Abstract

The crystal and molecular structure of two isomorphous mixed formates (Cu$_x$M$_{1-x}$)(HCOO)$_2$(H$_2$O)$_{1.33} \ (M = \text{Mg, Co}, \ x = 0.74)\) are presented. The cationic sites are occupied by a mixture of divalent cations (Cu, M) and the structure is built up by double layers of aqua-less, Cu rich polyhedra separated by single layers of M rich ones containing both formate ions and coordinated water molecules.

The infrared spectra of isotopically dilute (matrix-isolated HDO molecules) formates are analyzed in the region of the OD stretching modes. A discussion of the different strength of hydrogen bonds present in the structure is made at the light of the influence that the metal ions exert both onto the hydrogen bond donors, through direct coordination (synergetic effect) as well as onto hydrogen bond acceptor strength of the formate oxygens through the M–OCHO interactions.

Keywords: Mixed formates; Crystal structure; IR-hydrogen bonding

1. Introduction

In previous papers of one of the authors, it has been established that the co-crystallization of Cu(HCOO)$_2$·2H$_2$O with the isomorphous formate dihydrates M(HCOO)$_2$·2H$_2$O (M = Mg, Mn, Co, Ni, Zn) at 50 °C leads to the formation of: (i) two series of mixed crystals in the Cu(HCOO)$_2$–M(HCOO)$_2$–H$_2$O systems (M = Mn, Ni, Zn) [1–3] and (ii) three series of mixed crystals in the Cu(HCOO)$_2$–M(HCOO)$_2$–H$_2$O systems (M = Mg, Co) [4,5]. The monoclinic copper formate dihydrate undergoes a change into a new crystal structure due to the inclusion of Co$^{2+}$ and Mg$^{2+}$ ions. The new type of solid phase (mixed crystals) is stable within narrow crystallization fields Cu$_{0.75}$Mg$_{0.25}$(HCOO)$_2$·2H$_2$O–Cu$_{0.70}$Mg$_{0.30}$(HCOO)$_2$·2H$_2$O and Cu$_{0.83}$Co$_{0.17}$(HCOO)$_2$·2H$_2$O–Cu$_{0.74}$Co$_{0.26}$(HCOO)$_2$·2H$_2$O according to the solubility in the corresponding three component systems. Infrared spectra of the metal formate dihydrates as well as those of mixed crystals formed among them are reported and discussed in detail with respect to the fundamental vibrations of the formate ions and the water molecules in a series of papers [1,6–8].
spectra of the new crystal phase (Cu/Mg and Cu/Co) exhibit an essential difference from those of mixed crystal having Cu(HCOO)\textsubscript{2}·2H\textsubscript{2}O and M(HCOO)\textsubscript{2}·2H\textsubscript{2}O as matrices in the region of the OH and OD vibrations.

In the present paper, the crystal and molecular structure of the two copper–magnesium and copper–cobalt formates of general formula Cu\textsubscript{x}M\textsubscript{1-x}(HCOO)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{1.33}, x = 0.74, M = Mg (1) and M = Co (2) are reported, as obtained from single crystal diffraction techniques, and the resulting hydrogen bonding systems analyzed using crystal matrix-spectroscopy (matrix-isolated HDO molecules).

2. Experimental

2.1. Sample preparation

The simple and mixed copper–magnesium and copper–cobalt formates were prepared as described in Refs. [4,5]. The isotopically dilute samples were prepared by crystallization in partly deuterated water (about 10% D\textsubscript{2}O). Single crystals of the mixed formates were obtained by isothermal decrease of supersaturation of solutions containing copper and magnesium (cobalt) formates within the concentration ranges in which the new crystal phases are stable.

2.2. Infrared spectroscopy

The IR spectra were recorded on a Bruker model IFS25 and IFS113 Fourier transform interferometer (resolution < 2 cm\textsuperscript{-1}) using KBr discs as matrices at ambient and liquid nitrogen temperature. Ion exchange or other reactions with KBr have not been observed.

