1674 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1674—1679 (1977) [Vol. 50, No. 7

Cation Distribution in Mixed Formates. I. Change in Lattice Constants and in Infrared Spectra with the Chemical Constitution of $(Cu,M^{II})(HCOO)_2 \cdot 2H_2O$

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(Received November 22, 1976)

Mixed crystals of formates, with the general formula of $(Cu,M^{II})(HCOO)_2 \cdot 2H_2O$, were found to show non-uniform changes in lattice constants with the change in the chemical constitution. The reason for this unusual change was sought in relation to a possible non-uniform distribution of the cations over the two non-equivalent sites for metal ions. A simple model based merely on the difference in the radii of metallic ions did not agree with the results of IR measurements nor with those of an ESR study by Wagner *et al.* Another model, incorporating the change in the direction of the longest axis of the octahedron coordinating to the Cu^{2+} ion at the M1-site, as suggested from the results of a related work (Part II), was found not only to explain the changes in lattice constants, but also to conform with other evidences; it seems to be an essentially correct interpretation.

It has been reported that formates of divalent transitional metals, such as Mn, Fe, Co, Ni, Cu, Zn, and Cd, form isomorphous crystals with the general formula of $M^{II}(HCOO)_2 \cdot 2H_2O$.[1-7] Figure 1 shows the crystal structure of the copper salt as an example. The crystals are monoclinic, with a space group of $P2_1/c$, and the metal ions occupy two sets of non-equivalent centers of symmetry: the M1-site at 0,0,0, *etc.* and the M2-site at 1/2, 1/2, 1/2, *etc.* The metal ion at the M1-site is coordinated by an octahedron of six oxygen atoms, all from formate ions, while that at the M2-site is coordinated by a second octahedron of four water molecules and two oxygen atoms from formate ions.

The existence of the two sets of metal sites with different surroundings suggested the possibility that, when mixed crystals were prepared among the members of this series, cations of different chemical species might occupy different sites with different occupancy. Such a phenomenon would be interesting not only because it has been observed frequently in minerals, but also because it reminds us of the selectivity of biologically important substances to metal ions.[8]

From a series of preliminary experiments made in this laboratory,[9] it has been found that mixed crystals containing copper ions as one of the components exhibit an unusual behavior in the change of lattice constants with the change in the molar ratio of cations. A systematic study was thus undertaken of copper-containing mixed crystals of dihydrated formates.

Description of the Results

Preparation and Chemical Constitution. Mixed crystals with various molar ratios were prepared for the Cu–Zn, Cu–Ni, and Cu–Mn systems by the slow evaporation of the corresponding mixed solution at 55±2 °C. Only a small portion from a large quantity of each solution was crystallized out so as not to cause a substantial change in the composition of the solutions during crystallization. The relative amount of metallic ions in mixed crystals and in the mother liquor, both before and after the crystallization, were determined by absorptiometric methods. Figure 2 shows the relations between the compositions of the solution and the mixed crystals obtained in this way.

Powder X-Ray Pattern and Lattice Constants. The mixed crystals obtained were studied by X-ray powder diffractometry; the results are shown diagrammatically in Fig. 3. It may be noted that the 2θ values of some of the reflections do not change uniformly, indicating that the change in the lattice constants with the chemical constitution is not uniform; this can be seen more clearly in Fig. 4. The results obtained here seem to indicate a non-uniform distribution of the metal ions over the two possible sites, but a detailed interpretation will be given later.

Study by Infrared Absorption. IR measurements were made in order to get some additional clue as to the possibility that either one of the two sites, M1 or M2, might be preferentially occupied by Cu^{2+} ions. The spectra that were found to be most useful for this purpose are those assigned to the wagging vibrations of the water molecules, as is shown in Table 1, where the assignment was obtained by studying the IR spectra

