231

INFRARED STUDY OF COBALT ACETATE DIHYDRATE AND ITS PARTIALLY DEUTERATED ANALOGUES*

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The infrared spectra of protiated cobalt acetate dihydrate and of a series of its partially deuterated analogues were recorded at room temperature (RT) and at temperatures down to the liquid-nitrogen temperature (LNT). An assignment of the acetate bands is proposed. Attention is paid to the bands due to internal and external vibrations of the water molecules. The spectra indicate that some of the water hydrons are involved in the formation of strong hydrogen bonds which are apparently among the strongest existing in crystallohydrates.

INTRODUCTION

The vibrational spectra of the hydrated cobalt, nickel, iron, manganese and magnesium acetates have been quite extensively studied [1-8]. As a rule, however, the *tetrahydrates* were investigated, the only reported data on the spectra of cobalt acetate *dihydrate* (in addition to the short account given by us [9]) seem to be those of Stoilova *et al.* [3].

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* Dedicated to professor Dušan Hadži on the occasion of his seventieth birthday with appreciation of what he has done for spectroscopy in general and for spectroscopy in Skopje in particular.

Unfortunately, the spectra reported by Stoilova *et al.* [3] are only fragmentary and of rather poor quality. Furthermore, the work of these authors has been devoted mainly to the search for reliable spectroscopic criteria for the prediction of the type of bonding (monodentate, bridging etc.) of the acetate ions in crystals.

In reference [9], on the other hand, the acetate bands were only briefly mentioned (mainly in the context of their apparent coupling with water modes), the emphasis being put to the appearance of the bands in the O-H stretching region and to the water librational bands. It was concluded that some of the protons must be involved in the formation of quite strong hydrogen bonds. No direct crystallographic evidence is available to corroborate such a conclusion.

In view of the interesting features characterizing the spectra of cobalt acetate dihydrate (especially the above-mentioned indication for the presence of quite strong hydrogen bonds) and the incompleteness of the existing spectral data, we decided to complement our previous studies by investigating more closely the spectra of the protiated and almost completely deuterated cobalt acetate dihydrate and those of a series of partially deuterated analogues with varying deuterium content. In addition to that, we tried to assign, as completely as possible, the acetate bands in the infrared spectrum of this compound.

EXPERIMENTAL

The preparation of cobalt acetate dihydrate was accomplished following the procedure described by Balarew *et al.* [10]. Solid commercial cobalt acetate was dissolved in an acetic acid-water mixture and left to crystallize. The composition of the ternary system was such as to ensure [10] that the crystals were those of the dihydrate rather than the tetrahydrate. The crystals were recrystallized from an analogous mixture of acetic acid and water. The almost completely deuterated analogue was prepared and recrystallized in a similar manner, but using a CH_3COOD/D_2O mixture as a solvent. During the preparation and the recrystallization of the partially deuterated analogues, mixtures with appropriate deuterium content were employed.

The identity of the samples was checked by elemental and thermogravimetric analysis.

The infrared spectra were recorded, from KBr pressed disks, on a Perkin-Elmer 580 infrared spectrophotometer. A VLT-2 cell cooled with liquid nitrogen was used for recording the low-temperature spectra.

RESULTS AND DISCUSSION

The infrared spectra of the protiated and almost completely deuterated cobalt acetate dihydrate, recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) are shown in Fig. 1 and Fig. 2 respectively. The wavenumber values ("frequencies") of the observed bands, together with a qualitative estimate of their intensity and a tentative assignment are listed in Table 1. The discussion which follows will be divided into parts dealing with the acetate vibrations and the water modes.

Acetate vibrations

The comparison of the spectra of the protiated and deuterated cobalt acetate dihydrate facilitates the differentiation between the bands which originate from vibrations localized mainly in the acetate ions from those due to modes which are predominantly internal water motions or hindered rotations or translations of the water molecules.

