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# Vibrational Spectra of $BaCd(HCOO)_4 \cdot 2H_2O$

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IR and Raman spectra of $BaCd(HCOO)_4 \cdot 2H_2O$ have been recorded and analyzed. Observation of three separate frequencies for every internal mode of the formate ion is indicative of three crystallographically nonequivalent formate ions. The frequency of the in-plane C–H bending mode is found to be higher than the symmetric $CO_2$ stretching mode. The correlation field effect is observed to be small. © 1991 Academic Press, Inc.

## Introduction

Inorganic formates possess very interesting physical properties such as piezoelectricity (*1*) (lithium formate monohydrate), antiferroelectricity (*1*) (copper formate dihydrate), and antiferromagnetism (*2*) (manganese formate dihydrate). The crystal structure and vibrational spectra of a number of simple formates have extensively been studied (*1, 3–11*). IR and Raman spectra of mixed crystals of formates of monovalent and divalent cations have not been studied systematically. Feliksinski, *et al.* (*12*) used the IR spectrum (650–4600 $cm^{-1}$) of Barium Cadmium Formate (BCF) to investigate the influence of a metal ion on the carboxylate stretching frequencies of the formate ion. In the present paper, a detailed study of the IR and Raman spectra of the title compound BCF have been presented.

## Experimental

BCF crystals, $BaCd(HCOO)_4 \cdot 2H_2O$, are prepared by the method suggested by Feliksinski and Kolasinski (*13*). Attempts made to record the polarized Raman spectra of single crystals have not been successful, probably due to the twinning present in large single crystals. The Raman spectra of polycrystalline samples have been recorded on a Cary 82 spectrometer using the 514.5-nm line of Spectra Physics Model 164 Ar ion laser (laser power 100 mW). The IR spectra are measured on a Nicolet 170 SX FT–IR Spectrometer in the 4000–400 $cm^{-1}$ region with the sample in KBr pellet and in Nujol mull. The far IR spectrum is recorded on a Digilab FTS-15B instrument.

## Factor Group Analysis

$BaCd(HCOO)_4 \cdot 2H_2O$ belongs to the monoclinic space group $P2_1/c(C_{2h}^5)$ with four molecules per unit cell (*12*). The cations and

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TABLE I

IRREDUCIBLE REPRESENTATION FOR BaCd $(HCOO)_4 \cdot 2H_2O$

| | $4 \times 4$ $HCOO^-$ | $4 \times 2H_2O$ | 4 Ba | 4 Cd | Acoustic modes | Σ |
|---|---|---|---|---|---|---|
| | | Raman | | | | |
| $A_g$ | $(4 \times 6 = 24) + 12T + 12R$ | $(2 \times 3 = 6) + 6T + 6R$ | 3T | 3T | — | 72 |
| $B_g$ | $(4 \times 6 = 24) + 12T + 12R$ | $(2 \times 3 = 6) + 6T + 6R$ | 3T | 3T | — | 72 |
| | | IR | | | | |
| $A_u$ | $(4 \times 6 = 24) + 12T + 12R$ | $(2 \times 3 = 6) + 6T + 6R$ | 3T | 3T | −T | 71 |
| $B_u$ | $(4 \times 6 = 24) + 12T + 12R$ | $(2 \times 3 = 6) + 6T + 6R$ | 3T | 3T | −T−T | 70 |
| | | Σ | | | | |
| | $96 + 48T + 48R$ | $24 + 24T + 24R$ | 12T | 12T | −3T | 285 |

*Note.* T—translations, R—rotations.

the formate ions are in general positions. In the unit cell, formate ions bonded to $Ba^{2+}$ cations are on two sets of 4-fold general positions, but all formate ions bonded to $Cd^{2+}$ cations are situated in equivalent sites (*12*). Factor group analysis (*14*) gives the distribution of irreducible representations (excluding the three acoustic modes) at $k = 0$ as in Table I. It shows that all vibrations of all ions and water molecules appear in all factor group species.

