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Influence of the Copper Ions on the $Cu_xZn_{1-x}(HCOO)_2 \cdot 2H_2O$ Solid Solution Formation

D. STOILOVA* AND G. GENTCHEVA

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

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It was established that the isostructural salts $Cu(HCOO)_2 \cdot 2H_2O$ and $Zn(HCOO)_2 \cdot 2H_2O$ form a discontinuous series of solid solutions. The deviation from the classical isomorphous theory rules is due to the properties of the Jahn–Teller copper ions, which cause a strong radial deformation of the comparatively regular zinc octahedra, replacing the zinc ions in the $Zn(HCOO)_2 \cdot 2H_2O$ crystal structure. The observed shift in the absorption maximum in the visible range is explained by the preferential occupation of the two available lattice sites by the copper ions when they replace the zinc ions. The shift in the absorption maximum toward higher energies is evidence in favor of the hypothesis that the copper ions prefer a mixed coordination environment. The crystal structure of the solid solution $Cu_{0.5}Zn_{0.5}(HCOO)_2 \cdot 2H_2O$ may be treated from a crystallochemical point of view as a double salt. © 1992 Academic Press, Inc.

Introduction

It is well known that the metal formate dihydrates $Me(HCOO)_2 \cdot 2H_2O$ (Me=Mg, Mn,Fe,Co,Ni,Cu,Zn,Cd) are an isostructural—monoclinic system, with 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 (*1–9*). The different coordination environments of the metal ions suggest the possibility that when solid solutions are formed among the above formates, cations, depending on their nature, preferentially occupy one of the two available positions. The same crystal structure of the salts $Me(HCOO)_2 \cdot 2H_2O$ defines the possibility for the formation of continuous series of solid solutions during their cocrystallization from aqueous solutions (*10–13*). However, some experimental results show a limited solubility of the salt components (discontinuous series of solid solutions) in the $Cd(HCOO)_2$–$Mg(HCOO)_2$–H_2O system at 25°C (*11*) and $Cu(HCOO)_2$–$Mg(HCOO)_2$–H_2O system at 50°C (*14*). The deviation from the classical isomorphous theory rules in the above systems is due to: (i) the difference in the ionic radii of the metal ions, resulting in bond lengths of Cd–O_m greater than those of Mg–O_m, and (ii) the properties of the Jahn–Teller copper ions, which cause a strong radial deformation of the metal coordination octahedra. As a result of this distortion, a new type of solid phase (solid solutions) is formed in the $Cu(HCOO)_2$–$Mg(HCOO)_2$–H_2O system at 50°C and has crystal structure considerably different from those of the simple salts. On

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* To whom correspondence should be addressed.

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the other hand, the cocrystallization of the pair $Cu(HCOO)_2 \cdot 2H_2O/Cd(HCOO)_2 \cdot 2H_2O$ obeys the classical isomorphous theory rules; i.e., a continuous series of solid solutions is formed (*13*).

The purpose of the present paper is to examine the influence of the copper ions on the type of solid solutions $Cu_xZn_{1-x}(HCOO)_2 \cdot 2H_2O$. There are no data in the literature on the solubility of the $Cu(HCOO)_2$–$Zn(HCOO)_2H_2O$ system at 50°C. It is known that the lattice parameters of the solid solutions $Cu_xMe_{1-x}(HCOO)_2 \cdot 2H_2O$ (*Me*=Mn,Zn,Ni) do not change uniformly with the change in chemical composition (*15*). There are no comments, however, on the type of solid solutions. According to Ogata *et al.* the copper ions are localized mostly at the *Me*(1)-site in the crystal structure of the solid solution $Cu_{0.5}Zn_{0.5}(HCOO)_2 \cdot 2H_2O$. In our previous paper we assumed that when the copper ions were included in the crystal structure of some metal formates they would occupy the *Me*(2)-site characterized by mixed (X_4Y_2) coordination (*13*). The argument for this hypothesis is the fact that only the copper formate crystallizes at room temperature as tetrahydrate, having one type of coordination octahedron in which the copper ions are coordinated by two water molecules and four oxygen atoms from formate ions (*16*). The higher stability of the copper formate tetrahydrate may be explained by the Jahn–Teller properties of the copper ions, which have a higher preference for mixed coordination. The aim of the present study is to confirm this hypothesis.

