Copper/Zinc Oxide Catalysts VIII. Crystal Structure of Zinc Maleate Dihydrate, $Zn(C_4O_4H_2)(H_2O)_2$ and its Comparison with the Structure of the Cu-Zn Analogue $Zn_{0.94}Cu_{0.06}(C_4O_4H_2)(H_2O)_2$

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Single crystals of $Zn(C_4O_4H_2)(H_2O)_2$ (ZMH) were prepared and the crystal and molecular structure was determined. ZMH exhibits a 2-dimensional structure formed of extended layers stacked perpendicularly to the [010] direction like the structure of the copper-zinc analogue $Zn_{0.94}Cu_{0.06}(C_4O_4H_2)(H_2O)_2$ (ZCMH). The layers are built up of zinc atoms, maleate anions, and the two water molecules; each bridging maleate ligand is coordinated to three different zinc atoms through three carboxylate oxygen atoms. The close coordination sphere of the zinc atom contains the water molecules as well as three carboxylate oxygen atoms with all Zn—O distances shorter than 2.137(2) Å. The fourth oxygen atom of the maleate anion is at a longer distance from zinc (2.658(2) Å) and this atom is involved in an interlayer hydrogen bond. The unit cell parameters and volume of ZMH are smaller than for ZCMH despite the higher ionic radii of Zn^{2+} in comparison with Cu^{2+}. This observation can be explained by the more deformed coordination polyhedron around the copper atom, which causes less efficient packing of the layers in the structure of ZCMH.

Cu/ZnO-based solid solutions containing copper in the range of 1 to 10 mole % may play an important role in the catalytic process of methanolization of syngas, but these solid solutions depend strongly on the preparation conditions [1, 2]. In order to find a well crystallized monophasic precursor of such solid solutions containing copper in the above-mentioned range, we have prepared, characterized and solved the crystal structure of a novel Cu-Zn bimetallic precursor $Zn_{0.94}Cu_{0.06}(C_4O_4H_2)(H_2O)_2$ (ZCMH) [3]. The preparation of the zinc analogue (ZMH) in the microcrystalline form was already described by *Allan et al.* [4]. As we succeeded recently in the preparation of single crystals of this compound, we report here the X-ray study results of ZMH as well as a comparison with the structure of the zinc-copper bimetallic analogue.

EXPERIMENTAL

Single crystals suitable for X-ray structure analysis were prepared as described in Ref. [3].

X-Ray powder diffraction (XRD) pattern was taken by using a computerized Siemens D-500 diffractometer in the 2Θ range 5—50°. CuK_α radiation ($\lambda(K_{\alpha1})$ = 1.540981 Å, $\lambda(K_{\alpha2})$ = 1.54439 Å; Sollers slits) was used and backmonochromatized with a graphite monochromator. The diffractogram was recorded in step mode (0.02°, 10 s). Data handling (peak fitting, Pseudo-Voigt profile function) was carried out with the software package EVA and FIT (Socabim, France). Refinement of the cell parameters was made by using the program U-FIT [5].

Crystal Structure Analysis

For data collection of ZMH on a Syntex $P2_1$ diffractometer a colourless prism with dimensions 0.25 mm × 0.50 mm × 0.50 mm was selected. Cell parameters were obtained from 25 reflections in the range $2.7 \leqq \Theta \leqq 15.5°$.

The density was measured using flotation method with a mixture of bromoform, chloroform, and acetone. The relevant crystal data are gathered in Table 1 which contains also the cell parameters of ZCMH measured under similar conditions along with published data.