Thus, in the region around 1600 cm^{-1} where the appearance of the antisymmetric COO stretches* is expected, a doublet is observed, the frequencies of the components being only slightly sensitive to deuteration. This, of course, shows that they are indeed due to *acetate* vibrations. On the other hand, a band is present around 1710 cm^{-1} in the spectra of the protiated compound but is absent in the spectra of the deuterated analogue so that it is clear that it originates from a water mode.

The separation of the components of the doublet attributed to the antisymmetric COO stretches is more clearly visible at LNT (the frequencies of the components being 1595 and 1554 cm^{-1}) but even at RT it is clear that more than one band exist in the corresponding region. We would like to stress that the appearance of two bands related to the antisymmetric COO stretching vibrations does not automatically *prove* that two types of acetate groups are present in the structure of cobalt acetate dihydrate. Other effects (e.g. strong correlation-field interactions), namely, may be responsible for the doubling and in the spectra of many acetates two (or even more) bands exist in the 1600 cm^{-1} region. As will be seen, in the spectrum of the presently studied compound a number of other acetate bands are also split, making the existence of non-equivalent acetate ions more plausible.

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* The descriptions of the modes are only *approximate*. They are based on the results of a normal-coordinate analysis for the "free" acetate ion [11], but only the coordinate with the major contribution to the normal mode is used as a label.
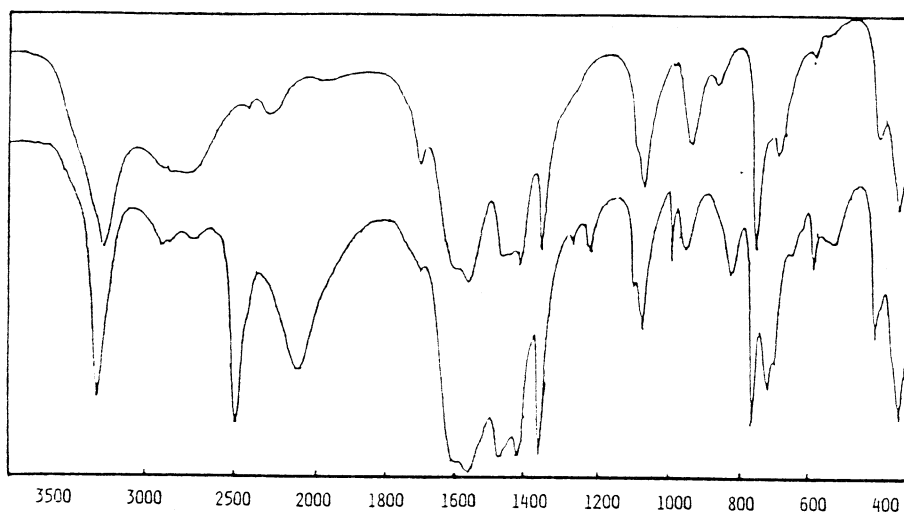
Fig. 1. Room-temperature (RT) spectra of the protiated (**a**)
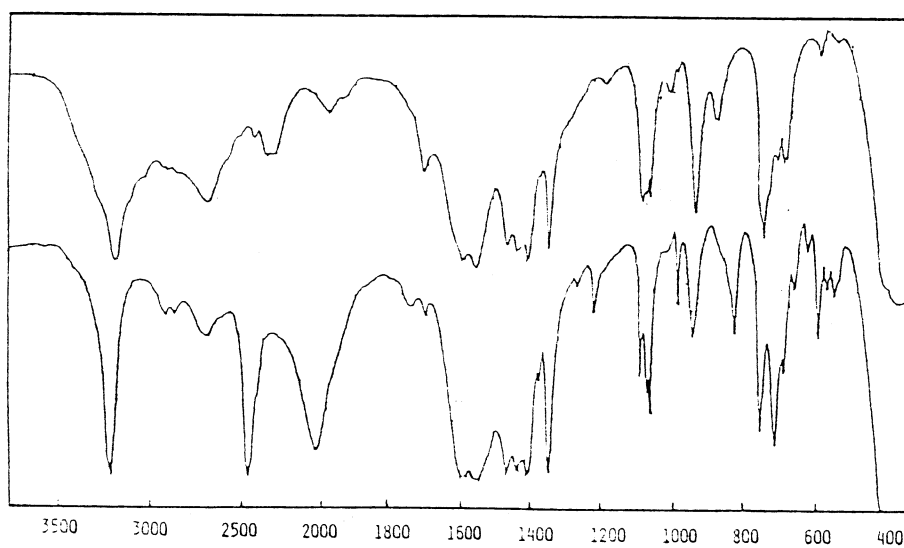and deuterated (**b**) cobalt acetate dihydrate