Experimental

The metal formates were obtained by neutralization of dilute formic acid solutions with the corresponding basic carbonates (in the case of copper formate) and metal oxide (in the case of zinc formate). Analytical grade reagents were used. The solubility of the $Cu(HCOO)_2$–$Zn(HCOO)_2$–H_2O system

TABLE I

SOLUBILITY IN THE $Cu(HCOO)_2$–$Zn(HCOO)_2$–H_2O SYSTEM AT 50°C

Liquid phase, wt.%		Solid phase calculated by (8), wt.%		Distribution coefficients	
$Cu(HCOO)_2$	$Zn(HCOO)_2$	$Cu(HCOO)_2$	$Zn(HCOO)_2$	$D_{Cu/Zn}$	$D_{Zn/Cu}$
1. —	8.06	—	—	—	—
2. 2.59	6.89	7.32	73.15	0.26	3.84
3. 5.88	5.80	13.26	67.90	0.19	5.26
4. 9.43	5.44	21.50	59.63	0.20	5.00
5. 13.63	3.79	30.54	50.53	0.17	5.88
6. 19.19	3.16	34.22	46.86	0.12	8.32
7. 23.85	3.00	42.38	38.72	0.14	7.14
8. 25.06	2.89	48.21	32.91	Eutonics	
9. 25.60	2.52	53.01	28.07	Eutonics	
10. 26.24	2.95	57.75	23.44	Eutonics	
11. 26.31	2.26	66.08	15.07	0.37	2.70
12. 27.63	1.17	72.79	8.38	0.37	2.70
13. 27.58	0.38	78.15	3.02	0.36	2.78
14. 26.92	0.20	79.38	1.79	0.33	3.03
15. 25.17	—	—	—	—	—

TABLE II

LATTICE PARAMETERS OF $Cu_xZn_{1-x}(HCOO)_2 \cdot 2H_2O$ SOLID SOLUTIONS

Solid phase	a (Å)	b (Å)	c (Å)	β (°)
$Zn(HCOO)_2 \cdot 2H_2O$	8.69	7.14	9.28(1)	97.76
$Cu_{0.09}Zn_{0.91}(HCOO)_2 \cdot 2H_2O$	8.70	7.14	9.26	97.72
$Cu_{0.18}Zn_{0.82}(HCOO)_2 \cdot 2H_2O$	8.63	7.15	9.29(2)	97.59
$Cu_{0.27}Zn_{0.73}(HCOO)_2 \cdot 2H_2O$	8.58	7.14	9.29(1)	97.52
$Cu_{0.33}Zn_{0.67}(HCOO)_2 \cdot 2H_2O$	8.56	7.16	9.30(2)	97.46
$Cu_{0.43}Zn_{0.57}(HCOO)_2 \cdot 2H_2O$	8.54(1)	7.17	9.30(3)	97.46
$Cu_{0.48}Zn_{0.52}(HCOO)_2 \cdot 2H_2O$	8.54(1)	7.14	9.26(3)	97.82
$Cu_{0.82}Zn_{0.18}(HCOO)_2 \cdot 2H_2O$	8.52(2)	7.13(1)	9.34(2)	97.41
$Cu_{0.94}Zn_{0.06}(HCOO)_2 \cdot 2H_2O$	8.48(2)	7.13(1)	9.31(2)	97.10
$Cu_{0.98}Zn_{0.02}(HCOO)_2 \cdot 2H_2O$	8.46	7.12	9.32	96.99
$Cu(HCOO)_2 \cdot 2H_2O$	8.49	7.12	9.34(1)	97.34

at 50°C was studied using the method for isothermal decrease of supersaturation. Equilibrium was reached in about 2 days. The experiments were carried out in a slight excess of formic acid (about 1–2 mass%) in order to suppress the salt hydrolysis. The liquid phase concentration and the wet solid phase concentration were determined as follows: the copper formate concentration was determined iodometrically; the sum of the copper and zinc formate concentrations was determined complexometrically at pH 5.5–6 using xylenol orange as indicator. The zinc formate concentration was calculated by difference. The variation of the Schreinemakers method of algebraic indirect identification of the solid phase was used to calculate the ideally dry solid phase concentration (*17*). The solid phases were washed with alcohol, dried in air, and analyzed as above. The X-ray diffraction analysis was carried out with a DRON-3 powder diffractometer using Co$K\alpha$ radiation. The 2θ diffraction range was 10–60°. The lattice parameters were calculated from the diffractometric data by least-squares refinements. The diffusive reflectance spectra of the powdery samples were recorded by a VSU-2P Carl Zeiss (Jena) spectrophotometer in the range 1000–300 nm. MgO was used as a reference medium with 100% reflection. The Kubelka–Munk function $F = (1 - R)^2/2R$ (R is relative reflectivity), characterizing the absorption coefficient, was calculated over the entire range.