## Interpretation of the Spectra

The frequencies, assignments, and relative intensities are summarized in Table II. The observed spectra show that all the fundamentals of the formate ions are split into three bands each. As all the modes are nondegenerate, this splitting can either be due to the presence of nonequivalent sets of ions or coupling between identical ions in the lattice. Since the ions are in three different sites, the splitting of the fundamentals into three bands each is due to their presence in nonequivalent sites. The additional splittings observed in the different modes are due to the vibrational coupling between identical formate ions (correlation splitting).

The C–H stretching frequency $\nu_1$, which appeared as very intense bands in Raman, is a triplet (2831, 2846, and 2927 $cm^{-1}$) with a splitting of about 100 $cm^{-1}$. Such a large splitting may not be due to vibrational coupling between identical ions. For this mode a splitting of the same order with four components has been observed in IR. These facts also support the inference that BCF contains three different types of formate ions. The large splitting (84 $cm^{-1}$) observed for the $\nu_6$ mode also supports this.

Controversy exists in the assignment of the symmetric C–O stretching mode $\nu_2$ and the in-plane O–C–H bending mode $\nu_5$. In certain compounds (*1, 5, 6, 8*) $\nu_2$ is assigned to be greater than $\nu_5$. However, in some others (*7, 9–11*) $\nu_5$ is assigned to be greater than $\nu_2$. Among the internal modes of the formate ion, $\nu_2$ is expected to be the most intense Raman band (*9*). Also, the C–H bending is usually much sharper than the C–O stretching band, since the latter is broadened by hydrogen bonding interactions. In order to check the bandwidths, a curve analysis of the group of bands between 1500 and 1250 $cm^{-1}$ in Raman (Fig. 1) is made. It shows that the component bands at 1377 and 1391 $cm^{-1}$ are sharper

TABLE II

SPECTRAL DATA ($cm^{-1}$) AND BAND ASSIGNMENTS[a]

| Raman | IR | Assignments |
|---|---|---|
| 43 m | | |
| 63 vs | 63 | Rocking librational mode of $HCOO^-$ |
| 81 s | 86 | |
| | 113 | |
| 130 s | 143 | Twisting librational mode of $HCOO^-$ |
| 157 m | 158 | |
| 173 sh | 170 | Wagging librational mode of $HCOO^-$ |
| | 255 | Ba–O stretch |
| 263 m | 267 | |
| 289 m | 283 | Translational mode of $HCOO^-$ |
| 291 sh | 291 | Cd–O stretch |
| | 660 wbr | Librations of water |
| | 668 w | |
| | 703 vwbr | |
| 768 w | 771 m | |
| 788 vw | 788 m | $\nu_3$ symmetric O–C–O deformation |
| 801 w | 800 m | |
| 1052 sh | vvw | |
| 1062 vw | 1060 vvw | $\nu_6$ out of plane C–H bend |
| 1075 vvw | 1074 vvw | |
| | 1144 vw | |
| 1333 m | 1330 s | |
| 1342 m | 1340 s | $\nu_2$ symmetric $CO_2$ stretch |
| 1355 m | | |
| 1365 vs | 1362 vs | |
| 1377 s | 1376 m | |
| 1390 m | 1384 m | $\nu_5$ in-plane C–H bend |
| 1565 w | 1570 sh | |
| | 1579 vvs | |
| | 1604 sh | $\nu_4$ asymmetric $CO_2$ stretch and $\delta$ $H_2O$ |
| | 1626 sh | |
| 2734 m | 2730 w | |
| 2748 w | 2742 vw | $2\nu_2$ |
| 2831 s | 2828 w | |
| 2846 vs | 2845 m | $\nu_1$ C–H stretch |
| 2927 m | 2910 sh | |
| | 2930 wbr | |
| 3120 wbr | 3260 sh | |
| 3225 wbr | 3420 sbr | $\nu$ $H_2O$ |
| 3300 wbr | | |

[a] Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; sh, shoulder; br, broad.

than others, and the bands at 1365 and 1355 $cm^{-1}$ are more intense than the 1377 $cm^{-1}$ one (Fig. 1-c). Hence the strong Raman bands at 1333, 1342, 1355, and 1365 $cm^{-1}$ are assigned to $\nu_2$, and the medium intensity bands at 1377 and 1390 $cm^{-1}$ to $\nu_5$. The absence of one component for the $\nu_5$ mode in IR may be due to accidental degeneracy or might have been overlapped with $\nu_2$. Bands around 2740 $cm^{-1}$ are found to be equal to 2 $\nu_2$.