Data from one half of the reciprocal space were collected (3275 reflections, Θ_{max} = 37.6°, $0 \leqq h \leqq 9$, $-27 \leqq k \leqq 27$, $-11 \leqq l \leqq 11$) using Θ—2Θ scan mode. The crystal stability during data collection was

Table 1. Crystal Data for ZMH and ZCMH

	ZMH	ZMH (powder)	ZCMH	ZCMH
Diffractometer	Syntex $P2_1$	Siemens D500	CAD4	Syntex $P2_1$
Radiation	Mo$K\alpha$	Cu$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
λ/Å	0.71069	1.540598	0.71069	0.71069
Space group	Cc	Cc	Cc	Cc
Cell parameters				
a/Å	5.702(2)	5.709(1)	5.725(1)	5.715(2)
b/Å	16.183(5)	16.187(2)	16.251(2)	16.257(6)
c/Å	6.801(3)	6.804(1)	6.825(1)	6.826(3)
β/°	90.81(3)	90.74(1)	90.72(1)	90.70(3)
V/Å^3	627.5(4)	628.7(2)	634.9(2)	634.2(4)
(D_o/D_c)/(g cm^{-3})	2.25/2.28		2.24/2.25	
Z	4	4	4	4

Table 2. Atomic Coordinates for ZMH along with U_{eq}, Equivalent Thermal Parameter or Isotropic Thermal Parameters (marked with asterisk)

Atom	x	y	z	U_{eq}/* U_{iso}
Zn	0.42482(4)	0.177440(1)	0.17524(3)	0.01838(8)
O1	0.7195(4)	0.1457(1)	0.0449(3)	0.0223(4)
O2	0.5292(4)	0.0272(1)	0.0443(3)	0.0275(3)
O3	1.2368(4)	0.2001(1)	−0.0934(3)	0.0226(3)
O4	0.9646(3)	0.1992(1)	−0.3275(3)	0.0202(3)
O5	0.5250(4)	0.1368(1)	0.4578(3)	0.0272(4)
O6	0.1025(4)	0.1616(2)	0.2846(3)	0.0263(4)
C1	0.7028(4)	0.0689(1)	0.0011(3)	0.0182(3)
C2	0.9007(4)	0.0307(1)	−0.1024(3)	0.0187(3)
C3	1.0727(4)	0.0719(1)	−0.1885(3)	0.0173(3)
C4	1.0925(4)	0.1632(1)	−0.1992(3)	0.0154(3)
H2	0.904(9)	−0.035(3)	−0.096(7)	0.022*
H3	1.202(8)	0.046(2)	−0.275(6)	0.021*
H51	0.590(14)	0.157(4)	0.506(11)	0.045(8)*
H52	0.514(10)	0.075(3)	0.493(8)	0.045(8)*
H62	0.084(14)	0.172(3)	0.388(11)	0.045(8)*
H61	0.000(14)	0.165(3)	0.227(10)	0.045(8)*

monitored with three standard reflections (171, 330, 2-23) measured every 100 reflections. 1782 unique reflections were obtained ($R_{int}(F_o^2) = 0.0285$), of these 1636 were "observed" with $I > 2\sigma(I)$ and used for refinement of 121 parameters. The data were corrected for Lorentz and polarization effects. Empirical absorption correction ($\mu(\mathrm{Mo}K_\alpha) = 3.98$ mm^{-1}) was used based on azimuthal ψ scans using the XP21 program [6], the maximum and minimum transmission coefficients were 0.995 and 0.506, respectively.

The atomic coordinates of the ZCMH [3] were taken as an initial model and were refined by least-squares methods using the SHELXL93 program [7]. Positions of hydrogen atoms were refined. Thermal parameters of H(C) atoms were set to be 1.2 times greater than the equivalent thermal parameter of the parent atom, while for the H atoms of the water molecules a common isotropic thermal parameter was refined.

The absolute structure was considered during refinement [8]. The first orientation yielded a Flack parameter $x_1 = 0.093(12)$, while the inverted one (c glide plane) a value of $x_2' = 0.213(15)$. The value of x_1, significantly different from the expected value of 0 (8 times e.s.d.) suggests the possibility of racemic twinning in the single crystal used for data collection. The value of the refined batch scale factor was 0.29(2). The final values were: $R1$(observed) = 0.0250, $R1$(all) = 0.0298, $wR2$(observed) = 0.0614 ($w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$), $wR2$(all) = 0.0627, S(all) = 1.013, $(\Delta/\sigma)_{max} = 0.000$. Extinction correction was used, with the extinction coefficient $x =$ 0.240(6) ($F_c^* = kF_c\,[1 + 0.001xF_c^2\,\lambda^3/\sin(2\Theta)]^{-1/4}$; k is the overall scale factor). The final difference map was featureless: $\Delta\rho(\mathrm{e}) \leqq 0.7(7)$ Å^{-3}. The scattering factors were those from International Tables included in the SHELXL93 program [7]. The programs PARST95 [9] and ORTEP [10] were used respectively for geometric analysis and for drawing of the figures. The atomic coordinates along with the equiv-