Fig. 2. Low-temperature (LNT) spectra of the protiated (**a**)
and deuterated (**b**) cobalt acetate dihydrate

TABLE 1

Infrared frequencies and a tentative assignment of the major
bands in the spectrum of cobalt acetate dihydrate (LNT values)

Frequency cm^{-1}	I*	Assignment**	Frequency cm^{-1}	I*	Assignment**
3310	vs	OH stretch	1330	vs	CH$_3$ s bend
2965***		CH$_3$ stretch	1230	vw	H$_2$O libration
2940***		CH$_3$ stretch	1165	w	H$_2$O libration
2750	vs	OH stretch	1055	sh	CH$_3$ rock
2390	m	OH stretch	1050	ms	(overlapped
2340	m	(see text)	1038	m	with H$_2$O
			1028	m	libration)
2055	vw		968	w	H$_2$O libration
2000	vw	see text			(coupled with
1955	vw		888	m	C-C stretch)
1713	w	HOH bend	830	w	H$_2$O libration
1610	sh	HOH bend	687	sh	
1595	vs	COO as stretch	680	s	OCO bend
1554	vs	COO as stretch	665	sh	
1460	s	CH$_3$ as bend	640	m	
1430	s	COO s stretch	622	m	COO wag
1420	sh	COO s stretch?	612	mw	
1395	vs	CH$_3$ as bend			
1355	vw	CH$_3$ s bend	515	vw	COO rock

* The abbreviations have the usual meaning : s - strong, m - medium,
w - weak, v - very, sh -shoulder.

** Only the major contributions to a given mode are listed. The abbre-
viations *as* and *s* mean *antisymmetric* and *symmetric* respectively.

*** Observed only on high degree of deuteration.

The frequency of the centroid of the doublet is close to the frequency (1575 cm^{-1}) reported [12] for sodium acetate.

Whereas the location of the bands which are related to the antisymmetric COO stretches is easy and unequivocal, the exact identification of the band(s) due to the symmetric COO stretching vibration(s) is, as in the case of other acetates, complicated and rather unreliable. The reason for this is clear : the expected frequency of the symmetric COO stretch, namely, is close to the frequencies of the methyl antisymmetric bendings and there is no straightforward way to distinguish the former from the latter without resorting to isotopic substitution of the carbon and/or oxygen atoms.
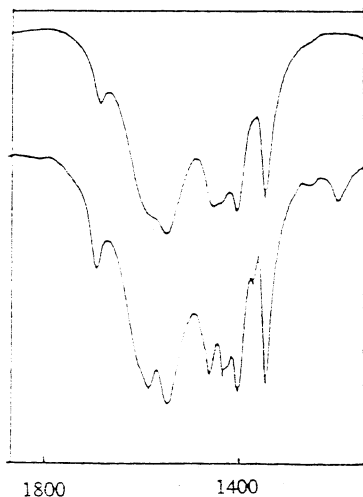
As seen in Figs. 1 and 2, and, more clearly, in Fig. 3, several bands are found in the 1500-1300 cm^{-1} region. The rather strong band located around 1330 cm^{-1} (and probably the weak one at 1355 cm^{-1}) are undoubtedly due to the *symmetric* CH$_3$ bending, leaving the three bands located between 1460 and 1380 cm^{-1} to be assigned to the antisymmetric CH$_3$ bending and to the symmetric COO stretching modes. The appearance of the presently studied spectra in this region is similar to that of the Cu$_2$(CH$_3$COO)$_4$·2H$_2$O spectrum studied by Heyns [13]. Analogous is even the temperature behavior of the bands, the one in the middle gaining in intensity when the temperature is lowered.