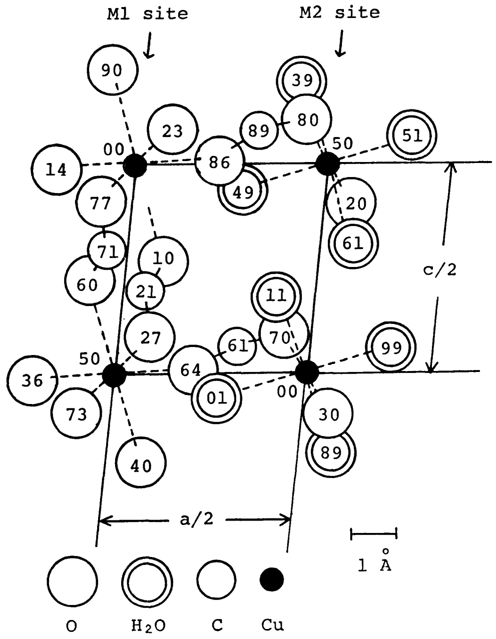

Fig. 1. Crystal structure of $Cu(HCOO)_2 \cdot 2H_2O$ projected on (010).

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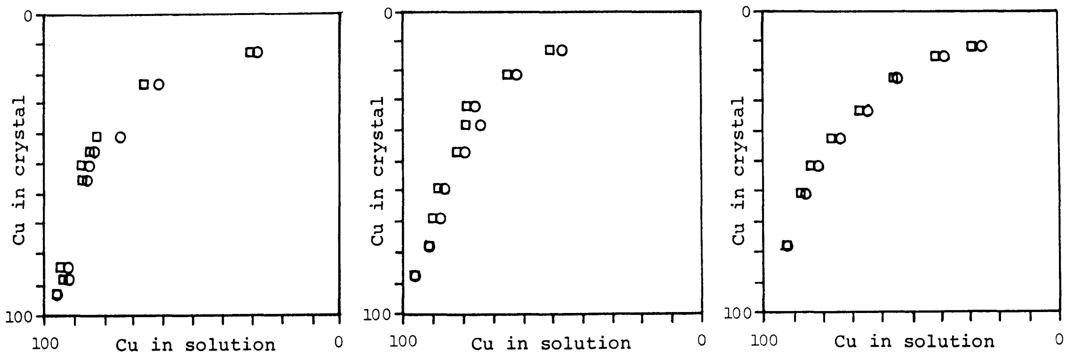
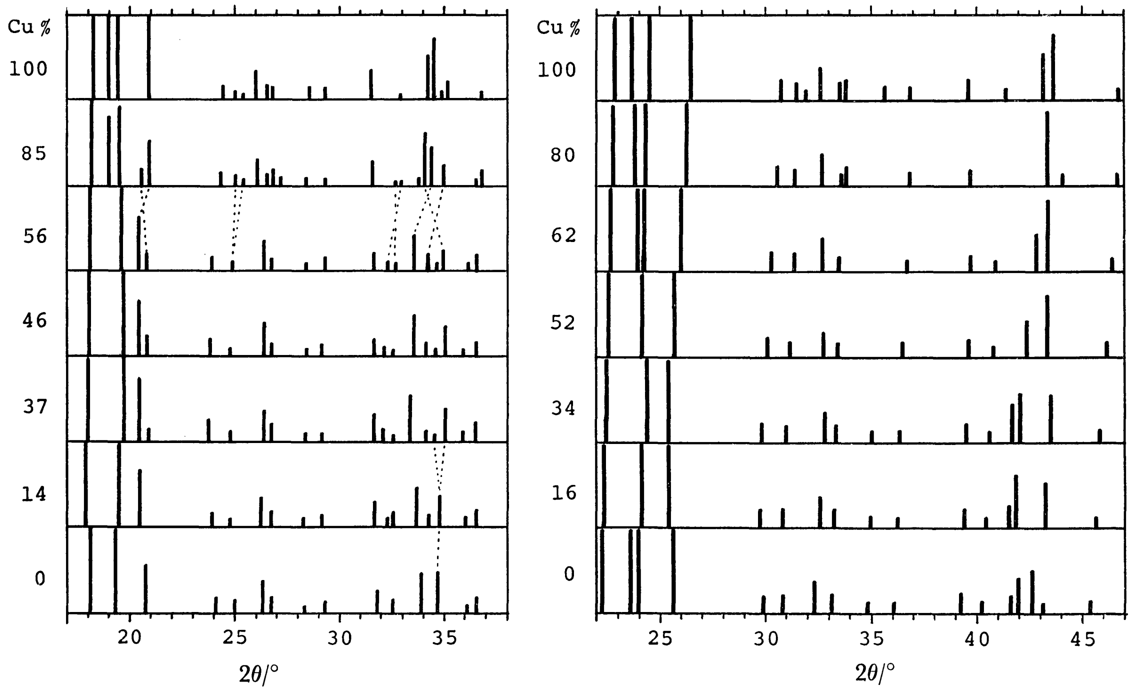