Table 3. Comparison of Selected Geometric Parameters in ZMH and ZCMH [3]

	ZMH	ZCMH
Zn—O1	1.979(2)	1.988(3)
Zn—O2	2.658(2)	2.682(3)
Zn—O3	2.137(2)^{i}	2.125(2)
Zn—O4	2.010(2)^{ii}	2.022(2)
Zn—O5	2.102(2)	2.109(3)
Zn—O6	2.009(3)	1.999(3)
O1—C1	1.282(3)	1.281(4)
O2—C1	1.237(3)	1.240(4)
O3—C4	1.239(3)	1.247(3)
O4—C4	1.270(3)	1.278(3)
C1—C2	1.474(3)	1.487(4)
C2—C3	1.329(3)	1.328(4)
C3—C4	1.484(3)	1.486(4)
O1—Zn—O3^{i}	94.60(9)	94.5(1)
O1—Zn—O4^{ii}	99.04(8)	98.2(1)
O1—Zn—O5	96.14(9)	95.6(1)
O1—Zn—O6	156.9(1)	157.3(1)
O4^{ii}—Zn—O3^{i}	82.92(7)	83.06(9)
O4^{ii}—Zn—O5	106.85(8)	105.9(1)
O5—Zn—O3^{i}	164.09(9)	165.4(1)
O6—Zn—O3^{i}	83.56(9)	84.1(1)
O6—Zn—O4^{ii}	103.5(1)	104.1(1)
O6—Zn—O5	82.0(1)	82.5(1)
C1—O1—Zn	107.2(2)	107.7(2)
C4—O3—Zn^{iii}	137.3(2)	136.8(2)
C4—O4—Zn^{iv}	120.8(1)	121.9(2)
O1—C1—O2	122.0(2)	122.1(3)
O1—C1—C2	117.6(2)	117.8(3)
O2—C1—C2	120.4(2)	120.2(3)
C1—C2—C3	125.0(2)	125.1(2)
C2—C3—C4	125.4(2)	125.6(2)
O3—C4—O4	123.3(2)	122.8(2)
O3—C4—C3	120.1(2)	120.1(2)
O4—C4—C3	116.5(2)	117.0(2)

i: $x-1$, y, z; ii: $x-1/2$, $1/2-y$, $z+1/2$; iii: $x+1$, y, z; iv: $x+1/2$, $1/2-y$, $z-1/2$.

alent thermal parameters are displayed in Table 2. Selected geometric parameters are gathered in Table 3.

RESULTS AND DISCUSSION

The zinc-alone compound ZMH exhibits the same type of structure as the copper-zinc analogue ZCMH with very close atomic coordinates (Fig. 1, Table 2). The structure of ZMH is formed of extended layers running perpendicularly to the [010] direction (Fig. 2) with 2 layers per cell. The layers are built up of one crystallographically independent zinc atom, one maleate anion, and two water molecules. The maleate anion behaves as a bridging ligand joining three zinc atoms through three carboxylate oxygen atoms; the fourth oxygen atom (O2) is involved in an interlayer hydrogen bond (HB) network. If we assume only short Zn—O coordination bonds (shorter than 2.14 Å), the zinc atom exhibits pentacoordination by three oxygen atoms from three different maleate anions and two water molecules. The fourth oxygen atom of the maleate anion is placed at a rather long distance from zinc atom (2.658(2) Å), comparable to the equivalent distance in ZCMH (2.682(3) Å). These results suggest the possibility of weak Zn···O2 bonding interaction. The observed type of coordination in ZMH (and also ZCMH) is different from that found in copper maleate hydrate where all four oxygen atoms are involved in coordination bonds [11].