Fig. 3. The RT and LNT spectra in the 1500-1300 cm^{-1} region

Accepting the suggestion by Heyns [13] that the evident temperature sensitivity of the intensity of a band in the region around 1400 cm^{-1} can be used as a criterion for assigning it to the symmetric COO stretch, we can attribute the band at around 1430 cm^{-1} to such motions in the crystals of Co(CH$_3$COO)$_2$·2H$_2$O. In fact, there may be more than one band related to such vibrations. The above frequency is, as should be noted, slightly *higher* than in the case of the *ionic* acetates, 1414 cm^{-1} being the value reported [12] for sodium acetate.

A *complex* of overlapping bands centered around 1040 cm^{-1} is found in the spectrum of Co(CH$_3$COO)$_2$·2H$_2$O, again looking

quite alike the analogous bands in the spectrum of
Cu$_2$(CH$_3$COO)$_4 \cdot$2H$_2$O. *Two* different CH$_3$ rocking vibrations are
expected to appear in this region and the existence of
different acetates in the structure and/or vibrational in-
teractions could increase the number of observed bands. As
seen in Fig. 4, however, not all bands in this region are
due to the methyl rocking motions. In fact, both the tempe-
rature lowering (Fig. 4 **a**) and the gradual increase in the
deuterium content (Fig. 4 **b**) bring about changes in the
spectral picture. It is thus clear that in the spectrum of
the protiated compound a water librational band is overlap-
ped with the bands originating from the methyl rocking
motions as has already been pointed out [9]. The same is
true for the bands found around 900 cm^{-1} where the acetate
C-C stretches are expected to appear. These regions will be
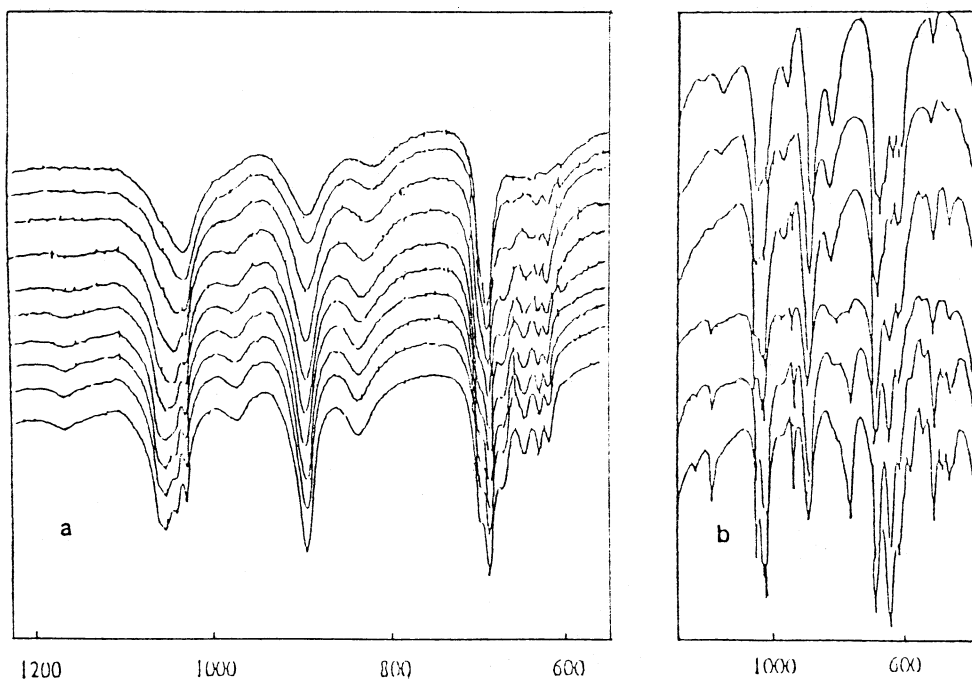discussed in more detail later.