Results and Discussion

Solubility in the $Cu(HCOO)_2$–$Zn(HCOO)_2$–H_2O system was studied at 50°C, the temperature at which the two salts crystallize as isostructural monoclinic dihydrates. The experimental results are shown in Table I and Fig. 1. The distribution curve of the components in molar units is shown in Fig. 2. The two branches of the curve lie on one side of the diagonal because the concentration of one component (copper formate) in the liquid phase remains higher than that in the solid phase over the entire concentration range.

The two branches of the curve indicate that two series of solid solutions are formed in the studied system, irrespective of the isostructure of the salts. Another argument in favor of this conclusion is the calculated distribution coefficients between the liquid and the solid phases, which are different for the two crystallization fields (Table I). The distribution coefficient of the copper for-

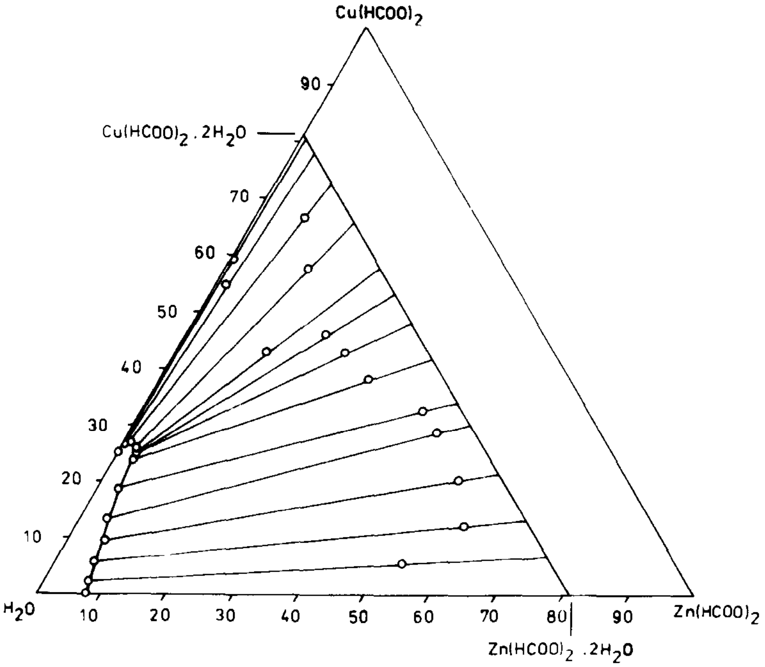

FIG. 1. Solubility diagram of the $Cu(HCOO)_2$–$Zn(HCOO)_2$–H_2O system at 50°C.

mate in the crystallization field of the solid solutions, having zinc formate dihydrate as a main component, has a mean value of 0.18, and that in the crystallization field of the solid solutions, having copper formate dihydrate as a main component, has a mean value of 0.36. Points 8, 9, and 10 are eutonic and lie on the vertical part of the distribution curve (Fig. 2). It is seen in Fig. 1 that the $Zn(HCOO)_2 \cdot 2H_2O$ matrix includes a maximum of 50 mole% copper formate.

The lattice parameters of the solid solutions $Cu_xZn_{1-x}(HCOO)_2 \cdot 2H_2O$ are given in Table II and Fig. 3. A mixture of the two types of solid solutions is formed within the concentration range limited by the crosses (eutonic area). The volume V is calculated for one formula unit and does not change with the chemical composition.

The interruption in the solid solution series may be explained in the following way: When the Jahn–Teller copper ions replace the zinc ions in the $Zn(HCOO)_2 \cdot 2H_2O$ matrix, they cause a strong radial deformation of the comparatively regular zinc octahedra. The distortion force created by this substitution does not substantially affect the zinc formate lattice up to copper formate concentrations of 50 mole% in the solid phase. At copper formate concentrations higher than about 24 mass% in the liquid phase, the production of solid solutions with $Cu(HCOO)_2 \cdot 2H_2O$ crystal structure increases stepwise.

