

The Crystal Structure of Copper(II) Formate Dihydrate

BY M. BUKOWSKA-STRZYŻEWSKA

Department of Inorganic Chemistry, Technical University, Łódź, Poland

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The crystal structure of $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ has been determined by two-dimensional projections. The compound is monoclinic, with space group $P2_1/c$ and cell dimensions $a=8.54$, $b=7.15$, $c=9.50$ Å, and $\beta=96^\circ 48'$, $Z=4$. The intensities were obtained from Weissenberg photographs about the three axes, with 59 of the 254 reflexions too weak to be recorded. The structure was refined in the projection (010) to $R=0.09$, in the projection (001) to $R=0.08$ and in the projection (100) to $R=0.10$. The overall isotropic temperature factor coefficients B are 2.40, 2.25 and 2.25 Å² respectively.

The crystal consists of three-dimensional chains of copper atoms joined together by formate groups in an *anti-syn* and *anti-anti* bridging arrangement. The environment of the Cu atoms has been shown to be distorted octahedral with distances: $\text{Cu}(1)-\text{O}(1)=2.02$ Å; $\text{Cu}(1)-\text{O}(2)=2.28$ Å; $\text{Cu}(1)-\text{O}(3)=2.03$ Å; $\text{Cu}(2)-\text{O}(4)=2.35$ Å; $\text{Cu}(2)-\text{O}(5)(\text{H}_2\text{O})=1.97$ Å; $\text{Cu}(2)-\text{O}(6)(\text{H}_2\text{O})=2.02$ Å. The distances C-O in the formate ions are not identical: $\text{C}(1)-\text{O}(1)=1.19$ Å, $\text{C}(1)-\text{O}(2)=1.29$ Å, $\text{C}(2)-\text{O}(3)=1.21$ Å, $\text{C}(2)-\text{O}(4)=1.27$ Å. A system of hydrogen bonding is suggested for the water molecules and the formate groups.

Introduction

The crystal structure investigation of copper(II) formate dihydrate was undertaken because of the interest in the stereochemistry of these and related copper(II) formates (Martin & Waterman, 1959). This research is a part of the study on space structure of formic and acetic cupric salts (Bukowska-Strzyżewska, 1963a, 1963b).

The pale-green crystals of $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ were obtained by prolonged exposure of the dark-green crystals of $\text{Cu}(\text{HCOO})_2 \cdot \frac{1}{2}$ dioxane to air. The dioxane molecule is replaced by four water molecules and the crystals turn pale green. An investigation of the structure of $\text{Cu}(\text{HCOO})_2 \cdot \frac{1}{2}$ dioxane was also undertaken.

Crystal data

The crystals of copper(II) formate dihydrate are monoclinic. The unit-cell dimensions were determined from Weissenberg photographs by applying Cu *K* radiation with sodium chloride as an internal standard. The density was measured by flotation in methylene iodide.

$\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$. $M=189.61$.

$a=8.54 \pm 0.02$, $b=7.15 \pm 0.01$, $c=9.50 \pm 0.02$ Å;
 $\beta=96^\circ 48'$.

Volume of the unit cell = 574.2 Å³; $Z=4$.

Density: calculated = 2.19 g.cm⁻³, experimental = 2.17 g.cm⁻³.

Linear absorption coefficients for X-rays,

$\lambda=1.5418$ Å $\mu=54.1$ cm⁻¹.

$\lambda=0.7107$ Å $\mu=38.4$ cm⁻¹.

Total number of electrons per unit cell, $F(000)=380$.

Systematic absences:

$h0l$ absent when $l=2n+1$ and

$0k0$ absent when $k=2n+1$.

The space group is $P2_1/c$.

Intensity data

For estimation the intensities the $h0l$, $hk0$ and $0kl$ were recorded on multiple-film Weissenberg photographs with unfiltered Cu *K* radiation. The intensities were estimated visually by comparison with a standard scale. The relative values of the structure amplitudes were derived by applying the usual Lorentz and polarization factors, the absolute scale being established later, by correlation with the calculated structure factors. The absorption correction was considered unnecessary, since the crystals used had a mean diameter of 0.05 mm.

Structure determination

A two-dimensional Patterson synthesis projected along a , b , and c axes gave unambiguously the positions of Cu at $2(a) 0 0 0$, $0 \frac{1}{2} \frac{1}{2}$ and $2(d) \frac{1}{2} 0 \frac{1}{2}$, $\frac{1}{2} \frac{1}{2} 0$.

In the case of such a configuration for heavy atoms, the Patterson projection $P(uw)$ should represent a picture corresponding to the superposition of two electron-density projections. Except for vectors $\text{Cu}_{00}-\text{X}$ related to the real positions of X atoms, vectors $\text{Cu}_{\frac{1}{2}\frac{1}{2}}-\text{X}$ connected with the previous ones by the centre of symmetry at $\frac{1}{4} \frac{1}{4}$ of the projection should be distinguished.

In connection with the symmetry of the electron-density projections corresponding to Patterson projections $P(uw)$ and $P(vw)$, they should give a picture related to the fourfold superposition of electron density. Vectors $\text{Cu}_{00}-\text{X}$ corresponding to the real positions of atoms are joined together by two symmetry planes $u=\frac{1}{4}$, $v=\frac{1}{4}$ and correspondingly $v=\frac{1}{4}$, $w=\frac{1}{4}$ with vectors $\text{Cu}_{0\frac{1}{2}}-\text{X}$, $\text{Cu}_{\frac{1}{2}0}-\text{X}$ and $\text{Cu}_{\frac{1}{2}\frac{1}{2}}-\text{X}$.