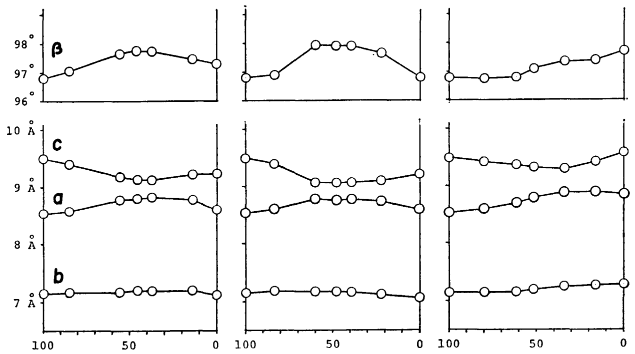
(a) Cu/Zn (b) Cu/Ni (c) Cu/Mn

Fig. 2. Relative concentrations of the metal ions in mixed crystals plotted against those in solutions before (○) and after (□) the crystallization. Ordinate and abscissa represent molar percentage of Cu ions in crystal and in solution, respectively.



(a) Cu/Zn (b) Cu/Mn

Fig. 3. Powder X-ray diffraction patterns of the mixed crystals.



(a) Cu/Zn (b) Cu/Ni (c) Cu/Mn

Fig. 4. Change of lattice constants with the chemical constitution.

Table 1. IR absorption frequencies ($\nu \times$cm) of $M^{II}(HCOO)_2 \cdot 2H_2O$ and their assignments

Salts in which M^{II} are				Assignments
Cu	Zn	Ni	Mn	
1580	1575	1580	1580	antisym. CO stretching
1390	1395	1400	1395	CH stretching in-plane
1325	1355	1355	1360	sym. CO stretching
	1380	1375	1375	
910	870	890	820	$M-H_2O$ rocking
875	830	850		
		795?		
785	765	770	750	OCO bending
600	555	550	568	$M-H_2O$ wagging
470	375	410	400	M-O stretching
400		360	365	
350			310	lattice deformation

