

Cation Distribution in $\text{Cu}_x\text{Cd}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ Mixed Crystals

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It was established that $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cd}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ form a continuous series of mixed crystals. The nonlinear dependence of the lattice parameters of the $\text{Cu}_x\text{Cd}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ mixed crystals on the composition and the observed shift of the absorption maximum in the visible range at $x > 0.5$ are explained well by the preferential occupation of the two available lattice sites by the copper ions. The shift of the absorption maximum at $x > 0.5$ toward the higher energy is evidence in favor of the hypothesis that the copper ions prefer a mixed coordination environment. © 1989 Academic Press, Inc.

Introduction

The formates of divalent metals Mg, Mn, Fe, Co, Ni, Cu, Zn, and Cd form isostructural monoclinic crystals with the general formula of $\text{Me}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ (space group $P2_1/c$). The metal ions occupy two sets of nonequivalent centers of symmetry: the metal ion at the *Me*(1)-site is coordinated by six oxygen atoms from formate ions; the metal ion at the *Me*(2)-site is coordinated by four water molecules and two oxygen atoms from formate ions (1–8).

The different coordination environment of the metal ions suggests the possibility that when mixed crystals are formed among the above formates, cations depending on their nature might occupy preferentially one of the two available positions. Ogata *et al.* found a nonlinear change in the lattice constants with the chemical composition in the cases of copper-zinc formate mixed crystals, resp. copper-nickel, resp. copper-manganese, considering these results as evidence that the copper ions are mostly

localized in the *Me*(1)-site (9). In a previous paper we have established that three series of mixed crystals are formed in the $\text{Cu}(\text{HCOO})_2\text{--Mg}(\text{HCOO})_2\text{--H}_2\text{O}$ system at 50°C. A new type of solid phase (mixed crystals) is formed within the concentration range $\text{Cu}_{0.85}\text{Mg}_{0.15}(\text{HCOO})_{12} \cdot 2\text{H}_2\text{O}\text{--Cu}_{0.74}\text{Mg}_{0.26}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$. The IR spectra of the mixed crystals show that when the copper ions replace the magnesium ions in the $\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ matrix they occupy predominantly the *Me*(1)-site in accordance with Ogata's suggestion due to the special affinity of the magnesium ions to the water molecules (10). However, this might not be the general case.

It is known that only the copper formate crystallizes at room temperature as tetrahydrate, all other metal formates crystallizing as dihydrates. The copper formate tetrahydrate crystal structure is built up by only one type of coordination octahedron in which the copper ions are coordinated by four oxygen atoms from formate ions and two water molecules (11). The higher sta-

bility of the copper formate tetrahydrate at room temperature may be explained by the Jahn-Teller properties of the Cu²⁺ ion determining a higher preference to a mixed (X_4Y_2) coordination. On the basis of these considerations we assume that when copper ions are included in the crystal structure of some metal formate and the partner metal ions do not show a strong affinity to the water molecules the copper ions would occupy preferentially the *Me*(2)-site with the mixed coordination, instead of the *Me*(1)-site having only one type of nearest neighbor.

In order to check this hypothesis we have studied the cocrystallization of copper and cadmium formate dihydrates, cadmium having no special affinity to water molecules. Diffuse reflectance spectroscopy in the visible range has been used to establish which metal site is occupied by the Cu²⁺ ions.

Experimental

The metal formates were obtained by neutralization of dilute solutions of formic acid with the corresponding normal or basic carbonates. Analytical grade reagents were used. The solubility in the Cu(HCOO)₂–Cd(HCOO)₂–H₂O system at 50°C was studied using the method of isothermal decrease of supersaturation. Equilibrium was reached in about 2 days. The study was carried out in an excess of formic acid (about 2 mass %) in order to suppress the hydrolysis of the salts. The composition of the liquid phase and the wet solid phase was determined as follows: the copper formate concentration was determined iodometrically; the sum of the copper and cadmium ions was determined complexometrically at pH 5.5–6 using xylenol orange as indicator. Cadmium formate concentration was calculated by difference. The composition of the ideally dry solid phase was calculated by the variation of Schreinemakers' method of

algebraic indirect identification of the solid phase (12). The X-ray diffraction analysis was carried out by means of a DRON-3 powder diffractometer using Fe-filtered CoK_α radiation. The 2θ diffraction range was 10–55°. The lattice constants were determined from diffractometric data by least-squares refinements. The diffuse reflectance spectra were recorded by a VSU-2P Carl Zeiss (Jena) spectrophotometer in the range 1000–300 nm. MgO was used as a reference medium with a 100% reflection. The Kubelka–Munk function $F = (1 - R)^2 / 2R$ (R is the relative reflectivity), characterizing the absorption coefficient, was calculated over the whole range.