The analysis of the $P(uv)$, $P(vw)$ and $P(uw)$ syntheses obtained allowed two different possible structural arrangements. In one both HCOO^- groups form the

bridging arrangement between copper atoms; in the other however, both oxygen atoms belonging to one HCOO^- group are coordinated to the same Cu atom. The second configuration variant of the formate groups is connected with a considerable deformation of the tetragonal-bipyramidal environment of Cu atoms. (The O-Cu-O angle changes from 90° to about 60° .) Since such a coordination around Cu atoms was previously found in the structure of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{NH}_3$ (Bukowska-Strzyżewska, 1963*a*), the possibility of its existence in this case too should be taken into consideration.

Fig. 1 shows the obtained Patterson projections $P(uv)$ and $P(uw)$ with the determination of both possible structural arrangements. During a refinement of the structure, arrangement II was rejected because it gave markedly higher values for the discrepancy factor R than arrangement I. The atomic scattering factors

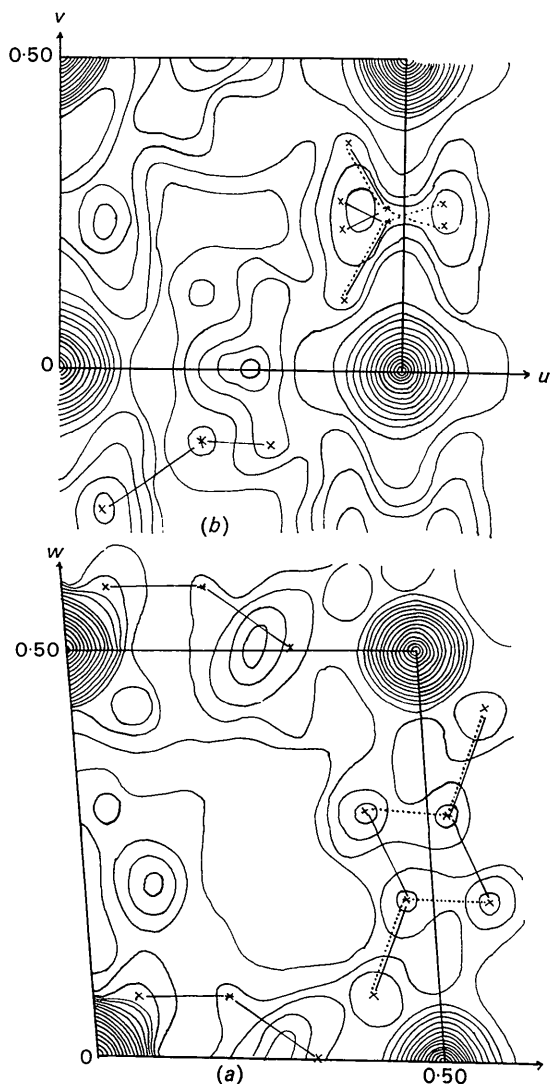


Fig. 1. Patterson projections along: (a) [010], (b) [001]. Full lines show variation I of the configuration of the formate groups; dotted lines show variation II.

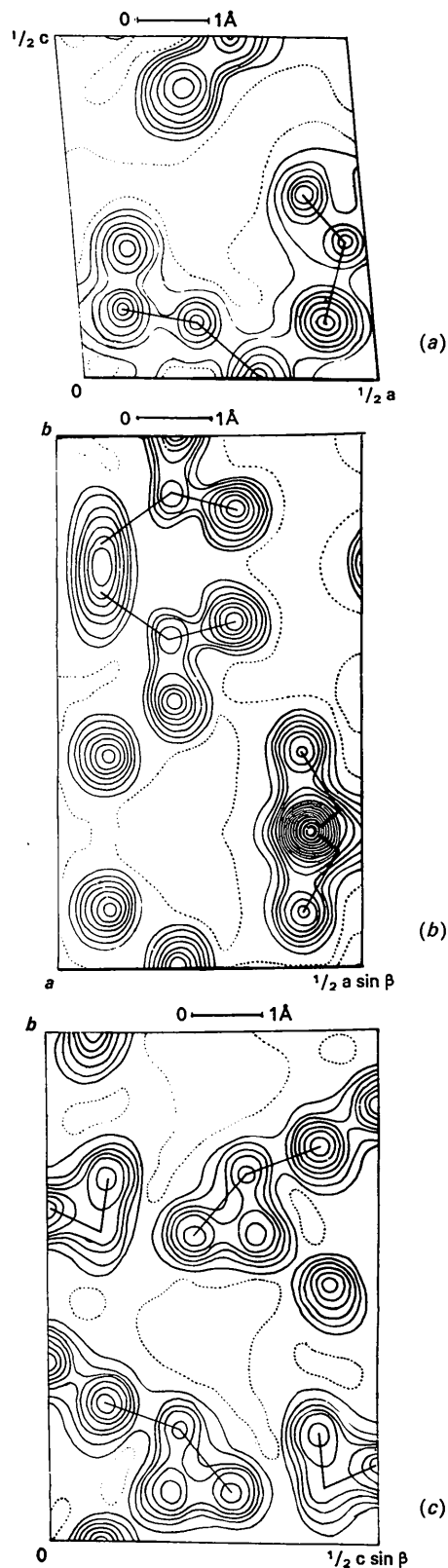


Fig. 2(a), (b), (c). Final $(F_{\text{O}} - F_{\text{Cu}})$ syntheses projected along [010], [001] and [100] respectively. Contours at intervals of $2 \text{ e} \cdot \text{Å}^{-2}$, zero contour omitted, $2 \text{ e} \cdot \text{Å}^{-2}$ contour dotted.

used for the structure factor calculations were: carbon and oxygen – Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), copper – Thomas & Umeda (1957).