The contacts between the layers are made by one HB of the O—H···O type (O5···O2^{v}; 2.719(3) Å, v: x, $-y$, $1/2+z$); further contacts of the C—H···O type (C2···O6^{i}; 3.409(4) Å, i: $x+1$, $-y$, $z-1/2$) with H···O distance of 2.48(5) Å are shorter than the sum of van der Waals radii (2.70 Å) [12]. These contacts are displayed in Table 4 along with the data concerning intralayer HB's.

In order to ascertain the phase homogeneity of ZMH, the powder diffraction pattern was recorded (Table 5), fully indexed and the refinement of the unit cell parameters yielded the same unit cell parameters (Table 1). We can conclude that ZMH in powder form is also monophasic.

The ionic radius for pentacoordinated Cu^{2+} (0.65 Å) is smaller than the ionic radius for pentacoordinated Zn^{2+} (0.68 Å). The same trend is valid also for hexacoordinated cations (Cu^{2+}: 0.73 Å and Zn^{2+}: 0.74 Å) [13]. On the basis of these values, shorter cell parameters for ZCMH than for ZMH could be expected, but the reverse was experimentally observed. All cell parameters of ZMH, but not the angle β, were observed to be smaller than those of ZCMH; the greatest difference being 0.068 Å for the b parameter. As it can be seen from the standard deviations, these differences are significant for a, b, and c unit cell parameters, and are on the border of significance for the value of angle β. The observed differences lead to a decrease of the unit cell volume from 634.9(2) Å^3 for ZCMH to 627.5(4) Å^3 for ZMH (1.2 % difference) and consequently to an increase of the calculated densities of ZMH and ZCMH (Table 1). In order to exclude any influence due to the use of different apparatus and experimental conditions for data collections, the cell parameters of ZCMH were measured again on the same diffractometer used for the data collection of ZMH. Almost the same values were found as reported previously (Table 1).

Porta et al. [14] studied the variation of the unit cell parameters by powder XRD for solid solutions of Cu^{2+} in hydrozincite phase $Zn_5(CO_3)_2(OH)_6$ for n(Cu) : n(Zn) ratios from 0 : 100 to 10 : 90. They observed an increase of the hydrozincite cell volume with increasing copper content. They explain the disagreement between the unit cell volume variation and the lower ionic radii for hexacoordinated copper(II) (0.73 Å) when compared with ionic radius of hexaco-

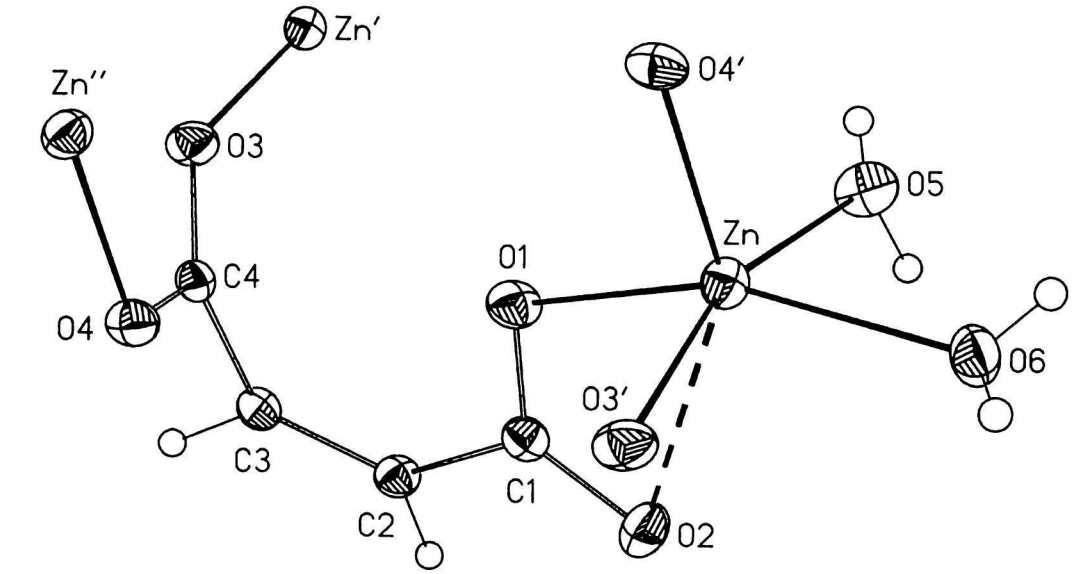

Fig. 1. An ORTEP view of the structure of zinc maleate dihydrate.