2.3. X-ray diffraction

The X-ray structural analysis was performed on very small crystals, as larger specimens seemed to present some kind of disordered layered stacking: only when smaller specimens were cut out from the bulk the data sets obtained allowed the resolution of the structures. Highly redundant data sets were collected at room temperature from crystals of ca. 10\textsuperscript{-3} mm\textsuperscript{3} (typical dimensions) up to a 2\theta max. of ca. 58° on a Bruker AXS SMART APEX CCD diffractometer using monochromatic Mo K\textalpha\ radiation, \(\lambda = 0.71069\) Å, and a 0.3° separation between frames. Data integration was performed using SAINT and a multi scan absorption corrections applied using SADABS, both programs in the diffractometer package. The structures were solved by direct methods and difference Fourier, and refined by least squares on \(F^2\) with anisotropic displacement parameters for non-H atoms. Formate hydrogen atoms were placed at their calculated positions and allowed to ride onto their host carbons both in coordinates as well as in thermal parameters. Those corresponding to water molecules were found in the final difference Fourier maps and refined with restrained O–H and H···H distances so as to ensure a reasonable geometry. The relative cationic composition was kept fixed at the values obtained from the chemical analysis, and the relative occupation of both sites was derived as explained in Ref. [9]. All calculations to solve the structures, refine the models proposed and obtain derived results were carried out with the computer programs SHELXS-97 and SHELXL-97 [10] and SHELXTL/PC [11]. Full use of the CCDC package was also made for searching in the CSD Database [12]. A survey of crystallographic and refinement data is presented in Table 1, while Table 2 shows the atomic positions and equivalent displacement factors and Table 3, relevant interatomic distances and angles.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 208628 and 208629. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Crystal structure

The compounds are isomorphous, and they crystallize in the monoclinic space group P2\textsubscript{1}/c. As usual in this type of compounds, there are two independent
Table 1
Crystal and structure refinement data for (1), (2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(1)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$C_{3}H_{3}Cu_{1.11}Mg_{0.39}O_{6}\cdot 2H_{2}O$</td>
<td>$C_{3}H_{3}Cu_{1.11}O_{6}\cdot 2H_{2}O$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>251.10</td>
<td>264.60</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>12.3280(14)</td>
<td>12.3202(13)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>7.2262(8)</td>
<td>7.2316(8)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>8.7217(10)</td>
<td>8.72559(9)</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>103.083(2)</td>
<td>103.121(2)</td>
</tr>
<tr>
<td>Volume ($Å^3$)</td>
<td>756.80(15)</td>
<td>757.10(14)</td>
</tr>
<tr>
<td>Calculated density (g/cm$^3$)</td>
<td>2.204</td>
<td>2.321</td>
</tr>
<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
<td>3.231</td>
<td>4.022</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>503</td>
<td>527</td>
</tr>
<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.22</td>
<td>0.14 × 0.10</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-12 \leq h \leq 16, -9 \leq k \leq 9, -10 \leq l \leq 7$</td>
<td>$-15 \leq h \leq 15, -9 \leq k \leq 9, -11 \leq l \leq 11$</td>
</tr>
<tr>
<td>Completeness to $θ$ max. (%)</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.66 and 0.52</td>
<td>0.62 and 0.55</td>
</tr>
<tr>
<td>Data parameters</td>
<td>1641/149</td>
<td>1698/149</td>
</tr>
<tr>
<td>$R$ indices ($Σ$)</td>
<td>$R^1 = 0.0295, wR^2 = 0.0615$</td>
<td>$R^1 = 0.0304, wR^2 = 0.0773$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R^1 = 0.0339, wR^2 = 0.064$</td>
<td>$R^1 = 0.036, wR^2 = 0.081$</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>$S = 0.984$</td>
<td>$S = 1.051$</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å$^{-1}$)</td>
<td>0.530 and − 0.476</td>
<td>1.002 and − 0.401</td>
</tr>
</tbody>
</table>

Common features to (1) and (2): temperature: 293(2) K, wavelength: 0.71073 Å, crystal system: monoclinic, space group: $P2_1/c$, $Z = 4$, absorption correction: empirical (SADABS), refinement method: full-matrix least-squares on $F^2$.