The refinement of the structure was carried out by successive two-dimensional Fourier syntheses. At the final stage Cu atoms were subtracted from the obtained projections in order to reduce the series termination errors and to estimate more exactly the positions of atoms situated near the Cu atoms. The relative values of experimental structure factors F_o were reduced to the absolute scale by comparison with F_c with the simultaneous introduction of the general isotropic temperature factor coefficient. The final projections of electron density after removal of Cu atoms are shown in Fig. 2(a), (b), and (c). The final values of R are: 0.08, 0.09, 0.10 for the $(hk0)$, $(h0l)$ and $(0kl)$ projections respectively. The temperature factor coefficients for the projections mentioned are 2.25, 2.40, 2.25 Å² which does not indicate anisotropic thermal vibration.

The atomic parameters in fractions of the unit-cell lengths are listed in Table 1. Standard deviations for the x , y , and z coordinates, calculated with Cruickshank's (1949, 1954) formulae are: $\sigma_x = \sigma_y = \sigma_z$

= 0.010 for oxygen and $\sigma_x = \sigma_y = \sigma_z = 0.014$ for carbon atoms.

Table 1. Atomic coordinates expressed as fractions of unit-cell edges

| | x | y | z |
|----------------------|-------|-------|-------|
| Cu(1) | 0.500 | 0 | 0.500 |
| Cu(2) | 0 | 0 | 0 |
| O(1) | 0.413 | 0.267 | 0.083 |
| O(2) | 0.406 | 0.096 | 0.277 |
| O(3) | 0.296 | 0.644 | 0.007 |
| O(4) | 0.075 | 0.705 | 0.094 |
| O(5)H ₂ O | 0.089 | 0.103 | 0.184 |
| O(6)H ₂ O | 0.211 | 0.484 | 0.425 |
| C(1) | 0.467 | 0.217 | 0.198 |
| C(2) | 0.192 | 0.600 | 0.078 |

Discussion

The crystals of $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ consist of three-dimensional chains of copper atoms joined by formate groups. All formate groups occupy a bridge position between Cu atoms; they approach Cu atoms by one oxygen atom at a distance 2.02–2.03 Å and by the other at a markedly longer distance 2.28, or 2.35 Å. Two Cu atoms in the unit cell are surrounded exclus-

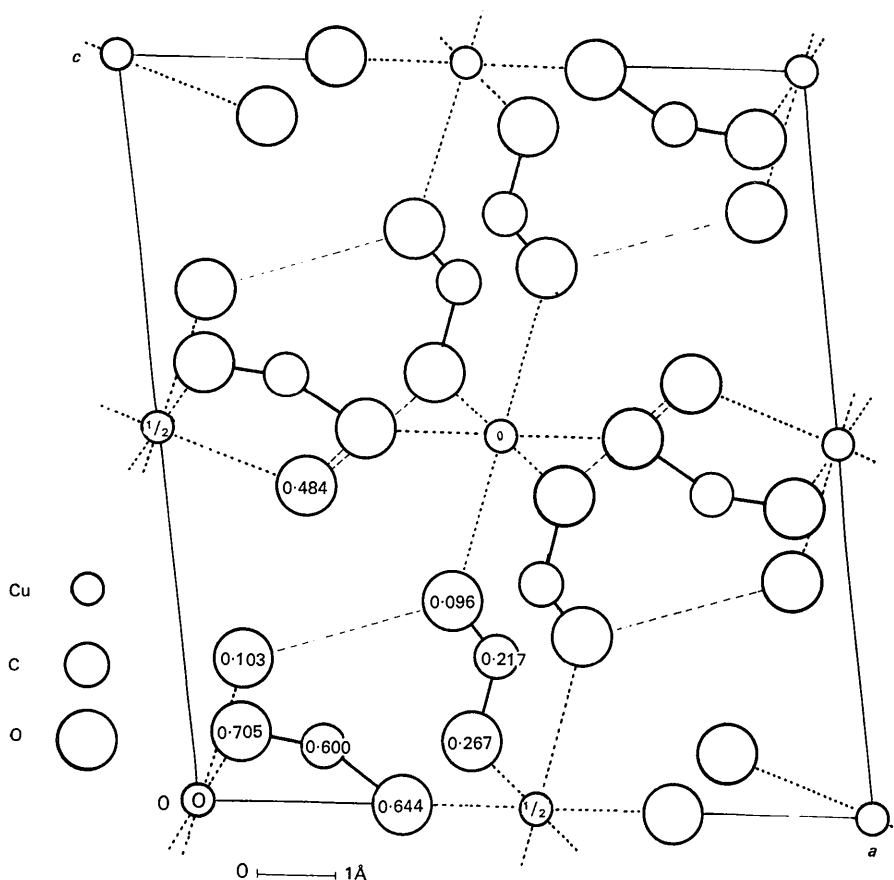


Fig. 3. Diagrammatic representation of contents of unit cell. y parameters in fractions of b . Full lines show the bonds to Cu within the coordination polyhedra Cu-6O, broken lines show the hydrogen bonds between $-\text{Cu}-\text{HCOO}-\text{Cu}$ chains.