Results and Discussion

Solubility data are given in Table I and a solubility diagram is shown in Fig. 1. The distribution curve of the salt components between the liquid and solid phases is shown in Fig. 2. It is seen from Fig. 1 that the solubility isotherm has a maximum at a composition of the solid phase Cu_{0.5}Cd_{0.5}(HCOO)₂ · 2H₂O. The X-ray diffraction patterns of the copper–cadmium formate samples show that a continuous series of mixed crystals Cu_xCd_{1-x}(HCOO)₂ · 2H₂O (0 ≤ x ≤ 1) is formed between the two salts during their cocrystallization from aqueous solutions (Fig. 3). However, the lattice constants change nonlinearly with the change in the chemical composition (Fig. 4). The replacement of cadmium by copper in the Cd(HCOO)₂ · 2H₂O crystal structure induces a contraction in the lattice parameters in agreement with the smaller ionic radius of the copper ions with respect to that of the cadmium ions. The nonlinear variation of the lattice parameters can be explained by the preferential distribution of the metal ions over the two possible *Me*(1)- and *Me*(2)-positions differing in their coordination environment. The type of the ligand environment preferred by the copper

TABLE I
SOLUBILITY IN THE $\text{Cu}(\text{HCOO})_2\text{-Cd}(\text{HCOO})_2\text{-H}_2\text{O}$ SYSTEM AT 50°C

Liquid phase (mass %)		Solid phase after (12) (mass %)		Solid phase composition
$\text{Cu}(\text{HCOO})_2$	$\text{Cd}(\text{HCOO})_2$	$\text{Cu}(\text{HCOO})_2$	$\text{Cd}(\text{HCOO})_2$	
25.17	—	—	—	$\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
24.98	3.00	76.51	4.74	$\text{Cu}_{0.96}\text{Cd}_{0.04}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
24.10	4.95	69.70	12.96	$\text{Cu}_{0.87}\text{Cd}_{0.13}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
23.55	7.06	62.82	19.14	$\text{Cu}_{0.81}\text{Cd}_{0.19}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
23.20	9.05	55.29	27.08	$\text{Cu}_{0.73}\text{Cd}_{0.27}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
22.50	12.50	46.86	35.93	$\text{Cu}_{0.63}\text{Cd}_{0.37}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
21.13	14.74	42.13	39.94	$\text{Cu}_{0.58}\text{Cd}_{0.42}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
20.20	14.98	36.20	41.98	$\text{Cu}_{0.5}\text{Cd}_{0.5}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
18.98	15.14	28.63	54.83	$\text{Cu}_{0.41}\text{Cd}_{0.59}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
16.89	17.89	25.05	58.59	$\text{Cu}_{0.36}\text{Cd}_{0.64}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
14.37	20.19	18.60	65.37	$\text{Cu}_{0.27}\text{Cd}_{0.73}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
10.15	22.49	13.65	70.54	$\text{Cu}_{0.20}\text{Cd}_{0.80}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
5.73	24.05	7.38	77.14	$\text{Cu}_{0.11}\text{Cd}_{0.89}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$
—	27.80	—	—	$\text{Cd}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$

ions can be deduced from the diffuse reflectance spectra of the mixed crystals in the visible range. The strength of the ligand field depends on the environment and the maximum in the optical absorption varies correspondingly (Table II). There are no published data on the structures containing only $\text{Cu}(\text{H}_2\text{O})_4(\text{HCOO})_2$ blocks. The com-

plex ion $\text{Cu}(\text{H}_2\text{O})_2(\text{HCOO})_4^{2-}$ exists in the lattices of the salts $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ and $2\text{Ba}(\text{HCOO})_2 \cdot \text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ and their spectra display maxima at the same energy. The hexaformate complex ion $\text{Cu}(\text{HCOO})_6^{4-}$ (building the lattice of the anhydrous copper formate) has a maximum at a higher energy. Thus, the optical spectra of the three arbitrating structures $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{HCOO})_2$, and $2\text{Ba}(\text{HCOO})_2 \cdot \text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ support the conclusion that in the case of tetragonal copper complexes the formate ions create a