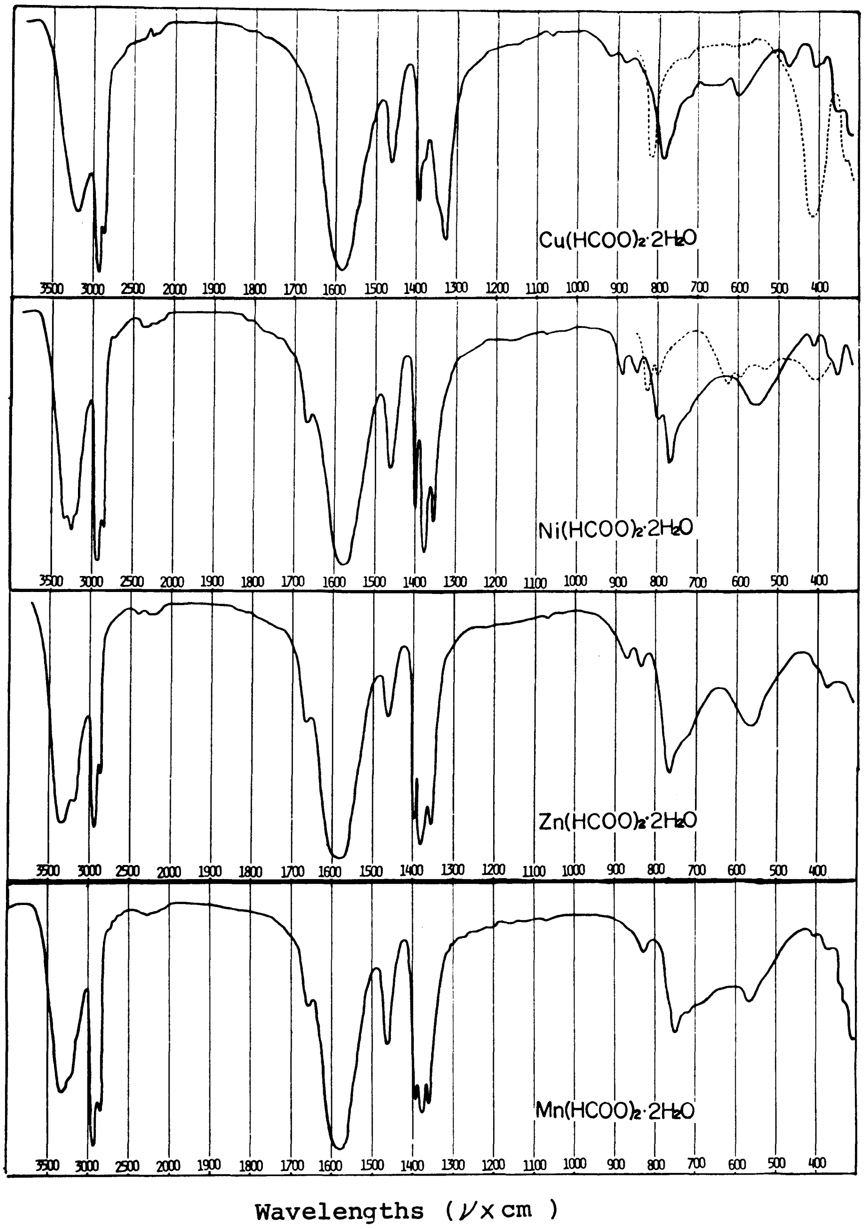


Fig. 5. Infrared absorption spectra of pure dihydrated formates. Dotted curves shown for Cu salt and for Ni salt are those of the anhydrous salt and of the deuterated salt, respectively.

reproduced in Fig. 5 with reference to some reports on related substances.[10,11]

Figure 6 shows how the spectra in this region change with the molar ratio of the cations. The relative amounts of the two kinds of metal ions occupying the M2-sites were determined from these spectra by comparing the optical densities at appropriate wavelengths (600, 555, 550, and 568 cm^{-1} for Cu, Zn, Ni, and Mn, respectively), assuming a 100% transmission at about 430 cm^{-1} and making use of the calibration curves prepared by mixing known amounts of the two kinds of pure substances corresponding to Fig. 5.

The results are shown in Fig. 7, in which the dotted lines, A, B, and C, correspond to the simple models described in the next section. Although there is some scattering of the observed points, it may be concluded that there is a definite tendency for the Cu^{2+} ions to occupy the M1-site rather than the M2-site.

Discussion

As has already been stated, the observed characteristic change of the lattice constants shown in Fig. 3 can not be explained by the uniform replacement of the metal ions in both M1- and M2-sites; some kind of structural change must be taken into account in order to explain the results obtained.

Model calculations were attempted of the lattice constants, *a* and *c*, of the Cu–Ni and Cu–Mn systems, for which the two extreme structures are shown in Fig. 8 in superposed projections. We assumed that the change in the lattice constants is mainly the result of the difference in metal-oxygen distances observed in Fig. 8. In the first place, calculations were made for the three simplest models:

(Model A) The two kinds of ions occupy the two sites without any preference;

(Model B) The Cu^{2+} ions occupy the M2-sites, and the other ions occupy the M1-sites, both with a 100% preference;

(Model C) The same as in model B, except that the M1- and M2-sites are interchanged.

In all three cases, it was assumed that the orientations of the Cu-octahedra at the M1- and M2-sites are the same as those found in the crystal structure of the pure Cu salt.[6]

The results of these model calculations are shown in Fig. 9. Of the three models given above, Model B appears to be in better agreement with the observed points than does A or C. However, this is just the opposite of the results of the IR measurements given above, and also contradicts the results of the ESR study by Wagner *et al.*[12] Moreover, it is noticed that the change in *a* in Fig. 9 (a) is too big to be explained even with Model B.