ively by oxygen atoms of HCOO⁻ groups, forming around them an elongated octahedral coordination. The remaining two are surrounded by 4 molecules of water, which form a square planar coordination with distances: Cu(2)-2O(5)_{H2O} = 1.97 Å, Cu(2)-2O(6)_{H2O} = 2.02 Å. As is shown in Fig. 3, this coordination is completed to the elongated octahedral coordination most typical for Cu atoms by two oxygen atoms from two different HCOO⁻ groups. The bond lengths (Å) and the angles in the bridging formate groups are given in Fig. 4(c) and (d). HCOO⁻ groups bonding Cu(1)-Cu(1) atoms have the *anti-anti* configuration; those bonding Cu(1)-Cu(2) atoms show the *anti-syn* configuration. This is a second example which was found of the *anti-syn* bridging arrangement of this group in cupric compounds. The first one was found by Barclay & Kennard (1961) in the structure of anhydrous copper(II) formate. The formate ions of the structure under examination have unequal C-O bond distances, unlike those in a series of known acetates and formates.

Some of the interatomic distances in structures of hydrated copper(II) formates are summarized in Table 3. It can be deduced from this comparison that the equalization of C-O bond lengths does not take place in all the compounds mentioned. An analysis of their structure reveals some regularity. Namely whenever a coordinate position more remote from the Cu atom is occupied not by a water molecule but by the oxygen atom of a HCOO⁻ group, it is bonded with the carbon

Table 2. Observed and calculated structure factors

| h | k | l | F _o | F _c | h | k | l | F _o | F _c | h | k | l | F _o | F _c |
|----|---|---|----------------|----------------|---|---|---|----------------|----------------|---|---|----|----------------|----------------|
| I | 0 | 0 | I2 | -I3 | 4 | 4 | 0 | 58 | 57 | 0 | 0 | 2 | II3 | II5 |
| 2 | 0 | 0 | IO2 | IO6 | 5 | 4 | 0 | II | II | 0 | 0 | 4 | 82 | 78 |
| 3 | 0 | 0 | II | -I4 | 6 | 4 | 0 | 35 | 35 | 0 | 0 | 6 | 36 | 33 |
| 4 | 0 | 0 | 57 | 60 | 7 | 4 | 0 | 6 | -6 | 0 | 0 | 8 | 28 | 26 |
| 5 | 0 | 0 | 9 | 8 | 8 | 4 | 0 | 30 | 28 | 0 | 0 | IO | 43 | 45 |
| 6 | 0 | 0 | 23 | 20 | 9 | 4 | 0 | 4 | 6 | 0 | 0 | 12 | 22 | 28 |
| 7 | 0 | 0 | 8 | -8 | | | | | | | | | | |
| 8 | 0 | 0 | 15 | 15 | I | 5 | 0 | 16 | -19 | 0 | I | I | 7 | -4 |
| 9 | 0 | 0 | 7 | -3 | 2 | 5 | 0 | 17 | 13 | 0 | I | 2 | 8 | -3 |