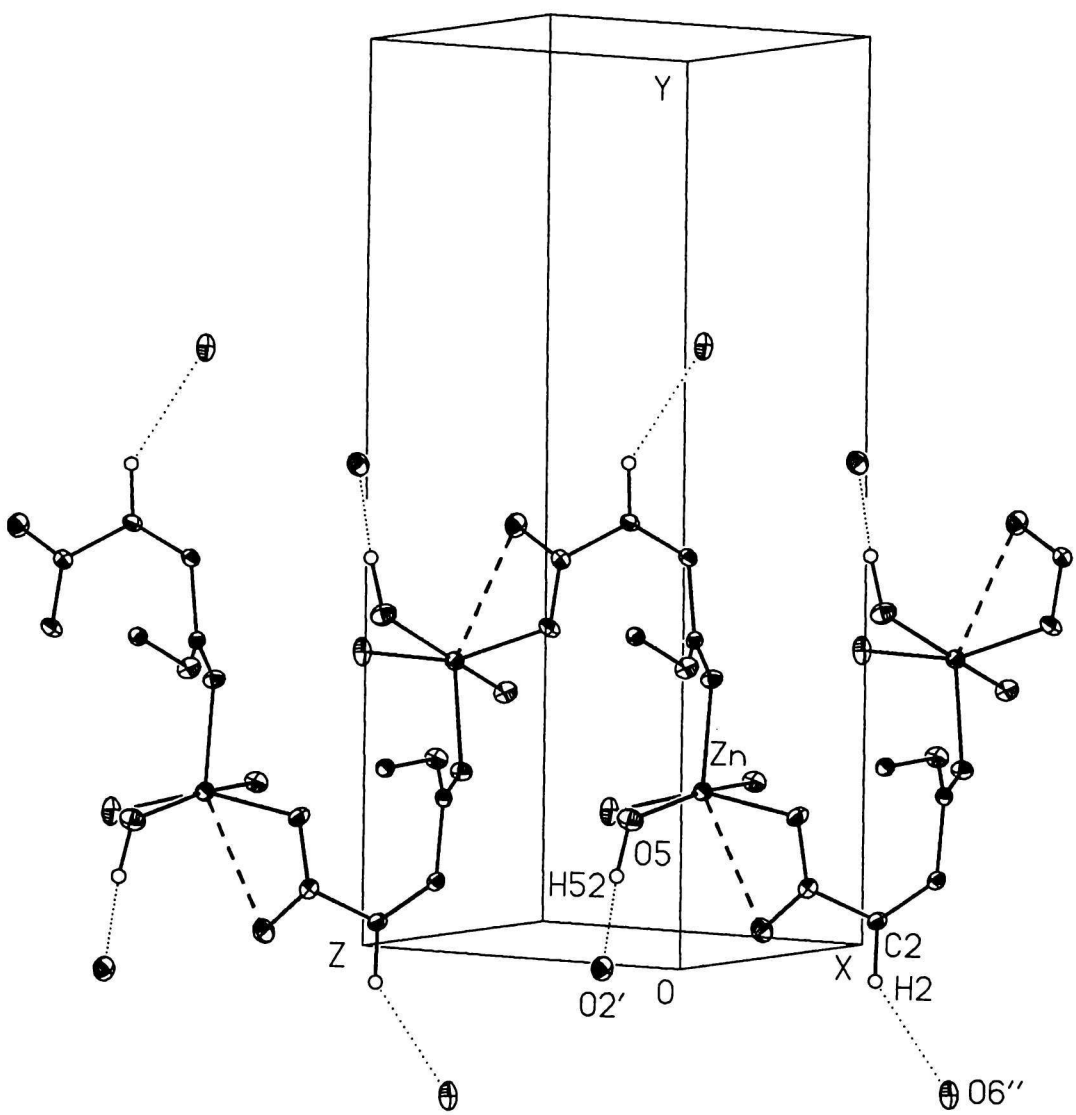

Fig. 2. Part of the layer formed in zinc maleate dihydrate. The possible interlayer hydrogen bonds are displayed as dashed lines.

