

INFRARED SPECTRA OF PROTIATED AND DEUTERATED COBALT ACETATE DIHYDRATE

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ABSTRACT

The infrared spectra of cobalt acetate dihydrate provide a direct evidence for the existence of quite strong hydrogen bonds formed by the water protons. An intense band is, namely, found around 2750 cm^{-1} , several additional bands are present at lower frequencies and bands originating from water librations appear above 1000 cm^{-1} . The existence of a band around 3310 cm^{-1} , on the other hand, indicates that much weaker hydrogen bonds are also present. On deuteration the protons involved in stronger hydrogen bonds are apparently replaced by deuterons to a higher degree than those forming weaker H-bonds.

INTRODUCTION

As part of our studies of various crystallohydrates, particularly of those interesting from the point of view of the hydrogen bonding in which the water protons take part [1-4], we now report the infrared spectra of protiated and deuterated cobalt acetate dihydrate recorded at room temperature (RT) and at temperatures down to that of liquid nitrogen (LNT). Parts of the infrared spectrum of the protiated form at RT have already been reported by Stoilova *et al.* [5], the agreement with our spectra being not always perfect.

EXPERIMENTAL

Cobalt acetate dihydrate was prepared (according to the method described by Balarew *et al.* [6]) by crystallization from acetic acid-water mixtures of appropriate composition and was recrystallized from the same solvent. The identity of the crystals was checked thermogravimetrically. Deuterated analogues were obtained similarly with mixtures of D_2O and CH_3COOD being used as a solvent. Partial deuteration was accomplished likewise using solvent mixtures with varying H/D ratios. The infrared spectra were recorded on a Perkin-Elmer 580 instrument equipped with a VLT-2 cell.

RESULTS AND DISCUSSION

The infrared spectra of cobalt acetate dihydrate, recorded at RT and LNT are reproduced in Fig. 1.

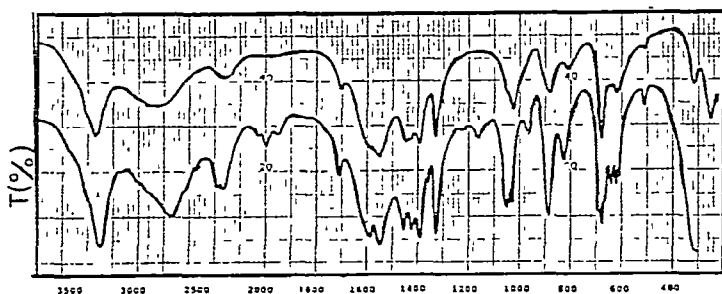


Fig. 1. Infrared spectra at RT (upper curve) and at LNT of cobalt acetate dihydrate

Immediately noticeable are the bands below 3000 cm^{-1} which are indicative of quite strong hydrogen bonding. Thus, the intense band around 2750 cm^{-1} is over 200 cm^{-1} lower than the corresponding band in the spectrum of cobalt acetate tetrahydrate and almost that much lower than the similar band in the spectrum of nickel acetate tetrahydrate, despite the fact that in the latter compound one of the protons is involved in a rather strong, linear hydrogen bond (the $O_w \cdots O$ distance being 261.9 pm) [7]. In fact, judging from the frequencies of the bands in the OH stretching region, it seems safe to conclude that the hydrogen bonds formed by some of the water protons in cobalt acetate dihydrate are quite strong and, perhaps, among the strongest ones formed by water hydrogens. It should be noted that in the OH stretching region a relatively sharp band at around 3310 cm^{-1} is also present and, thus, the existence of much weaker hydrogen bonds is also indicated.

In cases of $O-H \cdots O$ hydrogen bonds of considerable strength, a trio of bands (usually called A,B,C trio) is as a rule observed below 3000 cm^{-1} [8,9] and in our case the bands observed in this same region can probably be identified as the components of such a trio. It should be borne in mind, however, that in hydrates the analogues of $\delta(OH)$ and $\gamma(OH)$ have frequencies which differ from those in the usually studied hydrogen-bonded systems and that, con-

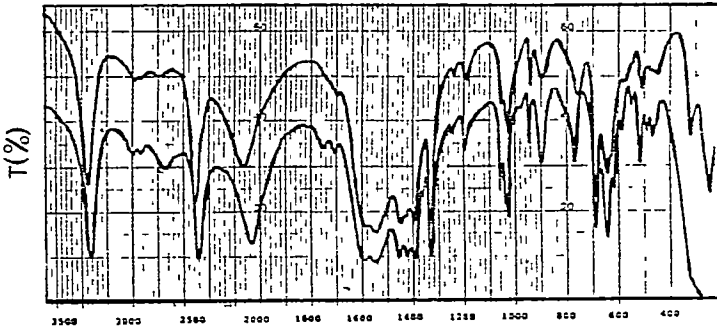


Fig. 2. Infrared spectra at RT and LNT of almost completely deuterated cobalt acetate dihydrate.

sequently, the explanation given for the origin of the trio [10] can not be used in its original form.

In line with the deduced strength of some of the hydrogen bonds is the appearance of water librational band(s) above 1000 cm^{-1} . Thus, a strong band which at RT overlaps the methyl rocking ones, clearly shows up at LNT (Fig. 1) and is shifted to $\approx 770\text{ cm}^{-1}$ in the spectrum of the deuterated analogue (Fig. 2), so that there is no doubt that it originates from a water librational motion. At least one additional band at even higher frequency is, however, observed in the RT spectrum of the protiated form. It too disappears on deuteration and must, therefore, be related to some water mode, probably again librational in character.



Fig. 3. Infrared spectra of partially deuterated samples of cobalt acetate dihydrate

Several other temperature- and deuteration-sensitive bands are found at lower frequencies (Fig. 3), the gradual increase on deuteration of the band around 945 cm^{-1} being an indication that here, just as in a number of other instances, a water-anion vibrational coupling between the carboxylate vibrations (in this case ν_4 of the acetate) and water librations is taking place.

It should be noted that on deuteration the protons involved in stronger hydrogen bonds are replaced by deuterons to a higher degree than those forming weaker H-bonds (see Fig. 2). Such a behaviour does not seem to be exceptional and has been observed in other systems as well [1].

ACKNOWLEDGEMENT

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