Fig. 4. Changes in the 1200-600 cm^{-1} region on lowering
the temperature (**a**) and gradual deuteration (**b**)

The methyl stretching bands are easy to observe (around 2965
and 2940 cm^{-1}) only in the spectra of the deuterated samples
with a high deuterium content. In the spectra of the proti-
ated compound these surprisingly weak bands are overlapped
by the intense water stretching bands (see below).

Three modes with COO character (OCO bending, COO wagging and COO rocking respectively) for each acetate ion are expected in the low-frequency region (below 700 cm⁻¹). A rather strong band (with two shoulders on it) observed around 700 cm⁻¹ can be attributed to the OCO bending modes of the acetates present in the structure, whereas the three much weaker bands with frequencies 640, 622 and 612 cm⁻¹ probably originate from the COO wagging ones. The latter assignment is somewhat tentative since in the spectrum of the deuterated analogue, a strong D_2O librational band appears in the corresponding region and the situation at intermediate degrees of deuteration is not entirely unambiguous.

A clear candidate for the rocking COO vibration is the weak and single band found around 515 cm⁻¹. In their paper (ref. [3]) Stoilova *et al.* proposed, as a spectroscopic criterion for the existence of *monodentate* acetates, the presence of a *strong* band around 540 cm⁻¹. The band observed here is certainly not strong and its frequency is lower than the value given in [3] so that it is difficult to decide whether or not the presence of the 515 cm⁻¹ band fits the criterion of Stoilova *et al.* [3]. We have shown [14], however, that the criteria proposed by these authors are (at least in some cases) based on an erroneous assignment of the observed bands.
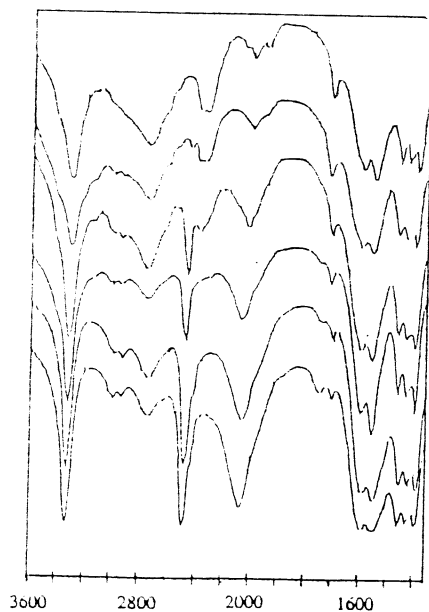

Fig. 5. The changes on deuteration in the 3600-1500 cm⁻¹

3600   2800   2000   1600

Water vibrations

Probably the most interesting point concerning the water vibrations is the appearance of bands in the stretching region whose shape and position strongly suggest that the hydrogen bonds in which some of the water protons take part are of quite considerable strength. The existence of an additional band at frequencies higher than 3300 cm⁻¹, on the other hand, show that weaker hydrogen bonds are also present. These features were briefly dealt with in [9].

The highest-lying of the water stretching bands has a frequency of ≈ 3345 cm⁻¹ at RT and ≈ 3310 cm⁻¹ at LNT. The positive temperature coeffi-

cient is not unexpected and is generally encountered, except, as pointed out by Falk *et al.* [15], in cases of weak and strongly bent or bifurcated hydrogen bonds formed by the water hydrons. When the deuterium content in the sample is gradually increased (Fig. 5), the shape and frequency of the band do not change to an appreciable degree, suggesting that it is due to a practically uncoupled O-H mode of water molecules in which the hydrons are involved in the formation of hydrogen bonds with quite different strength. That much stronger hydrogen bonds are indeed formed is beyond any doubt since bands are found at frequencies which are much lower than 3300 cm^{-1}.

