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IR study of dibarium copper formate tetrahydrate

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Abstract

The infrared spectra of $Ba_2Cu(HCOO)_6$ ·4H₂O and its deuterated analogues have been recorded and the internal modes of the formate groups and water molecules are reported. Some of the internal formate modes (ν_4 , ν_3 and ν_2) reflect the existence of three crystallographically independent formate ions. The frequency separations between the asymmetric and symmetric C–O stretching modes is explained in terms of different C–O bond lengths within each formate group. The number and positions of the bands in the high-frequency region (4000–2300 cm⁻¹) is evidence for the existence of two inequivalent water molecules. The librational modes of the water molecules are also discussed. © 1997 Elsevier Science B.V.

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1. Introduction

The great interest in the metal formates is determined by their interesting physical properties. For example, among the formates $LiHCOO\cdot 2H_2O$ [1], NaHCOO [2], $Sr(HCOO)_2$ [3], $Ba(HCOO)_2$ [4] are known as useful nonlinear materials for optical device applications. The metal (II) formates (simple or double) form the corresponding oxides at comparatively low temperatures which are used as catalysts.

While the simple metal (II) formates are widely studied by means of IR and Raman spectroscopy methods [5–12] the literature data of the double salts formed by two divalent metals are scanty. Data of vibrational spectra of BaCd(HCOO)₄·2H₂O are given in Ref. [13]. The purpose of the present paper is the infrared study of Ba₂Cu(HCOO)₆·4H₂O, the crystals of which are of interest because of their paramagnetic property.

2. Experimental

Barium formate and copper formate dihydrate were prepared by neutralization of barium carbonate and copper hydroxide carbonate with dilute formic acid solutions at $60-70^{\circ}$ C. The used reagents were "p.a." quality (Merck). The double salt Ba₂Cu(H-COO)₆·4H₂O was prepared by crystallization from mixed barium copper formate solutions according to the solubility data of the barium formate–copper formate–water system [14]. The crystals were filtered, washed with alcohol and dried in air. The metal contents were determined complexometrically resulting in 66.72% barium formate and 22.61% copper formate (calculated contents are: 66.83% barium formate and 22.57% copper formate). The double salt was

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identified by the X-ray powder diffraction method (DRON 3 diffractometer, Cu K α radiation). Anhydrous Ba₂Cu(HCOO)₆ was obtained by heating of the double salt crystals at about 90°C for several hours. The infrared spectra were recorded on a Bruker model IFS 25 Fourier transform interferometer (resolution < 2 cm⁻²) using KBr discs as matrices. Ion exchange or other reactions with KBr have not been observed.

3. Crystal structure and selection rules

 $Ba_2Cu(HCOO)_6$ ·4H₂O belongs to the triclinic space group $P\bar{1}$ (C_i^1) with Z = 1 [15]. Three crystallographically inequivalent formates exist in the crystal lattice. The formate groups show considerable differences in the C-O bond lengths and, hence, one of the bonds has more double bond character. Furthermore, the water molecules also fall in two sets $-H_2O(1)$ and $H_2O(2)$ molecules. $H_2O(1)$ molecules are bonded to copper atoms and $H_2O(2)$ to barium atoms. The structural data show the following $O-H\cdots O$ bond lengths: $W_1 - O_6'' = 2.88 \text{ Å}; W_1' - O_1 =$ 2.52 Å; $W_1 - O_6 = 2.72$ Å; $W_2 - O_6' = 2.97$ Å and $W_2 - O_6' = 0.97$ $O_5 = 2.97$ Å. It is important to point out that the hydrogen positions have not been determined [15]. The above mentioned structural data, however, indicate that the $H_2O(2)$ molecules are expected to form weaker hydrogen bonds than the $H_2O(1)$ molecules.

Six fundamental bands of internal vibrations of the formate group are expected to occur in the infrared spectra of metal formates, assuming $C_{2\nu}$ point group symmetry. In the case of Ba₂Cu(HCOO)₆·4H₂O crystals three sets of internal HCOO modes are expected to appear in the infrared spectrum as a result of the existence of three inequivalent formate groups. Each HCOO mode can theoretically split into $A_g + A_u$ components under PI symmetry of the crystal (C₁ site symmetry and C₁^l factor group symmetry).

As far as the water molecules are concerned three internal H–O modes of each type of water molecules are expected to occur. In addition three water librations are predicted for each type of water molecules – rock (R), wag (W) and twist (T). Each mode can also theoretically split into $A_g + A_u$ components (water molecules are in the same site symmetry as the formate groups). However, it has been shown that the correlation field splittings are not resolved in the vibrational spectra of the metal formates [7,8].

4. Results and discussion

The frequencies, assignments, half-widths and relative intensities of the bands of the formate groups in the IR spectrum of Ba₂Cu(HCOO)₆·4H₂O are summarized in Table 1. The assignments of the bands are done by analogy to the precise studies on metal formate dihydrates [7–10]. In these studies ν_5 is attributed to the C–H in-plane bending mode while in some other papers the same band is attributed to the asymmetric OCO bending mode [11–13].

