Cation Distribution in Mixed Formates. II. The Structure of the Mixed Crystal $Cu_{0.5}Zn_{0.5}(HCOO)_2 \cdot 2H_2O$

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The structure of the 1 : 1 mixed crystal between $Cu(HCOO)_2 \cdot 2H_2O$ and $Zn(HCOO)_2 \cdot 2H_2O$ has been determined on the basis of 878 visual intensity data. The space group is $P2_1/c$, with a=8.77, b=7.25, c=9.17 Å, β=98.0°, and Z=4. The structure is similar to that of $Cu(HCOO)_2 \cdot 2H_2O$, except that the two metal ions are distributed over two metal ion sites, the Cu^{2+} ions being mostly localized in the $[Cu(HCOO)_2]$ sheet, and except that the longest axis of the coordination octahedron around the Cu^{2+} ion in this sheet is nearly perpendicular to it. It is suggested that the type of sheet found in the mixed crystal as well as in $Cu(HCOO)_2 \cdot 4H_2O$ is more favorable than that in $Cu(HCOO)_2 \cdot 2H_2O$ for an independent $[Cu(HCOO)_2]$ sheet.

In Part I of this series,[1] it has been shown that the lattice constants of the mixed crystals with the general formula of $(Cu,M^{II})(HCOO)_2 \cdot 2H_2O$ do not change uniformly with the change in the chemical constitution, and that simple models based merely on the preferential occupation of the two non-equivalent sites by different metal ions were unsatisfactory in explaining the observed results. It was, therefore, hoped that a detailed structure study of a 1 : 1 mixed crystal of this series would provide some evidence which might help elucidate the problem.

Structure Determination

Apparently single crystals containing approximately equal amounts of Cu^{2+} and Zn^{2+} ions were obtained by the slow evaporation of a mixed solution with an appropriate molar ratio, as determined from Fig. 2 of Part I.

The lattice constants obtained from Weissenberg photographs are a=8.77±0.03, b=7.25±0.02, c=9.17±0.02 Å, and β=98.0±0.5°. There are four formula units in this unit cell with the space group of $P2_1/c$, just as in $Cu(HCOO)_2 \cdot 2H_2O$.[2] The intensity data, visually estimated on Weissenberg photographs and put on a common scale after necessary corrections, amounted to 878, excluding non-observed reflections.

An approximate structure was easily obtained with reference to those of related formates,[2,3] assuming averaged atoms at both metal sites. Refinements were performed with full-matrix least-squares for the two cases: one with Zn^{2+} at the M1-site and Cu^{2+} at the M2-site (case 1), and the other in which they are interchanged (case 2), in the hope that the slight difference in the number of electrons in the metal ions might give evidence as to which of these two cases corresponds to the true structure. The results are given in Table 1. The R value was 0.110 for both cases. No significant difference was found in the positions of the lighter atoms. From the smaller difference in the thermal parameters for the two metal sites, it might seem that Case 1 could be the correct structure. As a matter of fact, it turned out that the final model adopted after a detailed examination of the structure (to be described later) was closer to Case 2, though the localization of the metal ions was found to be incomplete. A reasonable interpretation of the above contradiction is that the large difference in the thermal parameters has upset the effect of the small difference in electron density.

The atomic scattering factors used were taken from the International Tables for X-ray Crystallography (Vol. 3), and dispersion corrections were applied to the real parts of the scattering factors for Cu^{2+} and Zn^{2+}. The

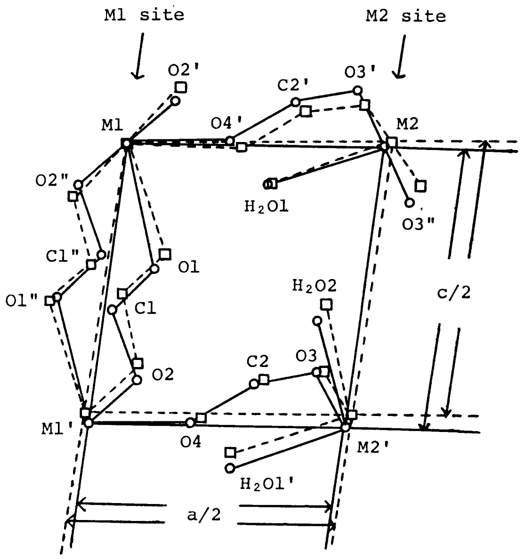

Fig. 1. Crystal structures of $Cu_{0.5}Zn_{0.5}(HCOO)_2 \cdot 2H_2O$ and $Cu(HCOO)_2 \cdot 2H_2O$ seen superposed in projection down the b-axis.