The most intense among these latter bands is located near 2750 cm^{-1}, but additional bands with considerable intensity exist at still lower frequencies, especially at LNT (Fig. 2). In fact, the feature centered around 2000 cm^{-1} is visible only at LNT, whereas in the RT spectrum there is hardly any trace of a band in this region. Several of the bands in the 3200-1900 cm^{-1} are split at LNT but the whole feature is highly reminiscent of the *A,B,C* trio [16-18] characteristic for systems in which there are hydrogen bond of considerable strength. We have encountered a similar spectral picture in the case of other crystallohydrates in which the water molecules are involved in rather strong hydrogen bonds but the components of the trio were at *higher* frequencies. Such is the case, for example, with nickel acetate *tetrahydrate* [19], in the structure of which there is a linear hydrogen bond with $R(O_w \cdots O) = 261.9$ pm [20], quite strong for a crystallohydrate. In the spectrum of this compound, however, the frequency of the *A* component of the trio is almost 200 cm^{-1} *higher* than in the presently studied compound. It thus seems that the hydrogen bonds in the case of cobalt acetate dihydrate should be considerably shorter than 260 pm, being among the *strongest* ones encountered in crystallohydrates.

On progressive deuteration, the analogue of the 2750 cm^{-1} band appears around 2080 cm^{-1} and gradually gains in intensity (Fig. 5). The fate of the other components of the trio is less clear, although the analogues of the 2390/2340 cm^{-1} doublet are certainly responsible for the appearance of one or more new bands around 1750 cm^{-1} in the spectra of the deuterated compounds.

It must be pointed out (as has already been done [9]) that in the case of crystallohydrates, the explanation for the origin of the trio proposed by Claydon and Sheppard [18] can not be applied in its original form. Namely, the fundamentals whose overtones are to interact with the O-H stretch, in the case of *water molecules* have not only different form, but also different frequencies than the in-plane and out-of-plane O-H bendings in systems in which *O-H* rather than *H-O-H* hydrons are involved in the formation of hydrogen bonds with similar strength.

As seen in Fig. 1 and Fig. 2 (and as has already been mentioned), the band observed above 1700 cm^{-1} in the spectrum of the protiated form has practically disappeared in the RT spectrum of the highly deuterated analogue. In view of the considerable strength of the hydrogen bonds formed by some of the water hydrons, it would not be unreasonable to attribute the 1710 cm^{-1} band to an H-O-H bending vibration. Its D-O-D analogue could be the band found around 1250 cm^{-1} in the LNT spectrum of the sample with high deuterium content. An additional, even more intense, new bands is present in the latter spectrum below 1200 cm^{-1} suggesting that either two types of water molecules are present in the structure or that, alternatively, multiple bands [21-23] appear in the H-O-H (and/or D-O-D) bending region.

As is well-known, the location of the librational bands is facilitated if the spectra are recorded at various temperatures. As the temperature is lowered, namely, the bands which are due to water librations shift towards higher frequencies and gain, at least apparently, in intensity.

The changes of the spectral picture in the 1100-600 cm^{-1} region on lowering the temperature are shown in Fig. 4 **a**. As seen, the above-described behaviour is characteristic for a number of bands in this region. Such are, for example, the bands at 1165, 970 and 830 cm^{-1} (LNT values) but also some of those below 700 cm^{-1} and, particularly important, of those found around 1050 cm^{-1} and 890 cm^{-1}. All these temperature-sensitive bands must be, in one way or another, related to water librations.

The last two of the above-mentioned regions are, as recalled, those in which the CH_3 rocking and the C-C stretching vibrations are expected to appear. The situation is simpler in the 1100-1000 cm^{-1} region where the three bands remaining in the spectrum of the almost completely deuterated sample have shapes and frequencies which are almost identical with those of three of the components of the feature present in the spectrum of the protiated compound. The librational band around 1050 cm^{-1} is, then, simply overlapping the methyl rocking ones without entering into vibrational interactions with them.

Contrary to that, the deuteration produces more pronounced changes in the 1000-800 cm^{-1} region. On deuteration, namely, a sharp band appears around 945 cm^{-1} and gradually gains in intensity as the deuterium content in the sample increases (cf. Fig. 4 b). The latter frequency is quite close to that expected for an acetate mode, mainly C-C stretching in character. The changes observed on deuteration, however, show that in the protiated compound this mode interacts with the librational water mode appearing in the same region. The

situation is, thus, similar to that encountered in the spectrum of nickel acetate tetrahydrate [7] where a similar interaction between the acetate C-C stretch and one of the librations of the water molecules takes place.