The difference in solid solutions of the type $Cu_xZn_{1-x}(HCOO)_2 \cdot 2H_2O$ (a discontinuous series) and the type Cu_xCd_{1-x} $(HCOO)_2 \cdot 2H_2O$ (a continuous series) is probably due to the difference in the ionic radii of the cadmium and zinc ions, which determine different bond lengths. At this stage in our study we may only assume that the larger cadmium octahedra handle the distortion caused by the copper ions more easily than do the zinc octahedra, resulting

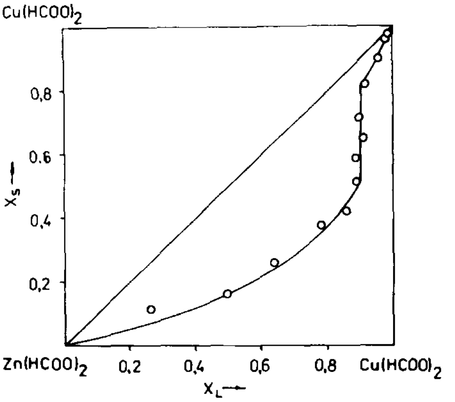

FIG. 2. Distribution curve of the salt components.

in the formation of a continuous series of solid solutions. Evidently, more detailed investigations are needed in order to determine the influence of the bond length change with the chemical composition on the type of solid solution.

As mentioned above, in the previous paper we assumed that the copper ions preferentially replace the cadmium ions characterized by mixed coordination. The type of ligand environment preferred by the copper ions was deduced from the diffusive reflectance spectra of the solid solutions in the visible range. The strength of the ligand field depends on the coordination environment, thus varying the maximum of the optical absorption correspondingly. The spectra of the different known arbitrating crystal structures support the conclusion that in the case of tetragonal copper complexes the formate ions create a ligand field that is stronger than that of water molecules (*13*). The inclusion of the copper ions in the $Zn(HCOO)_2 \cdot 2H_2O$ crystal structure up to 50 at.% (i.e., an equimolar mixture of the two salts) does not influence the position of the absorption maximum. A shift in the absorption maximum toward higher energies is observed when the copper formate concentration increases more than 50 mole%. The solutions $Cu_{0.90}Zn_{0.10}(HCOO)_2 \cdot 2H_2O$, $Cu_{0.96}Zn_{0.04}(HCOO)_2 \cdot 2H_2O$, and $Cu_{0.98}Zn_{0.02}(HCOO)_2 \cdot 2H_2O$ display an absorption maximum at the same energy as $Cu(HCOO)_2 \cdot 2H_2O$. The unchanged position of the absorption maximum in the spectra of solid solutions having zinc formate dihydrate as a main component shows that the copper ions predominantly occupy one of the two available positions. The shift toward higher energies, i.e., stronger ligand fields, is evidence that the copper ions replacing the zinc ions in the $Zn(HCOO)_2 \cdot 2H_2O$ matrix prefer the mixed coordination environment. When all the zinc ions at the *Me*(2)-site are replaced by copper ions, the latter begin to occupy the *Me*(1)-site and, as a consequence, the absorption maximum is shifted (Table III).

Conclusion

It was established that a discontinuous series of solid solutions is formed in the Cu

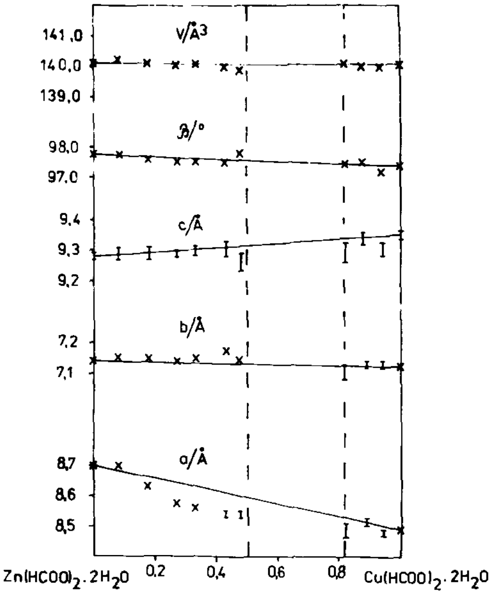

FIG. 3. Lattice parameters of the solid solutions $Cu_xZn_{1-x}(HCOO)_2 \cdot 2H_2O$.