Table 4. Possible Hydrogen Bonds/(Å and °) and Contacts for ZMH and ZCMH. (Data for ZCMH are given in italic.)

Donor-H	Donor···Acceptor	H···Acceptor	Donor-H···Acceptor
C2—H2	C2···O6^{i}	H2···O6^{i}	C2—H2···O6^{i}
1.06(4)	3.409(4)	2.48(5)	145(3)
1.060(3)	*3.420(5)*	*2.499(3)*	*144.7(2)*
O5—H51	O5···O4^{iv}	H51···O4^{iv}	O5—H51···O4^{iv}
0.59(8)	3.055(3)	2.50(8)	158(9)
0.69(7)	*3.084(4)*	*2.49(6)*	*146(7)*
O5—H52	O5···O2^{v}	H52···O2^{v}	O5—H52···O2^{v}
1.04(5)	2.719(3)	1.69(5)	173(5)
1.06(6)	*2.722(5)*	*1.66(7)*	*177(5)*
O6—H61	O6···O1^{vi}	H61···O1^{vi}	O6—H61···O1^{vi}
0.70(8)	2.719(3)	2.04(8)	166(5)
0.64(6)	*2.743(4)*	*2.18(6)*	*149(7)*
O6—H62	O6···O4^{vii}	H62···O4^{vii}	O6—H62···O4^{vii}
0.73(7)	2.830(3)	2.11(7)	170(8)
0.87(6)	*2.839(4)*	*2.00(6)*	*164(5)*

Equivalent positions:
i: $x + 1, -y, z - 1/2$; ii: $x + 1, y, z$; iii: $x - 1/2, -y + 1/2, z + 1/2$; iv: $x, y, z + 1$; v: $x, -y, z + 1/2$; vi: $x - 1, y, z$; vii: $x - 1, y, z + 1$.

ordinated zinc(II) (0.74 Å) by M—O bond covalency decrease and/or by greater octahedral site distortion around the Cu atom when copper replaces zinc.

A quantitative study of the variation of the cell parameters as a function of Cu content was performed in the case of the dihydrates of copper and zinc formates (CFH = copper formate hydrate and ZFH = zinc formate hydrate), which form continuous solid solutions. They crystallize in the monoclinic space group $P2_1/c$ with two independent metal sites in the asymmetric part. The variations of the unit cell parameters are displayed graphically as a function of the n(Cu) : n(Zn) atomic ratio and it can be seen that small copper substitution of zinc (approx. 14 mole %) causes an increase of a, b, and β unit cell parameters, while a small decrease was observed in the case of the c parameter; these changes indicate an increase of the unit cell volume [15] with increasing copper content for hexacoordinated metal atoms. The results of this study agree well with our results and those reported for the hydrozincite phase.

Moreover, the results of structure analysis of the mixed salt ZCFH [16] indicate that the distribution of the two metal cations over the two metal ion sites (the ions are pseudooctahedrally coordinated) is not uniform, but preferential, and the longest axes of the Cu octahedra are oriented in a different manner than in CFH. This observation supports the assumption that the distortion of the coordination polyhedron due to the Jahn—Teller effect is the more important factor influencing the unit cell volume increase.

In order to find possible reason(s) for such unit cell volume increase in the case of hexacoordinated central atoms of zinc and copper, we have compared the published M—O bond distances in crystal structures of CFH [17], ZFH [18], and mixed (1 : 1) formate dihydrate (ZCFH = zinc-copper formate hydrate) (Table 6) [16]. As it can be seen from Table 6, the two CuO_6 octahedra in CFH exhibit the largest differences between axial and equatorial bonds (0.28 Å and 0.40 Å) and thus are more deformed than ZnO_6 and $(Zn,Cu)O_6$ octahedra. The corresponding values in the zinc compound ZFH are only 0.074 Å and 0.112 Å indicating a more regular shape of the octahedron. These differences may be ascribed to the Jahn—Teller effect and are reflected in variation of the unit cell parameters in the corresponding compounds. Consequently the unit cell volume increases with increasing copper content from 574.6 Å^3 (ZFH) through 577.4 Å^3 (ZCFH) to 581.5 Å^3 (CFH).