It is seen from Fig. 1 that the ν_2 and ν_4 modes split into three bands at 1328, 1343 and 1360 cm⁻¹ and 1575, 1604 and 1615 cm⁻¹ respectively, corresponding to the three types of formate groups. According to Heyns [7] ν_3 and ν_4 reflect the existence of the crystallographically inequivalent formate groups in Cu(HCOO)₂·2H₂O and the latter mode shows two components which are separated by as much as ~30 cm⁻¹ thus reflecting a significant difference in the C-O bond lengths of two formate groups. The ν_4 component separations in the Ba₂Cu(HCOO)₆·4H₂O spectrum have magnitudes of

Table 1

Infrared wavenumbers (cm⁻¹) for fundamental vibrations of formate groups in $Ba_2Cu(HCOO)_6.4H_2O^{a,b}$

BCF	BF	CF	Assignment
1615 sh	1607sh	1587	$\nu_4(\nu_{as}COO)$
1604 (100 × 30)	1599		
1575 (70×113)	1576		
1393 (36 × 8)	1400	1397	$\nu_5(\delta C - H)$
1380 (27 × 4)	1389	1391	
~1360 sh	1361	1339	$\nu_2(\nu_{as}COO)$
1343 (49 × 6)	1353	1328	
1328 (66 × 12)			
1068 vw	1076	1070	$\nu_6(\nu C-H)$
1057 vw	1068		
810 or 802 sh	770	791	$\nu_{3}(\delta COO)$
788 (16 × 5)	760	775	
757 (21 × 6)			

^a The relative intensities (normalized with respect to $\nu_4(\nu_{as}COO)$ and half-widths of the bands are given in parentheses.

^b The bands for BF and CF are taken from our measurements and the results coincide well with those given in Refs. [7,11,13].



Fig. 1. The infrared bands of the formate groups in the region 2000–1000 cm^{-1} .

30-40 cm⁻¹ indicating different C–O bond lengths of the three formate groups. On the other hand, the $\nu_4 - \nu_2$ frequency separation between the asymmetric and symmetric C-O stretching modes points to different C-O bond lengths within each formate group [7]. In the case of equal bond lengths of HCOO groups (C_{2v} symmetry) this separation has a value of 234 cm⁻¹. In Ba₂Cu(HCOO)₆·4H₂O spectrum $\nu_4 - \nu_2$ frequency separation has a value 250-260 cm^{-1} indicating different C–O bond lengths within each formate group. As far as ν_3 is concerned, a study of $Cu(HCOO)_2 \cdot 2H_2O$ [7] and $Zn(HCOO)_2 \cdot 2H_2O$ [8] has revealed that extensive coupling occurs between this mode and the librations of water molecules. In the spectrum of Ba₂Cu(H- COO_{6} ·4H₂O the two bands at 788 and 757 cm⁻¹ and the shoulder at 810 or 802 cm^{-1} can be assigned to ν_3 (Table 1, Fig. 3). The librational modes of the water molecules (rocking vibrations) overlap with the ν_3 mode thus resulting in a broad band with a maximum at 814 cm^{-1} and two shoulders at 810 and 802 cm^{-1} . The sample highly deuterated (about 90%) exhibits three well-defined bands at 807, 786 and 757 cm⁻¹ (attributed to ν_3 modes).

In Fig. 2 the IR spectra of $Ba_2Cu(HCOO)_6.4H_2O$ and its deuterated analogues are shown in the high frequency range of 4000–2300 cm⁻¹ where O–H



Fig. 2. The infrared bands in the O-H and O-D stretching frequency range of: 1 Cu(HCOO)₂·2H₂O; 2 Ba₂Cu(HCOO)₆·4H₂O; 3 Ba₂Cu(HCOO)₆·4HDO (\sim 7%D); 4 Ba₂Cu(HCOO)₆·4HDO (\sim 20%D); 5 Ba₂Cu(HCOO)₆·4HDO (\sim 50%D); 6 Ba₂Cu(HCOO)₆·4HDO (\sim 90%D).

and O–D stretching modes occur. The assignments of the O–H and O–D modes are done by analogy with those in Cu(HCOO)₂·2H₂O [9] and in the spectra of the isomorphous family Me(HCOO)₂·2H₂O (Me = Mn,Co,Ni,Zn) [10]. For comparison the IR spectrum of Cu(HCOO)₂·2H₂O is shown and it is seen that only a broad intense peak centered at 3200 cm⁻¹ and a weakly defined shoulder at 3300 cm⁻¹ occur in its spectrum. Good explanations of the shape of the bands and the positions of the O–H and O–D modes can be found in Ref. [9]. In the copper formate dihydrate the H₂O(1) molecule exhibits bands at higher frequencies than the H₂O(2) molecule. In the other metal (II) formate dihydrates, however, the bands corresponding to the H₂O(1) molecule occur



Fig. 3. The infrared bands in the 1000–400 cm⁻¹ frequency range of: 1 Cu(HCOO)₂·2H₂O; 2 Ba₂Cu(HCOO)₆; 3 Ba₂Cu(HCOO)₆·4H₂O; 4 Ba₂Cu(HCOO)₆·4HDO (\sim 7%D); 5 Ba₂Cu(HCOO)₆·4HDO (\sim 20%D); 6 Ba₂Cu(HCOO)₆·4HDO (\sim 50%D); 7 Ba₂Cu(HCOO)₆·4HDO (\sim 90%D).