The contacts therein must be considered only as a first approximation to the real state of affairs: as will be discussed below, the difference in cationic environments defines a ‘fine structure’ around these values, detectable by IR but not through the less sensitive X-ray techniques.
The fact that both cationic sites are partially occupied by the species present (Cu and Mg/Co) posed a hard problem to the refinement process, as both the overall as well as the local composition of each site were (in principle) unknown parameters. In order to minimize the number of variables, it was decided to take as the overall composition of the crystal the values obtained from chemical analysis of the bulk (Cu: 0.74, Mg/Co: 0.26), thus disregarding possible sample fluctuations, and with this restrain in force only the composition of each site was refined as reported elsewhere [9]. The results on the internal drift of the cations are presented in Table 5.

The symmetry transformations used to generate equivalent atoms:

- #1: x, y - 1/z, z - 1/2;
- #2: x, y + 1/z, z + 1/2;
- #3: x, y - 1/2, - z + 3/2;
- #4: x, y, - z + 2.

Inspection of these values confirms that there is more mixing in (2), but an important amount of copper coordinated to water molecules can be found in both structures, viz.: in (1), 0.14465/0.5000 (29%, or 1 copper for each 2.5 Mg); in (2), 0.23914/0.5000 (47%, or 1 copper for each 1.1 Co).
3.2. Hydrogen bonding

The analysis of the infrared spectra of isostructural metal formate dihydrates (M(HCOO)$_2$·2H$_2$O, M = Mg, Mn, Fe, Co, Ni, Cu, Zn) reveals that the hydrogen bonds of the type M–OH$_2$···OCHO–Cu (M$^{2+}$ as guest ions) are considerably weaker as compared to those of the type Cu–OH$_2$···OCHO–M (Cu$^{2+}$ as guest ions) due to the stronger synergetic effect of the copper ions.

IR spectra of the compounds (1) and (2) in the O–H and O–D stretching mode regions are shown in Fig. 3. Two groups of bands are distinguished in the spectra of isotopically dilute samples in the region of matrix-isolated HDO molecules which are separated by 47 and 76 cm$^{-1}$ for the compounds (1) and (2), respectively (liquid nitrogen temperature, see Fig. 3B and D). Six bands are observed in the spectra of both compounds at ambient temperature due to the uncoupled OD vibrations (2565, 2526, 2512, 2450 (shoulder), 2423 and 2357 cm$^{-1}$ for the copper–magnesium formate and at 2543, 2530 (shoulder), 2510, 2420, 2370 and 2347 cm$^{-1}$ for the copper–cobalt formate). Nine and seven bands are observed in the spectra of the compound (1) and (2), respectively, at liquid nitrogen temperature. The red-shift of the OD modes at liquid nitrogen temperature as compared to ambient temperature (dndT > 0) evidences for the formation of linear hydrogen bonds, i.e. O–H···O$^{140}$ in coincidence with the structural data. The compounds (1) and (2) could be considered as mixed crystals having Cu$_{1.5}$(HCOO)$_3$·2H$_2$O as a matrix in which the metal ions are distributed over the two metal positions with different occupancy factors. Then, the three bands at frequencies lower than 2450 cm$^{-1}$ (compound (1)) and 2417 cm$^{-1}$ (compound (2)) could be assigned to hydrogen bonds formed by water molecules bonded to Cu$^{2+}$ ions and the bands at higher frequencies to those formed by water molecules bonded to Mg$^{2+}$ and Co$^{2+}$ ions, respectively (liquid nitrogen temperature).

