen from Table I, the r.m.s. displacements of Cr are highly anisotropic and the calculated value for one axis of the thermal ellipsoid for the O atom is, for all practical purposes, equal to the O-H bond length in the majority of crystalline hydrates, which is absolutely unrealistic (even the isotropic *B*-factor for the O atom is unusually large). In addition, the thermal ellipsoids of Cl₂, Cl₃ and O are not even real. This, of course, means that the displacement parameters of these atoms do not have any physical significance. It seems that both findings (three OD stretching bands in the LNT IR spectra and either highly anisotropic displacements or lack of their physical meaning at all)

indicate that the structure is incorrectly determined. This assumption is further supported by the fact that the conditions limiting the possible reflections are consistent with three different space groups: $C2$, Cm and $C2/m$. Finally, the R value was found to be 12.6%, thus showing a rather poor agreement between the calculated and observed structural factors.

As far as the IR spectra are concerned, it should be noted that, as in *trans*- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ [2] and in many other hydrates, multiple bands exist in the HOH bending region of the IR spectra. The reasons for the appearance of these bands are still not clear, although it was proposed [3] that the existence of multiple bands in the water bending region could be taken as an evidence for a pronounced anharmonicity of the H_2O normal modes.

The investigation of the IR spectra of the isomorphous [4] vanadium compound is in progress.

REFERENCES

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ИЗВОД

ИСПИТУВАЊЕ НА ВОДАТА ВО *trans*- $\text{Cs}[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$
СО ПОМОШ НА ИНФРАЦРВЕНА СПЕКТРОСКОПИЈА

Виктор Стефов, Бојан Шоптрајанов и Владимир Петрушевски

Институт за хемија, ПМФ, Архимедова 5, 91000 Скопје

Испитувани се инфрацрвените спектри на комплексното соединење *trans*- $\text{Cs}_2[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$, снимени на собна и на ниска температура. Спектрите на парцијално деутерираните соединенија не се во согласност со објавените податоци за структурата на соединението [1]. Макар што ова може да укажува на постоење на несреденост на молекулите вода во ова соединење, веројатно е дека структурата на соединението не е точно определена.