at lower frequencies than those of H₂O(2). Four bands at 3490, 3364, 3301 and 3246 cm⁻¹ (shoulder) could be distinguished in the spectrum of the double salt. According to the structural data of Ba₂Cu(H-COO)₆·4H₂O, the H₂O(2) molecule which forms longer OH···O bond lengths is expected to exhibit bands at higher frequencies than the H₂O(1) molecule. So the bands at 3490 and 3364 cm⁻¹ are attributed to H₂O(1) vibrations (ν_1 and ν_3 respectively) and those at 3301 and 3246 cm⁻¹ to H₂O(1) vibrations (ν_1 and ν_3 , respectively). One interesting feature of the spectrum is that the $H_2O(1)$ molecule which is bonded to the copper ions exhibits bands just at the same frequencies as in the Cu(HCOO)₂·2H₂O spectrum. Isotopically dilute Ba₂Cu(HCOO)₆·4H₂O (about 7%) shows four well-defined bands at 2566, 2488, 2453 and 2417 cm⁻¹ corresponding to four uncoupled O-D modes of HDO molecules, respectively the water molecules are asymmetric. It is worth to point out that the frequencies at which most of the uncoupled O-D modes occur in Ba₂Cu(H- COO_{6} ·4H₂O are close to those in the isomorphous family Me(HCOO)₂·2H₂O [10] while in Cu(H- COO_{2} ·2H₂O these frequencies shift downwards [9]. In Fig. 2 the changes in the shape and the positions of the bands with increasing D concentrations are shown. It is seen that the D concentration increase leads to broadening of the bands and in the spectrum of the sample deuterated about 90% only three comparatively broad bands at 2641, 2605 and 2479 cm^{-1} occur attributed to stretching modes of D₂O molecules. The intensity of the bands at 2566 and 2417 cm⁻¹ decreases with increasing D concentration and the two bands disappear in the spectrum of the fully deuterated sample. In the spectrum of the sample deuterated about 50% two shoulders at 2419 and 2400 cm⁻¹ occur which are attributed to the stretching mode and $2\nu_2$, respectively. The bending mode of the water molecules is absent in the spectrum of $Ba_2Cu(HCOO)_6.4H_2O$. In the spectrum of the sample containing about 50% D₂O, however, two weak bands at 1183 and 1190 cm⁻¹ occur which are assigned to the ν_2 bending mode.

The librational modes of water molecules occur in the region of 1000-400 cm⁻¹. Several procedures are suggested in the literature for the assignments of the water librations: (i) different intensities of these vibrations in both infrared and Raman spectra [16]; (ii) H_2O/D_2O and H_2O/HDO isotopic shifts [17,18]; (iii) trends obtained by force constant calculations [19]. In the case of metal formates the intensifies of the librational modes should vary in the sequence wag > rock > twist and the frequency sequence of these modes is rock > twist > wag [9]. So the two bands at 814 and 810 or 802 cm⁻¹ are attributed to rocking vibrations and the two bands at 770 and 767 cm^{-1} to twisting vibrations, respectively. It could be seen from Fig. 3 that the frequencies of rocking and twisting modes in Ba₂Cu(HCOO)₆·4H₂O are

significantly lower than those in Cu(HCOO)₂·2H₂O. The bands at 669 (shoulder), 639 and 522 cm^{-1} are assigned to wagging modes. It is quite difficult to assign the librational modes in the spectra of the deuterated samples because of the broadening of the bands. Using the given ratio $W_{(H2O)}/W_{(D2O)}$ for wagging modes 1.36 in Zn(HCOO)₂·2H₂O [8] and 1.35-1.39 in $Cu(HCOO)_2 \cdot 2H_2O$ [9] the bands at 493 (shoulder) and 465 cm⁻¹ could be assigned to wagging modes of D₂O molecules. For the twisting modes this ratio has a magnitude of 1.44 [8] and then the shoulder at 530 cm^{-1} could be assigned to the twisting mode. The broad band at 585 cm⁻¹ could be assigned to the rocking mode (the ratio $R_{(H2O)}/R_{(D2O)}$ has a value of 1.39). These assignments must, however, be regarded with a great deal of caution and thus we leave them open for discussion.

5. Conclusions

The analysis of the infrared spectrum of Ba₂Cu(H-COO)₆·4H₂O indicates that some of the internal formate modes (ν_4 , ν_3 , ν_2) reflect the existence of three crystallographically independent formate ions. The comparatively large frequency separations between the asymmetric and symmetric C–O stretching modes is a criterion for the different C–O bond lengths within each formate group. As far as the crystallization water is concerned four bands in the high-frequency region occur corresponding to two inequivalent water molecules. The H₂O(1) molecule bonded to copper atoms forms stronger hydrogen bonds than the H₂O(2) molecule. The four uncoupled O–D modes of HDO molecules are an indication of the asymmetry of the water molecules.

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