TABLE III

Nature of solid phase	Structural element	ν_{max} (cm^{-1})
$Cu(HCOO)_2$	$Cu(HCOO)_6$	14,700
$Cu(HCOO)_2\cdot 4H_2O$	$Cu(HCOO)_4(H_2O)_2$	12,820
$Ba_2Cu(HCOO)_6\cdot 4H_2O$	$Cu(HCOO)_4(H_2O)_2$	12,820
$Cu(HCOO)_2\cdot 2H_2O$	$Cu(HCOO)_6$ $Cu(HCOO)_2(H_2O)_4$	12,500
$Cu_{0.98}Zn_{0.02}(HCOO)_2\cdot 2H_2O$		12,500
$Cu_{0.96}Zn_{0.04}(HCOO)_2\cdot 2H_2O$		12,500
$Cu_{0.90}Zn_{0.10}(HCOO)_2\cdot 2H_2O$		12,500
$Cu_{0.82}Zn_{0.18}(HCOO)_2\cdot 2H_2O$		12,200
$Cu_{0.52}Zn_{0.48}(HCOO)_2\cdot 2H_2O$		11,900
$Cu_{0.42}Zn_{0.58}(HCOO)_2\cdot 2H_2O$		11,900
$Cu_{0.38}Zn_{0.62}(HCOO)_2\cdot 2H_2O$		11,900
$Cu_{0.26}Zn_{0.74}(HCOO)_2\cdot 2H_2O$		11,900
$Cu_{0.16}Zn_{0.84}(HCOO)_2\cdot 2H_2O$		11,900
$Cu_{0.11}Zn_{0.89}(HCOO)_2\cdot 2H_2O$		11,900

$(HCOO)_2$–$Zn(HCOO)_2$–H_2O system at 50°C. The interruption in the solid solution series is due to the properties of the Jahn–Teller copper ions, which cause a strong radial deformation of the comparatively regular zinc octahedra, replacing the zinc ions in the $Zn(HCOO)_2\cdot 2H_2O$ crystal structure. At copper formate concentration higher than 24 mass% in the liquid phase, the production of solid solutions with $Cu(HCOO)_2\cdot 2H_2O$ crystal structure increases stepwise. The shift in the maximum in the optical spectra toward higher energies is evidence in favor of the hypothesis that when the copper ions replace the zinc ions they predominantly occupy the *Me*(2)-site; i.e., they prefer the mixed coordination environment. The structure of the solid solution $Cu_{0.5}Zn_{0.5}(HCOO)_2\cdot 2H_2O$ may be treated from a crystallochemical point of view as a double salt—the structure is built up by alternating Cu and Zn octahedra containing different ligand coordinations.

References

1. K. Krogmann and R. Mattes, *Z. Kristallogr.* **118,** 291 (1963).
2. K. Osaki, Y. Nakai, and T. Watanabe, *J. Phys. Soc. Jpn.* **19,** 717 (1964).
3. M. Bukowska-Strayzewska, *Acta Crystallogr.* **19,** 357 (1965).
4. A. C. Anzushkina, M., Gussenova, and M. A. Porai-Koshiz, *Zh. Struckt. Khim.* **8,** 365 (1966).
5. M. L. Post and J. Trotter, *Acta Crystallogr. B* **30,** 1880 (1974).
6. G. With, S. Harkema, and G. J. van Hummel, *Acta Crystallogr. B* **32,** 1980 (1976).
7. N. Burger and H. Fuess, *Z. Kristallogr.* **145,** 346 (1977).
8. G. Weber, *Acta Crystallogr. B* **36,** 3107 (1980).
9. G. Weber, *Z. Kristallogr.* **158,** 315 (1982).
10. D. Stoilova, Chr. Balarew, V. Vassileva, and St. Russeva, *Zh. Neorg. Khim.* **26,** 1641 (1981).
11. Chr. Balarew, V. Vassileva, and D. Stoilova, *Commun. Dep. Chem.* (*Bulg. Acad. Sci.*) **14,** 57 (1981).
12. Chr. Balarew, D. Stoilova, and V. Vassileva, *C.R. Acad. Bulg. Sci.* **35,** 933 (1982).
13. D. Stoilova and S. Angelov, *J. Solid State Chem.* **82,** 60 (1989).
14. D. Stoilova, Chr. Balarew, and V. Vassileva, *Commun. Dep. Chem.* (*Bulg. Acad. Sci.*) **18,** 3 (1985).
15. T. Ogata, T. Taga, and K. Osaki, *Bull. Chem. Soc. Jpn.* **50,** 1674, 1680 (1977).
16. N. Burger and H. Fuess, Ferroelectrics **22,** 847 (1976).
17. D. Trendafelov and Chr. Balarew, *Commun. Dep. Chem.* (*Bulg. Acad. Sci.*) **1,** 73 (1968).