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The Crystal Structure of Topotactically Dehydrated Copper(II) Formate Tetrahydrate

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Thermal dehydration of copper(II) formate tetrahydrate leads to a modification of the anhydrous salt different from that produced by direct preparation of the latter. As the dehydration is a topotactic process, the known crystal structure of the tetrahydrate and the topotactic orientation relations can be used to deduce the crystal structure of the product. Single-crystal X-ray diffraction patterns of decomposed pseudomorphs yield the following unit cell for the dehydrated formate: monoclinic, $a = 8.195 \mp 0.006$ Å, $b = 7.925 \mp 0.006$ Å, $c = 3.620 \mp 0.005$ Å, $\beta = 122.21 \mp 0.09°$, probable space group $P2_1/a = C_{2h}^5$. The structure contains copper formate layers very similar to those in the tetrahydrate, stacked in such a way that columns of distorted coordination polyhedra, linked by formate bridges, are formed. The topotactic dehydration occurs in such a way that two-dimensional elements of the structure are unaltered but the mode of stacking is changed.

Introduction

Crystalline copper(II) formate phases have been the subjects of a number of investigations relating to their thermal decomposition (*1–4*). The structural aspects of these reactions are, however, not yet understood. This is mainly due to the fact that the structures of certain anhydrous copper(II) formate modifications are still unknown and even their number is controversial. Whereas the crystal structures of the tetrahydrate (*5*, *6*) and the dihydrate (*7*, *8*) have been determined, crystallographic data of the anhydrous salt are available only for the one phase obtained by direct preparation from solution (*9*). Various authors mention one or two other anhydrous phases, occurring as dehydration products of the di- and tetrahydrates (*1*, *2*, *9*, *10*), but their characterizations are rather vague, probably because single crystals could not be prepared. However, there is some evidence that the dehydration of copper(II) formate tetrahydrate is a topotactic process, leading to well-oriented pseudomorphs (*1*, *2*, *4*). As the careful examination of such topotactic reactions has enabled us to derive unknown crystal structures in several similar cases (*11–13*), in the present investigation we attempted to apply the same procedure to the dehydration product of copper(II) formate tetrahydrate.

Experimental

Copper(II) formate tetrahydrate crystals were prepared by dissolving copper hydroxide carbonate in formic acid and precipitating the formate by slow evaporation. Recrystallization from water at room tem-

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perature yielded single crystals of the tetrahydrate of up to 5 mm in length.

The dehydration was continuously investigated on a Mettler Thermoanalyzer TA-1 and a Perkin–Elmer thermogravimetric system TGS-2, as well as on a focusing high-temperature X-ray diffraction camera of the Guinier–Lenné type (Nonius, Delft) with Cu$K\alpha$ radiation.

X-Ray diffraction patterns were registered on a focusing Guinier FR 552 camera (Nonius, Delft) with Cu$K\alpha_1$ radiation for powders and on Weissenberg and Precession cameras with Cu$K\alpha$ and Mo$K\alpha$ radiation, respectively, for single crystals and pseudomorphs.

Intensities of powder diffraction lines were measured on a Joyce–Loebl double-beam microdensitometer. Scanning electron micrographs were recorded by means of a Stereoscan S-4 microscope (Cambridge Scientific Instruments Ltd.).

Results

The crystals of copper(II) formate tetrahydrate are of light blue color, transparent, and generally of the shape shown in Fig. 3 of Ref. (*6*). When dried in air, they turn opaque within few hours.

Thermogravimetric measurements show that the weight loss corresponds to four molecules of water per formula unit and proceeds in a single step, both on isothermal dehydration at 50°C and on continuous heating at 5°C/min, when the loss of water is completed at about 110°C. The lack of an intermediate with the composition of the dihydrate disagrees with (*1*), but agrees well with (*2, 10*). This absence of a dihydrate is quite remarkable, as a stable phase of this composition can easily be prepared from solution (*4, 10*).