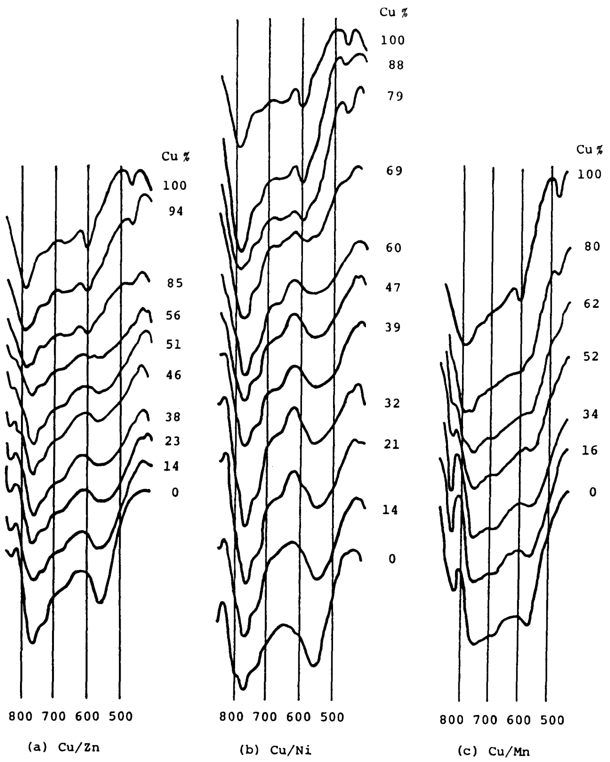


Fig. 6. Changes of the IR spectra assigned to wagging vibrations of water molecules, caused by the change in the molar ratio of metal ions. The abscissa are the wavelengths ($\nu \times$cm).

As a matter of fact, it has been shown, from the single crystal study described in Part II,[13] that, in the 1 : 1 mixed crystal of Cu and Zn salts, most of the Cu-octahedra occupying the M1-site have their longest axis pointing normal to the $[Cu(HCOO)_2]$ sheet, unlike those in the pure Cu salt. This is a possibility that has not been taken into account thus far, so model calculations were also tried for the following two models:

(Model D) Similar to Model C, except that the orientation of the Cu-octahedron at the M1-site is varied according to the Zn/Cu ratio; the longest axis of the Cu octahedron mostly lies along the bc-plane, while the Zn/Cu ratio is low, but as the Zn/Cu ratio increases the proportion of the longest axis pointing normal to the bc-plane becomes larger, attaining to a 70 to 80% orientation at Zn/Cu=1 : 1 (Part II);

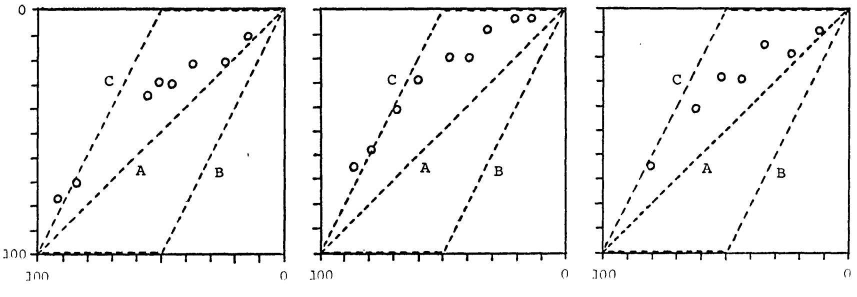
(Model E) Both ions occupy both M1- and M2-sites without any preference, as in Model A, but the longest axis of the Cu-octahedron at the M1-site changes its direction, just as in Model D.

In both cases, the longest axis of the Cu-octahedron at the M2-site always corresponds to M2–O3′. The results for these models, also shown in Fig. 9, seem to indicate that the best model lies somewhere between D and E. This result is also in accord with that of the IR measurements and seems to be the most reasonable interpretation of the mixed crystal formation in the $(Cu,M^{II})(HCOO)_2 \cdot 2H_2O$ system.