| IO | 0 | 0 | 35 | 37 | 3 | 5 | 0 | - | 2 | 0 | I | 3 | 2I | -2I |
| | | | | | 4 | 5 | 0 | - | 6 | 0 | I | 4 | 2I | 22 |
| I | I | 0 | 6 | 9 | 5 | 5 | 0 | - | -3 | 0 | I | 5 | 5 | -8 |
| 2 | I | 0 | 47 | 46 | 6 | 5 | 0 | - | 4 | 0 | I | 6 | 9 | -6 |
| 3 | I | 0 | 48 | -47 | 7 | 5 | 0 | - | -3 | 0 | I | 7 | 5 | -3 |
| 4 | I | 0 | 38 | 40 | 8 | 5 | 0 | - | -4 | 0 | I | 8 | 3 | -3 |
| 5 | I | 0 | 7 | -8 | 9 | 5 | 0 | 5 | 5 | 0 | I | 9 | 16 | II |
| 6 | I | 0 | - | 4 | | | | | | 0 | I | IO | 9 | -6 |
| 7 | I | 0 | 12 | II | I | 6 | 0 | 6 | 6 | 0 | I | II | - | 4 |
| 8 | I | 0 | - | -2 | 2 | 6 | 0 | 26 | 23 | 0 | I | 12 | - | 2 |
| 9 | I | 0 | - | -4 | 3 | 6 | 0 | - | 0 | | | | | |
| IO | I | 0 | - | -2 | 4 | 6 | 0 | 45 | 46 | 0 | 2 | I | 60 | -58 |
| | | | | | 5 | 6 | 0 | 5 | -2 | 0 | 2 | 2 | 63 | 75 |
| I | 2 | 0 | 26 | 26 | 6 | 6 | 0 | 36 | 37 | 0 | 2 | 3 | 12 | 6 |
| 2 | 2 | 0 | 35 | 4I | 7 | 6 | 0 | 4 | -2 | 0 | 2 | 4 | 66 | 78 |
| 3 | 2 | 0 | 15 | -12 | 8 | 6 | 0 | 12 | 19 | 0 | 2 | 5 | IO | -IO |
| 4 | 2 | 0 | 66 | 73 | | | | | | 0 | 2 | 6 | 59 | 58 |
| 5 | 2 | 0 | 17 | 15 | I | 7 | 0 | - | 2 | 0 | 2 | 7 | - | 5 |
| 6 | 2 | 0 | 58 | 58 | 2 | 7 | 0 | 4 | -6 | 0 | 2 | 8 | 3I | 32 |
| 7 | 2 | 0 | 8 | -8 | 3 | 7 | 0 | 14 | 16 | 0 | 2 | 9 | 6 | 8 |
| 8 | 2 | 0 | 39 | 36 | 4 | 7 | 0 | - | 3 | 0 | 2 | IO | 23 | 19 |
| 9 | 2 | 0 | 7 | 4 | 5 | 7 | 0 | - | 4 | 0 | 2 | II | - | -2 |
| IO | 2 | 0 | 26 | 24 | 6 | 7 | 0 | - | -3 | | | | | |
| | | | | | 7 | 7 | 0 | IO | -7 | 0 | 3 | I | 40 | 4I |
| I | 3 | 0 | - | 0 | | | | | | 0 | 3 | 2 | 15 | 12 |
| 2 | 3 | 0 | 22 | -27 | I | 8 | 0 | - | -2 | 0 | 3 | 3 | 25 | 22 |
| 3 | 3 | 0 | 23 | -22 | 2 | 8 | 0 | 17 | 18 | 0 | 3 | 4 | 22 | 22 |
| 4 | 3 | 0 | 24 | -25 | 3 | 8 | 0 | - | -3 | 0 | 3 | 5 | 18 | -16 |
| 5 | 3 | 0 | - | -4 | 4 | 8 | 0 | 20 | 2I | 0 | 3 | 6 | 12 | II |
| 6 | 3 | 0 | 8 | -8 | 5 | 8 | 0 | - | 6 | 0 | 3 | 7 | 8 | -8 |
| 7 | 3 | 0 | 14 | 12 | | | | | | 0 | 3 | 8 | 8 | -7 |
| 8 | 3 | 0 | - | 4 | I | 9 | 0 | - | 2 | 0 | 3 | 9 | 6 | 5 |
| 9 | 3 | 0 | - | 4 | 2 | 9 | 0 | - | -2 | 0 | 3 | IO | - | 2 |
| IO | 3 | 0 | - | 2 | | | | | | 0 | 3 | II | - | 6 |
| | | | | | 0 | 2 | 0 | 57 | 55 | | | | | |
| I | 4 | 0 | 12 | -6 | 0 | 4 | 0 | 60 | 6I | | | | | |
| 2 | 4 | 0 | 65 | 72 | 0 | 6 | 0 | 39 | 33 | | | | | |
| 3 | 4 | 0 | 17 | -14 | 0 | 8 | 0 | 36 | 37 | | | | | |