The above-mentioned observations led us to a closer inspection of geometric parameters of both ZCMH and ZMH structures (Table 3). The individual observed differences between corresponding bond distances and angles are rather small, and generally are within 3σ error range. The greatest observed differences are in decreasing order (the difference as multiples of σ is given into parentheses): angle O3—Zn—O5 (13σ), interaction M···O2 (11σ), angles O4—M—O5 and O1—M—O4 (9σ), bonds M—O3 and M—O4 (6σ) (see Table 3), the other differences do not exceed 5σ. These values suggest that partial substitution of zinc by copper (at 6 mole % level) in the central atom position causes minor but significant changes in the geometry of the coordination polyhedron. The changes in the geometry of the coordination polyhedron induce also minor changes in the geometric parameters of the maleate anion (the sum of bond distances in the

Table 5. X-Ray Powder Diffraction Data on ZMH

$2\Theta_{obs}/°$	$(100I/I_0)/\%$	$d_{obs}/Å$	h	k	l	$(2\Theta_{calc}-2\Theta_{obs})/°$
10.928	73	8.08980	0	2	0	−0.005
16.448	5	5.38499	1	1	0	0.004
17.011	100	5.20800	0	2	1	0.000
20.890	69	4.24899	1	1	−1	0.011
21.154	71	4.19655	1	1	1	−0.002
21.946	46	4.04676	0	4	0	−0.000
22.654	32	3.92193	1	3	0	0.004
25.589	33	3.47842	0	4	1	0.003
26.099	6	3.41150	1	3	−1	0.009
26.165	4	3.40313	0	0	2	0.012
26.310	10	3.38459	1	3	1	0.001
28.449	30	3.13489	0	2	2	−0.010
30.895	8	2.89202	1	1	−2	0.005
31.264	55	2.85867	1	1	2	−0.016
31.749	9	2.81613	1	5	0	0.000
33.189	98	2.69718	0	6	0	−0.009
34.361	5	2.60782	1	5	−1	−0.000
34.515	2	2.59652	1	5	1	0.004
35.047	12	2.55828	1	3	2	−0.002
35.712	10	2.51218	2	2	−1	−0.018
35.775	14	2.50791	0	6	1	0.000
38.567	2	2.33250	2	4	0	0.001
40.724	10	2.21380	2	4	−1	0.005
40.979	8	2.20064	2	0	−2	0.003
41.310	6	2.18377	0	2	3	0.002
41.517	7	2.17336	2	0	2	0.011
41.735	4	2.16248	1	5	2	−0.000
42.122	2	2.14352	1	7	0	0.005
42.534	15	2.12369	2	2	−2	0.006
42.744	6	2.11374	0	6	2	−0.001
43.065	10	2.09874	1	1	−3	−0.006
43.449	19	2.08106	1	1	3	0.003
44.201	10	2.04742	1	7	−1	0.008
44.327	10	2.04188	1	7	1	0.010
44.751	23	2.02352	0	8	0	0.003
45.837	8	1.97808	0	4	3	−0.006
46.291	7	1.95972	2	6	0	−0.023
46.388	5	1.95586	1	3	3	0.005
46.804	8	1.93944	0	8	1	−0.000
46.963	2	1.93321	2	4	−2	0.001
47.447	1	1.91464	2	4	2	0.008
48.115	1	1.88960	3	1	0	−0.006
48.382	2	1.87980	2	6	1	0.007
49.869	12	1.82716	3	1	−1	0.008

maleate anion in ZCMH is by 0.032 Å higher than in ZMH), which in turn influence the packing within and between the layers.