Experimental and Calculational Details

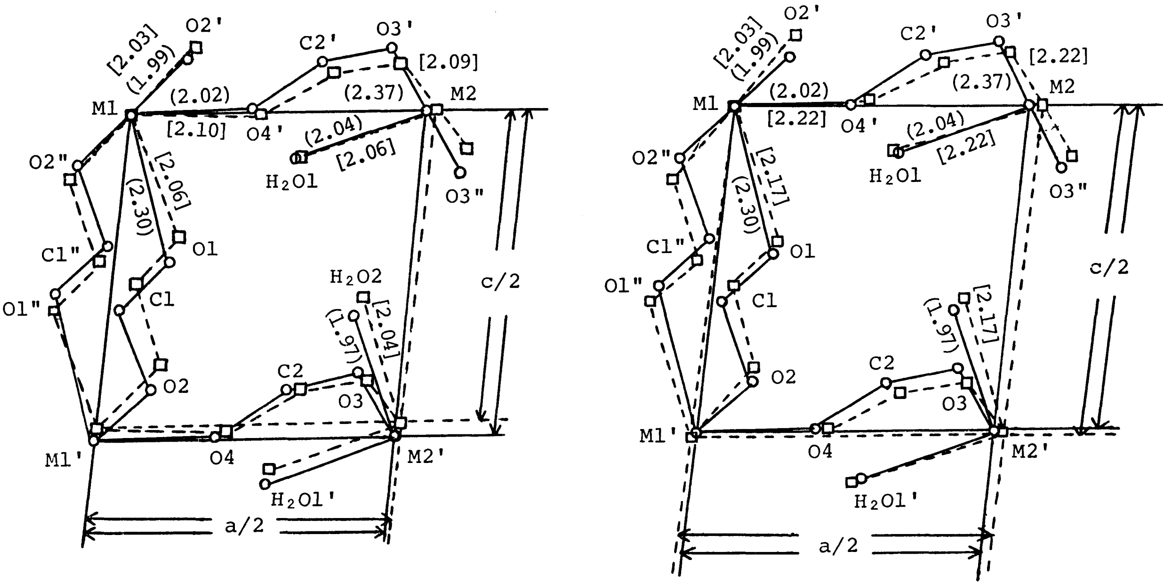
Preparation of Mixed Crystals. A mixture of calculated amounts of the starting substances, carbonates for Zn and Mn or basic carbonates for Cu and Ni, was decomposed in water with a slight excess of formic acid. The solution thus obtained (pH 3—4) was then evaporated in a constant-temperature box at 55±2 °C.

Chemical Analysis. Mixed crystals from each batch were dissolved in water and analyzed by absorptiometric methods,



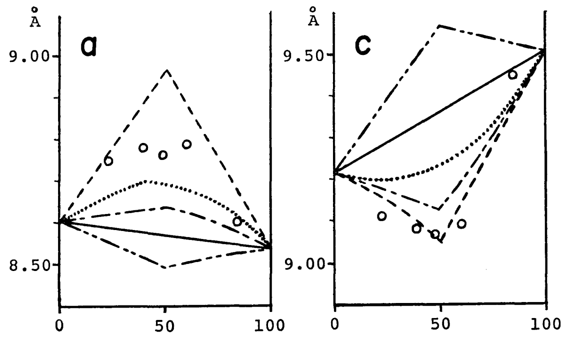
(a) Cu/Zn (b) Cu/Ni (c) Cu/Mn

Fig. 7. Relative amount of metal ions coordinated by water molecules (in M2-sites) against the total amount contained in the mixed crystals.

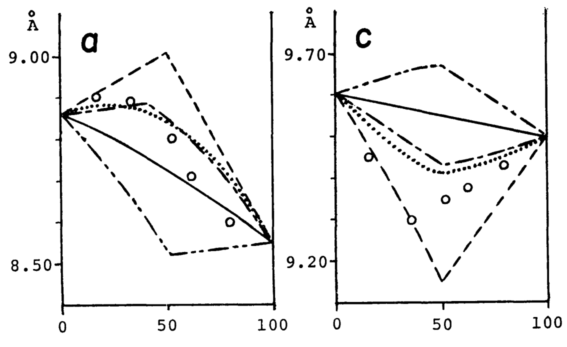


(a) Cu/Ni (b) Cu/Mn

Fig. 8. Crystal structures of $Cu(HCOO)_2 \cdot 2H_2O$ and of $M^{II}(HCOO)_2 \cdot 2H_2O$, shown superposed in b-axis projections. Figures in ( ) and in [ ] are those for the Cu salt and for the salt of the other metals, respectively.