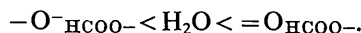
Table 2 (cont.)

| h | k | l | F _o | F _c | h | k | l | F _o | F _c | h | k | l | F _o | F _c |
|---|---|----|----------------|----------------|----|---|----|----------------|----------------|-----|---|----|----------------|----------------|
| 0 | 4 | I | 4 | -5 | I | 0 | 2 | I3 | -9 | -5 | 0 | 2 | I4 | I8 |
| 0 | 4 | 2 | 62 | 75 | 2 | 0 | 2 | 5 | I2 | -6 | 0 | 2 | 46 | 42 |
| 0 | 4 | 3 | IO | 12 | 3 | 0 | 2 | 50 | -42 | -7 | 0 | 2 | - | -I |
| 0 | 4 | 4 | 3I | 30 | 4 | 0 | 2 | 73 | 67 | -8 | 0 | 2 | 24 | 20 |
| 0 | 4 | 5 | 5 | -2I | 5 | 0 | 2 | 2I | -24 | -9 | 0 | 2 | 8 | -7 |
| 0 | 4 | 6 | 20 | 2I | 6 | 0 | 2 | 54 | 54 | -IO | 0 | 2 | I4 | I3 |
| 0 | 4 | 7 | - | -6 | 7 | 0 | 2 | - | 5 | -II | 0 | 2 | - | -6 |
| 0 | 4 | 8 | 23 | 26 | 8 | 0 | 2 | 24 | 28 | | | | | |
| 0 | 4 | 9 | - | -4 | 9 | 0 | 2 | 9 | 6 | -I | 0 | 4 | 34 | -25 |
| 0 | 4 | IO | 2I | 25 | IO | 0 | 2 | 26 | 26 | -2 | 0 | 4 | 39 | 36 |
| | | | | | | | | | | -3 | 0 | 4 | 38 | 34 |
| 0 | 5 | I | - | 2 | I | 0 | 4 | 36 | -35 | -4 | 0 | 4 | 64 | 57 |
| 0 | 5 | 2 | 7 | -8 | 2 | 0 | 4 | 86 | 8I | -5 | 0 | 4 | 12 | -8 |
| 0 | 5 | 3 | 5 | 4 | 3 | 0 | 4 | - | I | -6 | 0 | 4 | 55 | 55 |
| 0 | 5 | 4 | 6 | -4 | 4 | 0 | 4 | 6I | 57 | -7 | 0 | 4 | IO | 9 |
| 0 | 5 | 5 | 8 | 6 | 5 | 0 | 4 | 8 | -5 | -8 | 0 | 4 | 54 | 49 |
| 0 | 5 | 6 | - | -4 | 6 | 0 | 4 | 37 | 37 | -9 | 0 | 4 | I2 | -IO |
| 0 | 5 | 7 | II | -8 | 7 | 0 | 4 | 8 | I4 | -IO | 0 | 4 | 25 | 24 |
| 0 | 5 | 8 | 4 | 2 | 8 | 0 | 4 | - | 3 | | | | | |
| 0 | 5 | 9 | 6 | 5 | 9 | 0 | 4 | - | 5 | -I | 0 | 6 | - | I |
| 0 | 5 | IO | - | I | | | | | | -2 | 0 | 6 | 6I | 62 |
| 0 | 6 | I | 6 | 6 | I | 0 | 6 | 5 | 4 | -3 | 0 | 6 | 14 | 12 |
| 0 | 6 | 2 | 54 | 56 | 2 | 0 | 6 | 43 | 44 | -4 | 0 | 6 | 64 | 58 |
| 0 | 6 | 3 | - | -2 | 3 | 0 | 6 | 14 | 14 | -5 | 0 | 6 | 37 | -32 |
| 0 | 6 | 4 | 32 | 35 | 4 | 0 | 6 | 40 | 39 | -6 | 0 | 6 | 36 | 37 |
| 0 | 6 | 5 | 6 | 6 | 5 | 0 | 6 | 3I | -28 | -7 | 0 | 6 | II | 13 |
| 0 | 6 | 6 | 38 | 3I | 6 | 0 | 6 | 44 | 44 | -8 | 0 | 6 | 27 | 23 |
| 0 | 6 | 7 | - | -2 | 7 | 0 | 6 | - | I | -9 | 0 | 6 | - | 4 |
| 0 | 6 | 8 | 29 | 28 | 8 | 0 | 6 | 25 | 29 | -IO | 0 | 6 | II | II |
| 0 | 6 | 9 | - | -I | | | | | | | | | | |
| 0 | 7 | I | 4 | 4 | I | 0 | 8 | - | -9 | -I | 0 | 8 | - | -4 |
| 0 | 7 | 2 | 5 | 5 | 2 | 0 | 8 | 36 | 34 | -2 | 0 | 8 | 3I | 27 |
| 0 | 7 | 3 | 4 | -2 | 3 | 0 | 8 | 18 | 18 | -3 | 0 | 8 | 7 | 6 |
| 0 | 7 | 4 | - | 0 | 4 | 0 | 8 | 27 | 28 | -4 | 0 | 8 | 40 | 33 |
| 0 | 7 | 5 | 15 | -12 | 5 | 0 | 8 | - | 0 | -5 | 0 | 8 | 13 | -IO |
| 0 | 7 | 6 | - | -I | 6 | 0 | 8 | 26 | 25 | -6 | 0 | 8 | 34 | 33 |
| 0 | 7 | 7 | IO | -7 | 7 | 0 | 8 | 8 | 9 | -7 | 0 | 8 | - | 6 |
| 0 | 7 | 8 | - | I | | | | | | -8 | 0 | 8 | 23 | 24 |
| 0 | 8 | I | IO | 12 | I | 0 | IO | 23 | 25 | -9 | 0 | 8 | - | -3 |
| 0 | 8 | 2 | 30 | 30 | 2 | 0 | IO | 16 | 13 | -I | 0 | IO | 4 | -5 |
| 0 | 8 | 3 | 3 | -3 | 3 | 0 | IO | 18 | 17 | -2 | 0 | IO | 36 | 30 |
| 0 | 8 | 4 | 20 | 23 | 4 | 0 | IO | - | -I | -3 | 0 | IO | 15 | -15 |
| 0 | 8 | 5 | - | I | -I | 0 | 2 | 35 | 40 | -4 | 0 | IO | 32 | 27 |
| 0 | 8 | 6 | 15 | 16 | -2 | 0 | 2 | 50 | 54 | -5 | 0 | IO | IO | -8 |
| | | | | | -3 | 0 | 2 | 58 | 56 | -6 | 0 | IO | I3 | 14 |
| | | | | | -4 | 0 | 2 | IOI | IO0 | -I | 0 | 12 | 7 | 9 |
| | | | | | | | | | | -2 | 0 | 12 | 13 | 12 |
| | | | | | | | | | | -3 | 0 | 12 | - | 2 |

atom by a distinctly longer bond than is the other oxygen atom of this group.