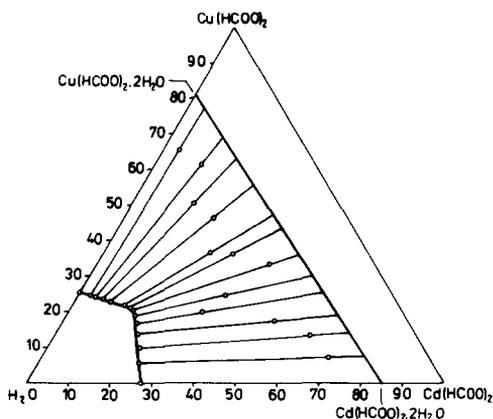


FIG. 1. Solubility diagram of the $\text{Cu}(\text{HCOO})_2\text{-Cd}(\text{HCOO})_2\text{-H}_2\text{O}$ system at 50°C .

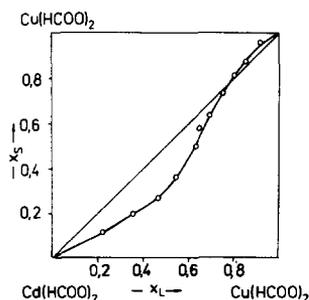


FIG. 2. Distribution curve of the salt components.

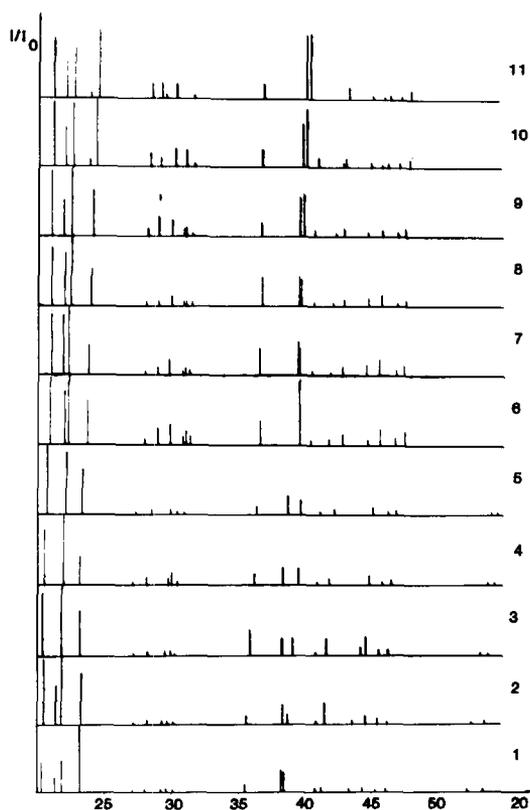


FIG. 3. Stick diagram of the mixed crystals $\text{Cu}_x\text{Cd}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$. (1) $\text{Cd}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (2) $\text{Cu}_{0.04}\text{Cd}_{0.96}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (3) $\text{Cu}_{0.14}\text{Cd}_{0.86}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (4) $\text{Cu}_{0.26}\text{Cd}_{0.74}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (5) $\text{Cu}_{0.38}\text{Cd}_{0.62}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (6) $\text{Cu}_{0.52}\text{Cd}_{0.48}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (7) $\text{Cu}_{0.59}\text{Cd}_{0.41}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (8) $\text{Cu}_{0.62}\text{Cd}_{0.38}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (9) $\text{Cu}_{0.71}\text{Cd}_{0.29}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (10) $\text{Cu}_{0.87}\text{Cd}_{0.13}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$; (11) $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$.

ligand field stronger than that of water molecules. Accordingly, in the spectrum of $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ one would observe two maxima due to the $\text{Cu}(\text{HCOO})_6^{4-}$ and $\text{Cu}(\text{H}_2\text{O})_4(\text{HCOO})_2$ complexes. The appearance of only one maximum means that the water molecules and the formate ions are very close in the spectrochemical series at tetragonal symmetry, rather similar to the case of octahedral symmetry.