Looser packing within the layers of ZCMH manifests itself by longer intralayer HB's (Table 4), especially O5···O4^{iv} (3.055(3) Å, iv: x, y, $z+1$) and O6···O1^{vi} (2.719(3) Å, vi: $x-1$, y, z) as well as by the "thickness" of the layer. This can be expressed as a difference between the y coordinates of C2 and C2^{viii} atoms (viii: $x-1/2$, $1/2-y$, $z-1/2$) (these atoms are placed on the "surface" of the layers) (Fig. 2). The thickness in ZMH is 7.0995 Å and in ZCMH 7.1244 Å (Table 7). As there are two layers in the cell, the total difference is 0.0498 Å. This value is still smaller

Table 6. Comparison of the Unit Cell Parameters (*a*) and Relevant Geometric Parameters for ZFH [18], ZCFH [16], and CFH [17] (*b*)

a)

Compound	$a/Å$	$b/Å$	$c/Å$	$\beta/°$	$V/Å^3$
ZFH	8.685	7.160	9.323	97.58	574.6
ZCFH	8.77	7.25	9.17	98.0	577.4
CFH	8.54	7.15	9.59	68.8	581.5

b)

Bond	ZFH	ZCFH	CFH
M1—O1	2.102(3)	2.10(2)	2.30(2)
M1—O2	2.071(3)	2.10(2)	1.99(2)
M1—O4	2.145(3)	2.22(1)	2.02(2)
M2—O3	2.166(3)	2.19(1)	2.37(2)
M2—W1	2.103(3)	2.10(1)	2.04(2)
M2—W2	2.054(4)	2.04(1)	1.97(2)

a) Cell parameters and volume of the unit cell, V of CFH, ZFH, and ZCFH. *b*) Bond distances in MO_6 coordination polyhedra in CFH, ZFH, and ZCFH (W = water molecule).

than the observed difference for the b parameters, so the rest corresponds to the difference in y coordinates of the C2 atoms of the neighbouring layers. A closer look at the interlayer contacts O2···O5 and C2···O6 in both compounds can be made (Table 7). While the O2···O5 contacts corresponding to weak hydrogen bonds are the same within experimental error in both structures, the contact C2···O6 in ZMH is shorter than in ZCMH and the difference for the y-axis component gives 0.0201 Å. Addition of these values to the previous value of 0.0498 Å gives 0.0699 Å, in good agreement with the observed difference 0.068 Å in b parameters of both structures. At the same time, this comparison indicates that the interlayer distances do not change uniformly and reflect the deformation of the layers due to copper substitution.

The corresponding geometric parameters of the carboxylate anions in ZMH and ZCMH, respectively, are the same within experimental error and all carboxylate anions are planar. On the other hand, the C—O bonds within the same carboxylate anion significantly differ, *e.g.* in ZMH C1—O1 (1.282 Å) and C1—O2 (1.237 Å). These differences are preserved independently from the fact that the oxygen atom is or is not a donor atom in coordination bond.

On the basis of the literature data and our results we can conclude that the introduction of the copper atom into the central atom site induces a small perturbation in the coordination sphere, which is compensated by small, but significant change of maleate anion conformation. These changes result in lower effectiveness of the packing within the layer. This lower effectiveness results in larger H-bonds and thus higher unit cell parameters are observed. These results also

Table 7. Comparison of Some Geometric Parameters in ZMH and ZCMH [Å] (see the text for explanation)

	ZMH	ZCMH	Difference pro cell
y(C2)···y(C2)^{viii}	7.0995	7.1244	$2 \times 0.0249 = 0.0498$
O2···O5	2.719(3)	2.722(5)	$2 \times 0.003 = 0.006$
	distance $*$ cos ϕ in the y direction		$= 0.0059$
C2···O6	3.409	3.420	$2 \times 0.011 = 0.022$
	distance $*$ cos ϕ in the y direction		$= 0.0201$

viii: $x - 1/2$, $1/2 - y$, $z - 1/2$.

indicate that simple comparison of the unit cell parameters of isostructural compounds based only on the ionic radii of the central atoms can be inadequate and the anisotropic character of the coordination polyhedron has to be accounted for.

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