The dehydrated pseudomorphous crystal aggregates show pronounced splitting parallel to the basal planes of the prisms, dividing them into piles of lamellae, resembling stacks of playing cards (Fig. 1).

Weissenberg and Precession X-ray diffraction patterns of these pseudomorphs yield lattice constants and space group for the dehydrated form, even though their reflections are strongly broadened. These unit cell parameters permit the complete indexing of the X-ray powder diffraction pattern (Table I). Refinement of the monoclinic unit cell parameters by least-squares calculations results in the following values:

$$a = 8.195 \mp 0.006\ \text{Å},$$
$$b = 7.925 \mp 0.006\ \text{Å},$$
$$c = 3.620 \mp 0.005\ \text{Å},$$
$$\beta = 122.21 \mp 0.09^\circ.$$

The space group is, according to the observed systematic absences of reflections, determined unambiguously as $P2_1/a$-C_{2h}^5 (No. 14) (as the data are derived from pseudomorphs and not from real single crystals, the possibility exists that $P2_1/a$ represents only a pseudo-space group).

FIG. 1. Scanning electron micrograph of a dehydrated copper(II) formate tetrahydrate crystal, showing pronounced splitting parallel to the basal plane.

TABLE I

X-RAY POWDER DIFFRACTION PATTERN OF DEHYDRATED COPPER(II) FORMATE TETRAHYDRATE

$d_{\text{obs.}}$ (Å)	$\sin^2\theta \times 10^4_{\text{obs.}}$	$\sin^2\theta \times 10^4_{\text{calc.}}$	$I/I_{0,\text{obs.}}$	$h\,k\,l$	$I/I_{0,\text{calc.}}$
5.236	216.4	217.8	100	1 1 0	100
3.969	376.6	377.8	2	0 2 0	2
		493.6		2 0 0	<1
3.444	500.3	501.2	3	1 2 0	2
3.348	529.2	530.9	4	$2\ 0\ \bar{1}$	3
3.282	550.9	552.7	10	$1\ 1\ \bar{1}$	14
3.184	585.3	588.0	2	2 1 0	2
		625.4		$2\ 1\ \bar{1}$	4
3.063	632.4	632.4	23	0 0 1	27
2.8553	727.7	726.9	6	0 1 1	8
2.6688	833.0	836.0	2	$1\ 2\ \bar{1}$	3
2.6099	871.0	871.2	20	2 2 0	17
2.5579	906.7	908.7	6	$2\ 2\ \bar{1}$	5
2.5061	944.7	944.8	10	$3\ 1\ \bar{1}$	7
2.4894	972.9	973.4	8	1 3 0	5
2.4212	1012	1010	2	0 2 1	3
2.2750	1146	1148	7	1 1 1	13
2.2254	1198	1205	2	3 1 0	1
2.1994	1226	1228	7	$3\ 2\ \bar{1}$	3
2.1324	1305	1308	3	$1\ 3\ \bar{1}$	3
2.1002	1345	1344	5	2 3 0	3
2.0741	1379	1381	1	$2\ 3\ \bar{1}$	<1
2.0460	1417	1417	7	$4\ 0\ \bar{1}$	4
		1431		1 2 1	⩽1
1.9960	1489	1488	<1	3 2 0	<1
		1511		$4\ 1\ \bar{1}$	<1
1.9815	1511	1511	7	0 4 0	3
1.9050	1635	1635	2	1 4 0	1
1.8681	1700	1700	8	$3\ 3\ \bar{1}$	4
1.8610	1713	1721	<1	2 0 1	<1
1.8175	1796	1794	12	$4\ 2\ \bar{1}$	5
1.7990	1833	1833	<1	$2\ 0\ \bar{2}$	2
1.7650	1904	1903	1	1 3 1	3
		1927		$2\ 1\ \bar{2}$	1
		1949		$3\ 1\ \bar{2}$	6
1.7406	1958	1960	5	3 3 0	5
		1974		4 0 0	1
1.7208	2003	2005	5	2 4 0	2
1.7039	2043	2042	3	$2\ 4\ \bar{1}$	5
1.6822	2096	2099	5	2 2 1	8
1.6695	2128	2124	2	$4\ 0\ \bar{2}$	4
1.6626	2146	2144	4	0 4 1	4
		2152		$1\ 1\ \bar{2}$	1
1.6407	2204	2211	<1	$2\ 2\ \bar{2}$	2
		2232		$3\ 2\ \bar{2}$	1
		2266		$4\ 3\ \bar{1}$	<1
1.5989	2321	2324	4	$5\ 1\ \bar{1}$	4
1.5926	2343	2352	1	4 2 0	3
		2435		$1\ 2\ \bar{2}$	<1
1.5452	2485	2485	3	1 5 0	2
1.5405	2500	2502	<1	$4\ 2\ \bar{2}$	2
		2530		0 0 2	1
		2565		1 4 1	<1
		2571		2 3 1	<1