The asymmetric C–O stretching frequency $\nu_4$ of the formate ion shifts upward from that of RbHCOO, if the metal–formate ion bond is covalent (*10*). Since barium formate is more ionic than cadmium formate, frequencies of $\nu_4$ modes bonded to $Ba^{2+}$ cations should be lower than those bonded to $Cd^{2+}$ cations (*10*). Therefore, the bands on the low frequency side may be taken as those due to $\nu_4$ of formates bonded to $Ba^{2+}$ cations. $\nu_3$ is also observed as three well-separated medium intensity bands at 771,

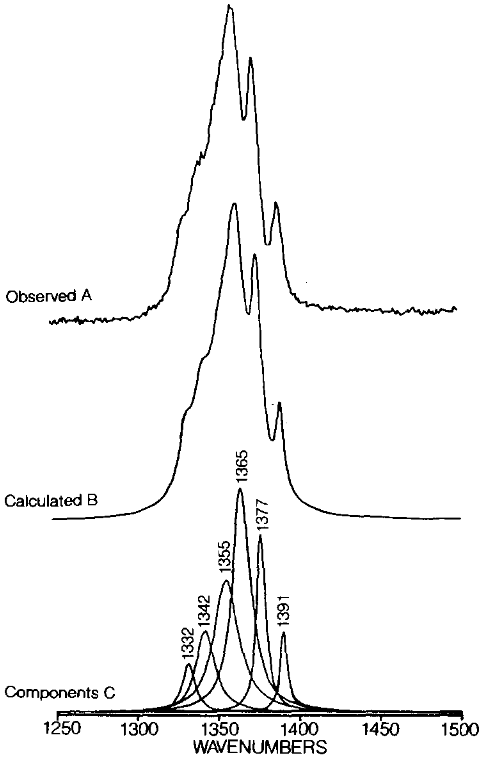

FIG. 1. Curve fitting of the formate $\nu_2$, $\nu_5$ region (Raman Spectrum).

788, and 800 $cm^{-1}$ in the IR and as weak bands at 768, 788, and 801 $cm^{-1}$ in the Raman spectra.

A single envelope with peaks at 3120, 3225, and 3300 $cm^{-1}$ in Raman and strong broad bands at 3260 and 3420 $cm^{-1}$ in IR arise from the stretching vibrations of water molecules. This large shifting of bands shows that fairly strong hydrogen bonds are present in the crystal.

Unambiguous assignment of the low frequency bands is very difficult, as mixing of lattice modes is expected to occur due to the low symmetry and the presence of three different types of formate groups. The intense Raman bands at 264 and 291 $cm^{-1}$ may be due to Ba–O and Cd–O vibrations, as water would not give rise to such intense Raman bands in this region. The band at 280 $cm^{-1}$ is assigned to the translational mode of the formate ion (*9*). The most intense bands below 200 $cm^{-1}$ are assigned to the librational modes (*1*). These librational modes of the formate groups are assigned on the basis of the fact that the frequencies of wagging > twisting > rocking (*9*).

## Results

(i) Splitting of all the internal modes of the formate ion into three components each indicates the presence of three crystallographically nonequivalent formate ions in conformity with the structural result.

(ii) The shifting of the asymmetric C–O stretching frequency of the formate ion to the high frequency side indicates the covalent character of the Cd–O bond.

(iii) From curve analysis it is found that the frequency of the in-plane C–H bending mode ($\nu_5$) is higher than the symmetric $CO_2$ stretching mode ($\nu_2$).

(iv) The correlation field effect is small in the compound.

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