The incorporation of the copper ions in the $\text{Cd}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ matrix up to 50 at.% (i.e., an equimolar mixture of both

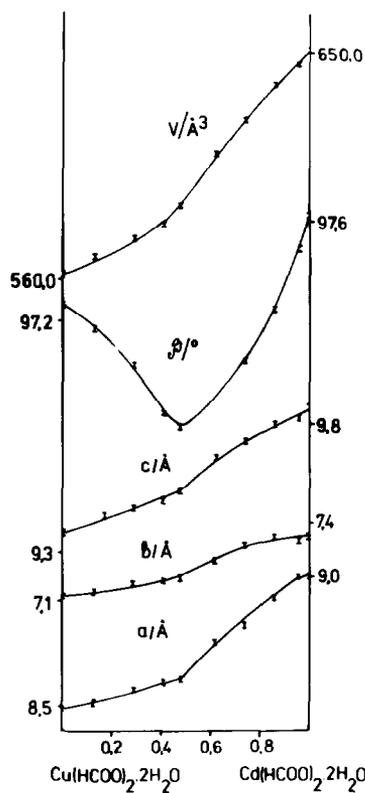


FIG. 4. Lattice parameters of the mixed crystals $\text{Cu}_x\text{Cd}_{1-x}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$.

components) does not influence the position of the absorption maximum in the visible range (Table II, Nos. 4–8). In the spectra of the mixed crystals containing more than 50 at.% of copper ions, a shift of the absorption maximum toward the higher energies is observed (Table II, Nos. 9–14). The mixed crystals $\text{Cu}_{0.95}\text{Cd}_{0.05}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}_{0.83}\text{Cd}_{0.17}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ display an absorption maximum at nearly the same energy as pure $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$. The unchanged position of the maximum in the spectra of the crystals containing less than 50 at.% of copper ions shows that the copper ions occupy preferentially one of the two available positions, which is in good agreement with the nonlinear change in the lattice parameters. When all the cadmium ions in the corresponding environ-

TABLE II

Nature of solid phase	ν_{\max} (cm ⁻¹)
1. 2Ba(HCOO) ₂ · Cu(HCOO) ₂ · 4H ₂ O	12,820
2. Cu(HCOO) ₂ · 4H ₂ O	12,820
3. Cu(HCOO) ₂	14,700
4. Cu _{0.03} Cd _{0.97} (HCOO) ₂ · 2H ₂ O	11,900
5. Cu _{0.22} Cd _{0.78} (HCOO) ₂ · 2H ₂ O	11,900
6. Cu _{0.30} Cd _{0.70} (HCOO) ₂ · 2H ₂ O	11,900
7. Cu _{0.46} Cd _{0.54} (HCOO) ₂ · 2H ₂ O	11,900
8. Cu _{0.52} Cd _{0.48} (HCOO) ₂ · 2H ₂ O	11,900
9. Cu _{0.60} Cd _{0.40} (HCOO) ₂ · 2H ₂ O	12,200
10. Cu _{0.64} Cd _{0.36} (HCOO) ₂ · 2H ₂ O	12,200
11. Cu _{0.73} Cd _{0.27} (HCOO) ₂ · 2H ₂ O	12,200
12. Cu _{0.83} Cd _{0.17} (HCOO) ₂ · 2H ₂ O	12,500
13. Cu _{0.95} Cd _{0.05} (HCOO) ₂ · 2H ₂ O	12,500
14. Cu(HCOO) ₂ · 2H ₂ O	12,500

ment are replaced by copper ions, the latter begin to occupy the second position and as a consequence the absorption maximum is shifted. The shift towards the higher energies, i.e., stronger ligand fields, is evidence in favor of the hypothesis that copper ions prefer the mixed coordination environment, i.e., the *Me*(2)-positions. More details on the structure of this environment will be given in a future publication using ESR data. As a result of this preference the solubility curve has a maximum.

Conclusion

The nonlinear dependence of the lattice parameters of the Cu_xCd_{1-x}(HCOO)₂ · 2H₂O mixed crystals on the composition and the observed shift of the absorption

maximum in the visible range at $x > 0.5$ are explained well by the preferential occupation of the two available lattice sites by the copper ions. The shift of the maximum toward the higher energies is evidence in favor of the hypothesis that in the matrix of Cd(HCOO)₂ · 2H₂O the copper ions prefer the octahedra built up by four water molecules and two formate ions. The structure of the mixed crystal Cu_{0.5}Cd_{0.5}(HCOO)₂ · 2H₂O is built up by alternating Cu- and Cd-octahedra containing different coordinations of ligands which may be treated from a crystallochemical point of view as a double salt.

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