Note. Cutoff at $d = 1.5000$ Å.

Topotaxy

The morphology of dehydrated particles (Fig. 1) closely resembles that of molybdenum trioxide prepared from its dihydrate (*11*). This might indicate similar reaction mechanisms in the two cases, controlled by preservation of layered parts of the parent structure (*14*). Evidence for this assumption is obtained by X-ray diffraction on one and the same sample before and after dehydration in identical orientation. Weissenberg and Precession photographs show the following orientation relation between the tetrahydrate single crystal (t) and its anhydrous pseudomorphous product (a):

$b^*_{\mathrm{a}} \; // \; b^*_{\mathrm{t}}$ and $c^*_{\mathrm{a}} \; // \; c^*_{\mathrm{t}}$ in reciprocal space,

or

$(001)_{\mathrm{a}} \; // \; (001)_{\mathrm{t}}$ and $[100]_{\mathrm{a}} \; // \; [100]_{\mathrm{t}}$ in real space.

A comparison of the lattice constants of the two phases reveals the close resemblance, in both length and orientation of the *a* and *b* axes of the two structures, whereas the *c* axes differ considerably:

$Cu(HCOO)_2 \cdot 4H_2O$ (t) (*5, 6*)	$Cu(HCOO)_2$ (a)
$a = 8.18 \mp 0.02$ Å	$a = 8.195 \mp 0.006$ Å
$b = 8.15 \mp 0.02$ Å	$b = 7.925 \mp 0.006$ Å
$c = 6.35 \mp 0.02$ Å	$c = 3.620 \mp 0.005$ Å
$\beta = 101°5' \mp 20'$	$\beta = 122.21° \mp 0.09°$

It should also be noted that the space group $P2_1/a$ remains the same. These results point to a topotactic reaction mechanism, in which two-dimensional structural elements of the hydrate remain essentially unaltered on dehydration, whereas their mode of stacking is changed.

The extreme similarity of the magnetic properties of the tetrahydrate and its dehydration product (*10*) also point to a strict conservation of the atomic arrangement within the copper formate layers, making possible a superexchange via formate ions in comparable extent in both structures.

Deduction of the Crystal Structure

The crystal structure of the parent phase, copper(II) formate tetrahydrate, was first determined by Kiriyama *et al.* (*5*) and later again by neutron diffraction by Okada *et al.* (*6*). The unit cell and space group have been given above. The structure is distinctly layered. Copper cations and formate anions are nearly coplanar in the (001) planes, each copper being surrounded by four oxygens of four different formate ions in an almost square configuration (cf. Fig. 2), and each formate ion thus connecting two copper ions. Above and below these planes, half of the water molecules complete the elongated octahedral coordination of the copper ions, and the other half, which are not directly coordinated to the metal ions, are linked with the coordinated water molecules by hydrogen bonds.