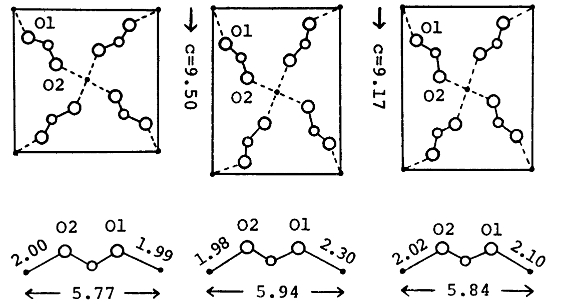

Fig. 2. The structure of thc $[Cu(HCOO)_2]$ sheets in the three related compounds.

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TABLE 1. POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	B/Å² Case 1	B/Å² Case 2
M1	0	0	0	1.72(05)	1.21(04)
M2	0.5	0.5	0	1.48(05)	2.07(05)
C1	0.034(1)	0.226(1)	0.277(1)	1.96(18)	1.97(18)
C2	0.324(1)	0.612(1)	0.438(1)	1.96(18)	2.01(18)
O1	0.095(1)	0.103(1)	0.207(1)	2.22(16)	2.16(13)
O2	0.087(1)	0.279(1)	0.405(1)	1.99(13)	2.00(13)
O3	0.436(1)	0.722(1)	0.420(1)	2.87(16)	2.90(16)
O4	0.214(1)	0.664(1)	0.502(1)	2.11(13)	2.17(13)
$(H_2O)1$	0.284(1)	0.474(1)	0.073(1)	2.19(13)	2.13(13)
$(H_2O)2$	0.413(1)	0.107(1)	0.300(1)	3.06(16)	3.15(16)

Case 1: Zn^{2+} in M1 and Cu^{2+} in M2, Case 2: Cu^{2+} in M1 and Zn^{2+} in M2.

TABLE 3. INTERATOMIC DISTANCES AND ANGLES

Atom pairs[a]	$Cu_{0.5}Zn_{0.5}$-$(HCOO)_2 \cdot 2H_2O$	Cu-$(HCOO)_2 \cdot 2H_2O$
M1-O1	2.10(2) Å	2.30(2) Å
M1-O2′	2.02(1)	1.98(2)
M1-O4′	2.22(1)	2.02(2)
M2-W1	2.10(1)	2.04(2)
M2-O3′	2.19(1)	2.37(2)
M2′-W2	2.04(1)	1.97(2)
O4-M1′-O1″	92.8(4)°	91.5(6)°
O1″-M1′-O2	91.2(6)°	89.2(7)°
O4-M1′-O2	93.4(7)°	93.2(7)°
O3-M2′-W1′	89.3(4)°	87.6(6)°
W1′-M2′-W2	90.5(8)°	87.5(7)°
O3-M2′-W2	90.1(5)°	86.9(6)°
C1-O1	1.26(1) Å	1.26(3) Å
C1-O2	1.27(1)	1.30(3)
C2-O3	1.29(1)	1.26(3)
C2-O4	1.25(1)	1.24(3)
O1-C1-O2	124(1)°	121(2)°
O3-C2-O4	121(1)°	130(2)°
W1′-O2	2.82(2) Å	2.82(2) Å
W1′-O4	2.75(1)	2.78(2)
W2-O1	2.79(2)	2.77(3)
W2-O3″	2.70(2)	2.67(2)

a) W in this column represents (H_2O).

TABLE 4. OBSERVED AND CALCULATED M-O DISTANCES

Bond	Observed	Calcd[a] 70%	Calcd[a] 80%	Calcd[a] 100%
M1-O4′	2.22 Å	2.20 Å	2.23 Å	2.27 Å
M1-O1	2.10	2.10	2.08	2.03
M1-O2′	2.02	2.03	2.03	2.03
M2-O3′	2.19	2.18	2.18	2.18
M2-W1	2.10	2.07	2.07	2.07
M2′-W2	2.04	2.07	2.07	2.07

a) The percentages given for the calculated values are the proportions of the longest axis orientated along M1-O4′.

observed and calculated structure factors are given in Table 2.**

Description and Interpretation of the Structure

The crystal structure of $Cu_{0.5}Zn_{0.5}(HCOO)_2 \cdot 2H_2O$ is similar to that of $Cu(HCOO)_2 \cdot 2H_2O$,[2)] as is shown in Fig. 1 in superposed projections along the b-axis. They both contain parallel sheets with the composition of $[M^{II}(HCOO)_2]$, interleaved with another kind of sheet with the composition of $[M^{II}(H_2O)_4]$ and linked together by a second formate ion. However, closer study shows that, in the mixed crystal, both the M1–O4′ and M2–O3′ listed in Table 3 are definitely longer than those to be expected for a Zn–O bond (0.74+1.40=2.14 Å), and that the longest axis (M1–O4′) of the coordination octahedron at the M1-site points almost normal to the $[M^{II}(HCOO)_2]$ sheet, which is quite different from that found in $Cu(HCOO)_2 \cdot 2H_2O$, where the longest axis M1–O1 lies along the sheet. The latter observation suggests that the longest axis of the Cu-octahedron at the M1-site changes its direction in relation with the relative concentration of the Cu atom and opens the possibility of some new models for the relation between lattice constants and chemical constitution which has been discussed in Part I.