Two different (long or short) positions occupied by oxygen atoms of HCOO⁻ groups in coordination polyhedra around Cu atoms prove that the oxygen atoms of HCOO⁻ groups can differ as ligands in their field strength. The oxygen atom more strongly attached to carbon shows the higher field strength. The different positions of the O_{HCOO-} and O_{H2O} atoms in the known structures of cupric formates can thus be understood. According to the ligand field theory it should be observed that the square planar coordination around Cu atoms in the structure under examination can be completed to an elongated octahedral coordination, not with water molecules, as in copper formate tetrahydrate (Sundara Rao, Sundaramma & Sivasankara Rao, 1958), but with oxygen atoms of HCOO⁻ groups as in barium-copper(II) formate tetrahydrate (Kiriyama, Ibamoto & Matsuo, 1960).

Thus, in the series of ligands arranged according their increasing ligand field strength, the O_{HCOO-} atom linked to carbon with predominantly double-bond should be placed after the water molecule, that with predominantly single-bond character before it:



An analysis of the O-O distances in Cu(HCOO)₂ · 2H₂O suggests that each water molecule forms two

hydrogen bonds with oxygen atoms. Distances: $O(6)_{H_2O}-O(1)=2.82$; $O(6)_{H_2O}-O(3)=2.85$ Å; $O(5)_{H_2O}-O(2)=2.79$; $O(5)-O(4)=2.99$ Å; angles $O(1)-O(6)-O(3)=108.9^\circ$; $O(2)-O(5)-O(4)=94.8^\circ$.

Recently Krogman & Mattes (1965) have reported the results of their examination of the structure of nickel formate dihydrate. The comparison of these data with those obtained in this research for $Cu(HCOO)_2 \cdot 2H_2O$.

$2H_2O$ seems to be interesting from the viewpoint of the stereochemistry of divalent nickel and copper.

The structure of the cupric compound shows a significant analogy to that of the nickel compound. The positions of Cu and Ni atoms, water molecules and $HCOO^-$ groups are analogous in both compounds. Considerable differences however can be seen in interatomic distances. Cu^{2+} ions tend to the distortion of the regular octahedral environment by elongation of

Table 3. Some of the interatomic distances in structures of hydrated copper(II) formates

| Formula | Distances in $HCOO^-$ groups | | Distances in Cu-6O octahedra | |
|------------------------------|---------------------------------|-----------|---------------------------------|------------|
| | $Cu(HCOO)_2 \cdot 2H_2O$ | C(1)-O(1) | 1.19 Å | Cu(1)-O(1) |
| | C(1)-O(2) | 1.29 | Cu(1)-O(2) | 2.28 |
| | C(2)-O(3) | 1.21 | Cu(1)-O(3) | 2.03 |
| | C(2)-O(4) | 1.27 | Cu(2)-O(4) | 2.35 |
| | | | Cu(2)-O(5) H_2O / | 1.97 |
| | | | Cu(2)-O(6) H_2O / | 2.02 |
| $Cu(HCOO)_2 \cdot 4H_2O$ | C(1)-O(1) | 1.26 | Cu-O(1) | 2.00 |
| | C(1)-O(2) | 1.25 | Cu-O(2) | 2.01 |
| | | | Cu-O(3) H_2O / | 2.36 |
| $CuBa_2(HCOO)_6 \cdot 4H_2O$ | C(2)-O(3) | 1.43 | Cu-O(3) | 2.18 |
| | C(2)-O(4) | 1.24 | Cu-O(6) | 2.02 |
| | C(3)-O(5) | 1.26 | Cu-O(7) H_2O / | 1.97 |
| | C(3)-O(6) | 1.35 | | |