(a) Cu/Ni



(b) Cu/Mn

Fig. 9. Model calculations on the lattice constants a and c.

——— model A, – – – model D,
— — — model B, ········· model E.
—·—·— model C,

as will be described below. The same method was used also for the analysis of the mother liquor.

For the case of Cu–Zn, the zincon method[14,15] was used. For the case of Cu–Ni, the absorbance of the solutions colored by EDTA (pH≈6) was measured at two suitable wavelengths selected from 740, 590, and 385 mμ according to the concentration adopted (from 10^{-3} to 4×10^{-2} mol/l). For the case of Cu–Mn, Mn was measured using the permanganic-acid method[16], while Cu was measured as in the case of Cu–Ni.

X-Ray Powder Diffractometry. The conditions of powder diffractometry were, for the Cu–Zn and Cu–Ni systems: Rigaku Geigerflex; Ni-filtered Cu*K* radiation; 30 kV; 15 mA; receiving slit, 0.15 mm; scanning speed, 1°/min; time constant, 4 s; for the Cu–Mn system: Norelco Diffractometer; Mn-filtered Fe*K* radiation, 35 kV; 10 mA; receiving slit, 0.006 inch; scanning speed, 1°/min; time constant, 8 s.

No signs of unusual line broadening were detected in the powder diagrams of mixed crystals; this suggests that the compositions of the powdered crystal grains in the same batch were fairly uniform and that local fluctuations in the lattice constants were not appreciable.

Indices were given at first only to lower-order, non-overlapping reflections, making use of the similarity in the powder patterns of the mixed crystals and of individual pure substances. The lattice constants calculated by the least-squares method from the observed spacings of these reflections made possible the indexing of additional reflections. This process was repeated until it became difficult to add new reflections.

Infrared Absorption Measurements. The IR spectra shown in Fig. 5 were obtained with a Perkin-Elmer Model 521, and those in Fig. 6, with a Koken DS-301, both using the nujol mull method. In Fig. 5, the spectra shown by dotted lines are those of the anhydrous salt in the case of $Cu(HCOO)_2 \cdot 2H_2O$ and those of the deuterates in the case of $Ni(HCOO)_2 \cdot 2H_2O$.

Model Calculations of the Lattice Constants. The following assumptions were also made:

1) The change in β can be ignored;

2) The change in the axial length, a, is mainly determined by the a-axis component of the variations in the M1–O4′ bond distances, though some additional corrections were also applied taking into consideration the differences in the M2–

O4′ distances which were actually observed in the Cu, Ni, and Mn salts;

3) The change in the axial length, *c*, is mainly determined by the c-axis component of the difference in the M1–O1 bond distances, though corrections similar to those above were also made for the change in the M1′–O1 distance.

The authors are indebted to Professor Emeritus Eiji Suito, Institute for Chemical Research, Kyoto University, and to Professor Katsunosuke Machida of this Faculty for their helpful advice in doing the IR measurements. The preliminary part of this work has been participated in by Miss Yoko Kokado (Mrs. Taga), Miss Miyako Yasuda (Mrs. Hoshiai), Miss Ouko Hamada (Mrs. Umemura), Miss Noriko Okudaira, Miss Yuriko Tanaka (Mrs. Ohno), Miss Yasuko Matsuo and Miss Yumiko Sumida, to all of whom the authors' thanks are also due.

One of the authors (K. O.) is also especially indebted to Professor Emeritus Isamu Nitta and Professor Emeritus Tokunosuké Watanabé, in the atmosphere of whose laboratories in the Faculty of Science, Osaka University, the idea of this work has emerged.

Most of the computations were performed on the HITAC 5020 at the Kyoto University Computation Center or on the FACOM 230-60 at the Data Processing Center, Kyoto University, using UNICS programs and those written by the authors.

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