The different number of the infrared bands corresponding to the OD vibrations in the spectra of both compounds needs some additional comments. The bands in the spectral region 2556–2497 cm$^{-1}$ (six OD oscillators) in the spectrum of compound (1) are assigned to hydrogen bonds formed by water molecules bonded to Cu$^{2+}$ ions and the bands at higher frequencies to those formed by water molecules bonded to Mg$^{2+}$ and Co$^{2+}$ ions, respectively (liquid nitrogen temperature).
hydrogen bonds can be formed by the two crystallographically equivalent water molecules labelled ‘2W’ (refer to Table 4), via its H(2WB) hydrogen atom, due to the three different possible combinations of site B cations, viz.: 

\[ \text{Cu(B)} - \text{O(1C)} \cdot \cdot \cdot \text{H(2WB)} \cdot \cdot \cdot \text{O} - \text{Mg} - \text{OH} \]

(2WB) \cdot \cdot \cdot \text{O(1C)} - \text{Cu(B)},

\[ \text{Cu(B)} - \text{O(1C)} \cdot \cdot \cdot \text{H(2WB)} \cdot \cdot \cdot \text{O} - \text{Mg} - \text{OH} \]

(2WB) \cdot \cdot \cdot \text{O(1C)} - \text{Cu(B)},

\[ \text{Cu(B)} - \text{O(1C)} \cdot \cdot \cdot \text{H(2WB)} \cdot \cdot \cdot \text{O} - \text{Mg} - \text{OH} \]

(2WB) \cdot \cdot \cdot \text{O(1C)} - \text{Cu(B)},

\[ \text{Cu(B)} - \text{O(1C)} \cdot \cdot \cdot \text{H(2WB)} \cdot \cdot \cdot \text{O} - \text{Mg} - \text{OH} \]

(2WB) \cdot \cdot \cdot \text{O(1C)} - \text{Cu(B)},

Table 4

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>d(D–H) (Å)</th>
<th>d(H···A) (Å)</th>
<th>d(D···A) (Å)</th>
<th>&lt;(DHA) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1W)–H(1WA)···O(2C)</td>
<td>0.76(2)</td>
<td>0.78(2)</td>
<td>1.97(2)</td>
<td>2.705(3)</td>
</tr>
<tr>
<td>O(1W)–H(1WB)···O(1A)#1</td>
<td>0.74(2)</td>
<td>0.79(2)</td>
<td>2.14(2)</td>
<td>2.847(3)</td>
</tr>
<tr>
<td>O(2W)–H(2WA)···O(2A)#2</td>
<td>0.76(2)</td>
<td>0.78(2)</td>
<td>2.10(2)</td>
<td>2.855(3)</td>
</tr>
<tr>
<td>O(2W)–H(2WB)···O(1C)#3</td>
<td>0.76(2)</td>
<td>0.77(2)</td>
<td>1.96(2)</td>
<td>2.717(3)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 x, –y+1/2, z+1/2; #2 x+1, y+1/2, –z+5/2; #3 x, –y+1/2, z+1/2.
Cu(B)–O(1C)· · ·H(2WB)O–Mg–OH
(2WB)· · ·O(1C)–Mg(B),
Mg(B)–O(1C)· · ·H(2WB)O–Mg–OH
(2WB)· · ·O(1C)–Mg(B).

This fact explains the appearance of three of the infrared bands in the above spectral region. The other three bands are due to hydrogen bonds formed between ‘1W’ water molecules in conjunction with the remaining ‘2W’ hydrogen atom H(2WA) and the O(2C), O(1A) and O(2A) proton acceptors coordinated only to Cu$^{2+}$ ions (the occupancy of site A by Mg$^{2+}$ ions being sufficiently low as to be safely ignored). With this line of reasoning, more infrared bands ought to be expected to appear in the spectrum of compound (2) as compared to those in the spectrum of the compound (1) due to the distribution of the copper and cobalt ions over the two metal positions; as a consequence the hydrogen bond acceptor strength of all oxygen atoms is expected to be different depending on the metal ion environment. However, only four bands are observed in the spectrum of the compound (2) in the region of 2534–2493 cm$^{-1}$ (see Fig. 3D). These facts could be explained if the chemical nature of the metal ions is taken into consideration. We believe that probably the close chemical nature of the copper and cobalt ions (they both belong to the first transition metal row) determines almost the same acceptor strength of the oxygen atoms. Contrarily, the considerably different chemical nature of the magnesium and copper ions influences strongly on the proton acceptor strength of O(1C) thus leading to the appearance of more infrared bands as was mentioned above.

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References