The observed length of M1–O4′ and M2–O3′ can only be explained if it is assumed that both M1 and M2 sites are occupied by Cu^{2+} ions to some extent and that the two bond lengths mentioned above are the average values including the contributions from the longest axis of the Cu octahedron. If we adopt the findings of our IR study described in Part I, that in a 1 : 1 mixed crystal between the Cu and Zn salts about 70% of the M1-site is occupied by Cu^{2+} ions, and make the further assumption that from about 70 to 100% of the Cu-octahedra occupying the M1-site are orientated with their longest axis along M1–O4′, we obtain the calculated M–O distances given in Table 4.

It will be seen that a satisfactory agreement between observed and calculated M–O lengths is obtained with

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** Table 2 is kept at the office of the Chemical Society of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo 113 (Document No. 7708).

a 70 to 80% orientation. In this calculation, it was further assumed that all the Zn–O bond is 2.10 Å, while for Cu–O, the longest axis is 2.35 Å and the shorter ones are 2.00 Å.

The conclusions obtained here, that in the 1 : 1 mixed crystals between Cu and Zn salts, the M1-site is preferentially occupied by Cu^{2+} ions and that most of the longest axes of the Cu-octahedra at the M1-site point to M1–O4′, while those at the M2-site point to M2–O3′, not only explain the observed changes in the lattice constants with respect to the chemical constitution (Part I), but are in agreement with the results of an ESR study of the Cu-doped $Zn(HCOO)_2 \cdot 2H_2O$ by Wagner *et al.*⁴⁾ if the principal axis of the magnetic field at the Cu^{2+} ion found by ESR coincides with the longest axis of the Cu-octahedron.

The structure of the 1 : 1 mixed crystal between Cu and Zn salts has now been elucidated including the distribution of the cations, but questions still remain as to why the Cu^{2+} ion occupies the M1-site preferentially and why the longest axis of the Cu-octahedron at the M1-site points to M1–O4′ and not to M1–O1, as in the pure Cu salt.

A sheet with the composition of $[M^{II}(HCOO)_2]$, similar to that found in the mixed crystal, is also found in $Cu(HCOO)_2 \cdot 4H_2O$;⁵⁾ it resembles the one in the mixed crystal also with respect to the orientation of the longest axis of the Cu-octahedron. The sheet in the tetrahydrate has been the subject of many investigations because of its remarkable anti-ferromagnetic nature,⁶⁻¹⁵⁾ and it seems generally accepted that the superexchange interaction by way of the delocalized π-electron cloud of the formate ion is responsible for the magnetic interaction between the neighboring Cu^{2+} ions in the sheet.⁴,¹⁶,¹⁷⁾ Since the Cu^{2+} ion is coordinated with an elongated octahedron, an arrangement with the long axis almost normal to the sheet will be most favorable for a better overlapping between the copper d-orbitals and oxygen π-orbitals of the formate ion. The very large exchange integrals observed for the tetrahydrate ($-54\ cm^{-1}$)¹²⁾ and for the Cu^{2+} ions in $Zn(HCOO)_2 \cdot 2H_2O$ ($-33\ cm^{-1}$)⁴⁾, as compared with the corresponding values for $Cu(HCOO)_2 \cdot 2H_2O$ (1.5 K),¹⁸⁾ seem to support this view.

A comparison among the $[Cu(HCOO)_2]$ sheets found in the three compounds discussed shows that the sheet in the mixed crystal is, in a sense, intermediate between those in $Cu(HCOO)_2 \cdot 4H_2O$ and in $Cu(HCOO)_2 \cdot 2H_2O$ (Fig. 2). Perhaps it may be said that the sheets found in $Cu(HCOO)_2 \cdot 4H_2O$ and in the mixed crystal represent the most stable structure for a single $[Cu(HCOO)_2]$ sheet, while that of the other type, found in $Cu(HCOO)_2 \cdot 2H_2O$, is probably a result of some additional interaction through the second formate linkages.

Most of the computations were made on the HITAC 5020 at the Kyoto University Computation Center, using programs written by the present authors.

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