It should be noted that the highest-lying of the water librational bands observed in the spectrum of $Co(CH_3COO)_2 \cdot 2H_2O$ has a frequency which is *very high* for such a mode. In view of the exceptionally strong hydrogen bonds present in the structure of this compound, such high frequencies of the water librations should not be surprising, since the hydrogen bonding must be a very important factor among those which determine the frequencies of the water librational modes.

REFERENCES

1. A.I. Grigor'ev, *Zh. Neorg. Khim.*, **8**, 802 (1963).

2. D.A. Edwards and R.N. Hayward, *Can. J. Chem.*, **16**, 3443 (1968).

3. D. Stoilova, G.St. Nikolov and Ch. Balarev, *Izv. Khim.*, **9**, 371 (1976).

4. P. Baraldi and G. Fabri, *Spectrochim. Acta*, **37A**, 89 (1981).

5. G.S. Raghuvanshi, M. Pal and H.D. Bist, *J. Raman Spectrosc.*, **14**, 1 (1983).

6. G.S. Raghuvanshi, M. Pal, M.B. Patel and H.D. Bist, *J. Mol. Struct.*, **101**, 7 (1983).

7. B. Šoptrajanov and M. Ristova, *J. Mol. Struct.*, **115**, 359 (1984).

8. G.S. Raghuvanshi and H.D. Bist, *Chem. Phys. Lett.*, **103**, 507 (1984).

9. M. Ristova and B. Šoptrajanov, *J. Mol. Struct.*, **115**, 355 (1984).

10. Chr. Balarew, D. Stoilova and L. Demirev, *Z. Anorg. Allgem. Chem.*, **410**, 75 (1974).

11. K. Nakamura, *J. Chem. Soc. Japan*, **79**, 1411 (1958).

12. K. Ito and H.J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).

13. A.M. Heyns, *J. Mol. Struct.*, **11**, 93 (1973).

14. L. Šoptrajanova and B. Šoptrajanov, to be published.

15. M. Falk, C.H. Huang and O. Knop, *Can. J. Chem.*, **52**, 2380 (1974).

16. D. Hadži, *Pure Appl. Chem.*, **11**, 435 (1965).

17. D. Hadži and S. Bratos in P. Schuster, G. Zundel and C. Sandorfy (eds.), *The Hydrogen Bond*, Vol. II, North-Holland, Amsterdam, 1976, p. 565.

18. S.F. Fischer, G.L. Hofacker and M.A. Ratner, *J. Chem. Phys.*, **52**, 1934 (1970).

19. M. Ristova, *MS Thesis*, University of Skopje, Skopje, 1981.

20. T.C. Downie, W. Harrison, E.S. Raper and M.A. Hepworth, *Acta Crystallogr.*, **B27**, 706 (1971).

21. B. Šoptrajanov, V. Petruševski, M. Ristova and M. Trpkovska, *Horizons in Hydrogen Bond Research, Poster Abstracts*, Sånga-Säby (Sweden), 1980.

22. M. Ristova and B. Šoptrajanov, *J. Mol. Struct.*, **142**, 75 (1986).

23. L. Šoptrajanova, B. Šoptrajanov and G. Jovanovski, *J. Mol. Struct.*, **142**, 63 (1986).

Povzetek

Infrardeče spektre kobaltovega acetata dihidrata in serije njegovih delno devteriranih analogov smo posneli pri sobni temperaturi in temperaturi vrelišča tekočega dušika. Poimenovali smo trakove acetatnih skupin, posebno pozornost pa smo namenili trakovom, ki jih povzročajo notranja in zunanja nihanja molekul vode. Spektri kažejo na to, da nekatere molekule vode sodelujejo pri nastanku močnih vodikovih vezi, ki spadajo med najmočnejše, kar jih poznamo pri kristalohidratih.