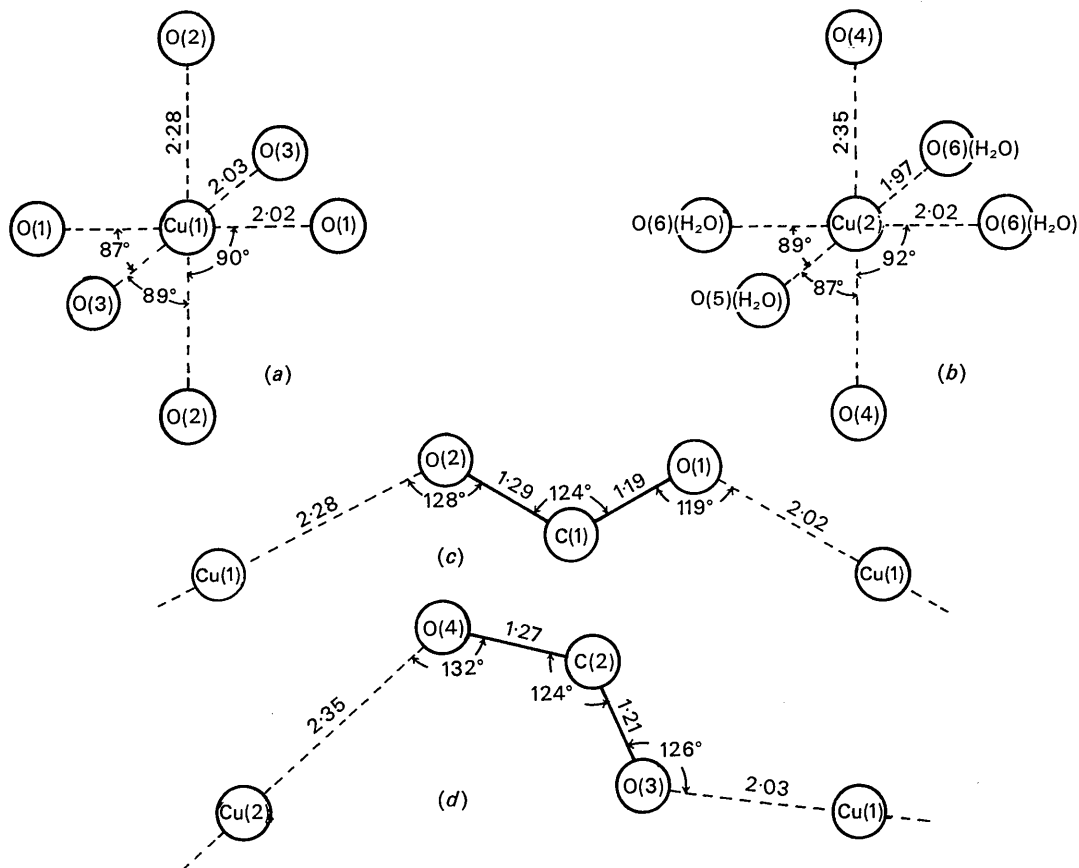


Fig. 4. (a) and (b) Bond lengths (Å) and bond angles in the environment of the copper atoms. (c) and (d) Bond lengths (Å) and bond angles in the formate bridging groups.

two bonds. This fact causes the increase of the bond lengths Cu(1)–O(2) and Cu(2)–O(4) by about 0.24 Å. The remaining distances Cu–O however are shorter by about 0.06 Å in comparison with the nickel salt. The bond distances C–O within the HCOO[−] groups of Cu(HCOO)₂ · 2H₂O are equalized to a lesser degree. The bond distances C(1)–O(1) and C(2)–O(3) are markedly shortened in comparison with the nickel salt. The bond distances C(1)–O(2) and C(2)–O(4) are elongated. It follows that for the distorted octahedral coordination around the Cu²⁺ ion the above mentioned differentiation of the role of oxygen atoms belonging to formate groups can appear. The configuration of hydrogen bonds is similar in both compounds. In spite of the facts that the dimensions of the elementary cell of copper formate are slightly larger than those of nickel formate and that the structure is more loose, the lengths of the hydrogen bonds are of the same order of magnitude.

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Die Struktur von Kaliumamidotriphosphat K₄P₃O₉NH₂ · 4H₂O

VON WALTRAUD HILMER

Institut für anorganische Chemie der Deutschen Akademie der Wissenschaften zu Berlin, Berlin-Adlershof, Deutschland

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K₄P₃O₉NH₂ · 4H₂O crystallizes in space group *P* $\bar{1}$ with cell dimensions $a=6.08$, $b=10.06$, $c=12.72$ Å, $\alpha=95.9^\circ$, $\beta=91.7^\circ$, $\gamma=107.1^\circ$ and two molecules K₄P₃O₉NH₂ · 4H₂O per unit cell. The triphosphate anion consists of three phosphate tetrahedra joined at corners to form a chain. Three potassium atoms are irregularly surrounded by seven oxygen atoms, one potassium atom by six oxygen atoms and one nitrogen atom. The structure consists of layers of triphosphate anions and potassium atoms alternating with layers of water molecules.

Untersuchungen von Quimby & Flautt (1958) & Feldmann & Thilo (1964) an Amidotriphosphaten zeigten, dass sich aus Amidotriphosphat leicht ringförmiges Trimetaphosphat bildet. Diese leichte Bildung von ringförmigen Anionen legte die Vermutung nahe, dass bereits in den Amidotriphosphat-Anionen durch die relative Lage der PO₄-Tetraeder die Ringe vorgebildet sind. Die Strukturbestimmung eines Amidotriphosphates sollte diese Frage klären.

Es wurde Kaliumamidotriphosphat K₄P₃O₉NH₂ · 4H₂O nach der Darstellung von Feldmann & Thilo (1964) untersucht. Die Gitterkonstanten sind

$$\left. \begin{array}{ll} a = 6,08 \pm 0,02 \text{ \AA} & \alpha = 95,9^\circ \\ b = 10,06 \pm 0,03 & \beta = 91,7 \\ c = 12,72 \pm 0,04 & \gamma = 107,1 \end{array} \right\} \pm 0,5^\circ$$

triklin, Raumgruppe *P* $\bar{1}$ (*I*-Statistik nach Howells, Phillips & Rogers, 1950); in der Elementarzelle sind

2 Formeleinheiten K₄P₃O₉NH₂ · 4H₂O enthalten. Die Dichte ergab sich pyknometrisch bei 25 °C zu $D=2,07$ g.cm^{−3}*, die berechnete Dichte beträgt 2,17 g.cm^{−3}. Die Intensitäten wurden aus Weissenberg-Aufnahmen (Cu-Strahlung) für die *h0l*-, *0kl*- und *1kl*-Reflexe bestimmt und auf Lorentz- und Polarisationsfaktor, sowie $\alpha_1\alpha_2$ -Aufspaltung korrigiert. Die untersuchten Kristalle hatten die Abmessung von 0,1 × 0,03 × 0,02 mm, so dass auf Absorptionskorrektur verzichtet werden konnte.

Strukturbestimmung

Zunächst sollte die Patterson-Projektion *P*(*v*, *w*) zur Bestimmung erster Atomlagen verwendet werden. Leider war diese Projektion – auch nach der Zuspitzung

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