In view of this layered atomic arrangement in the tetrahydrate, the experimentally found topotactic orientation relation can easily be interpreted. Both kinds of intercalated water molecules have relatively free pathways for diffusion parallel to the layers. If, however, they leave the lattice on dehydration, the only way to recomplete the (4 + 2)-fold coordination of the copper ions is a collapse of the layers. It is not quite trivial, however, if this collapse occurs perpendicular to (001), parallel to *c*, or involves some displacement of the layers

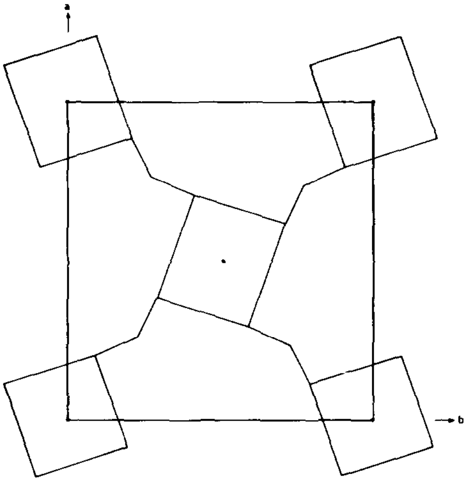

FIG. 2. (001) plane of $Cu(HCOO)_2 \cdot 4H_2O$ and its dehydration product: square planar coordination of Cu by formate ions.

parallel to each other. Obviously, the lattice constants and especially the angle β of the anhydrous phase indicate how this collapse actually occurs.

The structure resulting from such a dehydration mechanism again consists of copper formate layers with fourfold coordination of copper, almost identical to the initial ones (Fig. 2). The fifth and sixth neighbors of the copper ions are then formate oxygen atoms from the layers above and below (Fig. 3).

Alternatively, the structure may be described as an arrangement of edge-sharing, (4 + 2)-elongated coordination octahedra CuO_6 parallel to *c*, crosslinked by the formate ions (Fig. 4). This model allows an estimation of the atomic positional parameters in the dehydrated structure, by assuming the layers to remain unaltered and their stacking to fit the unit cell found. Space group $P2_1/a$:

Cu in 2 *a*: 0, 0, 0
C in 4 *e*: 0.237, 0.270, 0.033
O1 in 4 *e*: 0.177, −0.092, −0.163
O2 in 4 *e*: 0.143, 0.210, 0.180

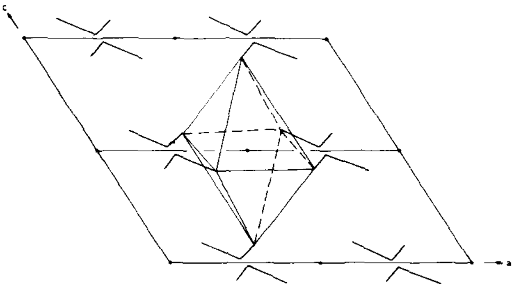

FIG. 3. Projection (010) of the suggested structure for anhydrous copper(II) formate. The typical (4 + 2)-fold distorted octahedral coordination of Cu is shown.

A structural model based on arguments similar to those given above needs further support. In the present case, where no single crystals are available, this can be

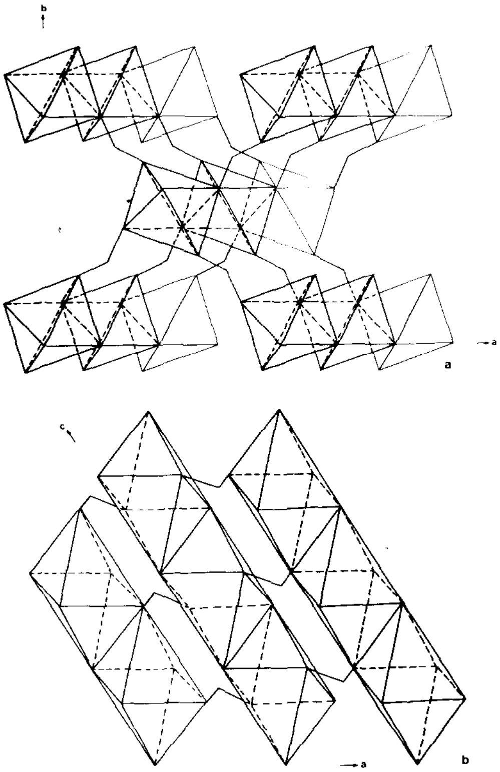

FIG. 4. (a) The columns of edge-sharing octahedra of the type shown in Fig. 3, projected onto (001). (b) Projection of the columns of edge sharing octahedra onto (010).

obtained in two ways:

(a) a detailed description of the resulting copper coordination polyhedron should not reveal any unreasonable bond distances or angles, and

(b) the intensities of the X-ray powder diffraction pattern should be roughly explicable by the model structure.

These two points shall subsequently be discussed in turn.

(*a*) *Bond Angles and Distances*

Bond angles and distances have been calculated by a subprogram of the XRAY program system (15), based on the atomic coordinates given above. They are represented in Fig. 5.

While the formate ions as such show their usual geometry, the copper coordination has to be looked at more closely. The central copper ion is surrounded by four oxygen atoms in an almost square arrangement, with distances Cu–O of 1.928 and 1.966 Å, and angles O(close)–Cu–O(close) of 90.4° and 89.6°. The two more distant oxygen atoms above and below this square are at 2.656 Å and include angles O(distant)–Cu–O(close) of 78.7° (101.3°) and of 89.2° (90.8°), respectively. Such values are not uncommon in the coordination chemistry of copper(II). A geometrically very similar atomic arrangement is found, e.g., in the compound $Cu(NH_3)_2Sn(OH)_6$, where copper has as its close neighbors two OH groups at 2.011 Å and two NH_3 molecules at 2.000 Å, and two more distant OH groups at 2.627 Å. The bond angles also compare well with the values for our suggested structure: N(close)–Cu–O(close) 91.8° and 88.2°, O(distant)–Cu–O(close) 75.1° (104.9°), O(distant)–Cu–N(close) 85.3° (94.7°) (*16*).

The geometry of the coordination polyhedron around the copper ion in the model structure therefore appears to be reasonably explained in comparison with other known structures.

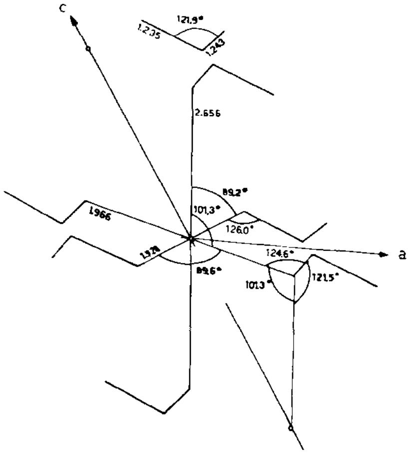

FIG. 5. Bond angles and bond lengths (in Å) in one of the distorted coordination octahedra around Cu in the suggested structure of $Cu(HCOO)_2$.

(*b*) *Powder X-Ray Diffraction Line Intensities*

The computer program LAZY PULVERIX (*17*) allows the calculation of X-ray powder diffraction patterns with their relative line intensities. It has been applied to the suggested model structure under the experimental conditions of the Guinier camera used. The result is compared with the observed diffraction pattern in Table I. The agreement between observed and calculated values is fair, when it is considered that the structure has been proposed on the basis of crystal chemical considerations only and has not been refined at all.

Thus it is shown that no arguments have been found which disprove the validity of the suggested structure of dehydrated copper(II) formate tetrahydrate deduced from its topotactic dehydration reaction. This additional example of the successful deduction of a structure of non-single-crystalline material encourages application of this procedure to other systems.

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