

in the molecule (bonds 1–2 and 8–9) and both are short, 1.352 and 1.342 Å respectively.

Although the molecule is approximately planar it is not as planar as some other aromatic condensed ring hydrocarbons; for example chrysene has a maximum deviation of 0.02 Å (Burns & Iball, 1960). There is overcrowding due to the H atoms attached to atoms 1 and 16 and this is relieved mainly by the slight twisting of the molecule so that atoms 1 and 16 are on opposite sides of the mean plane (separation normal to the plane, 0.044 Å) and there is no undue lengthening of the bond 17–18. In many similar compounds this kind of bond is greater than 1.46 Å.

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Copper(II) Formate–Urea–Water (1/2/2)

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Abstract. $\text{Cu}(\text{HCO}_2)_2 \cdot 2(\text{NH}_2)_2\text{CO} \cdot 2\text{H}_2\text{O}$, monoclinic, $P2_1/c$, $a = 8.275$ (4), $b = 8.346$ (3), $c = 8.018$ (3) Å, $\beta = 96.36$ (5)°, $Z = 2$, $D_m = 1.862$ (3), $D_x = 1.869$ g cm⁻³. The crystal consists of the same kind of copper formate layers, $[\text{Cu}(\text{HCO}_2)_2]_\infty$, as in $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$, between which urea and water molecules are held together by unique hydrogen bonds.

Introduction. Crystals suitable for X-ray studies were prepared from an aqueous solution of copper formate and a large excess of urea, at room temperature. The (100) plane is a pronounced cleavage plane and corresponds to (001) in copper formate tetrahydrate (hereafter abbreviated as CFTH).

Weissenberg and precession photographs showed the symmetry of monoclinic $P2_1/c$ (systematic absences: $h0l$ with l odd and $0k0$ with k odd). A blue 0.1 mm cubed crystal was mounted on a Rigaku automatic

four-circle diffractometer. The lattice parameters were determined from setting angles of the diffractometer with Mo $K\alpha_1$ radiation ($\lambda = 0.7093$ Å). Intensity data were collected on the same diffractometer by use of Mo $K\alpha$ radiation and of the ω - 2θ scan technique. The scan speed was 1°/min in 2θ and background intensities were measured for 10 s at both ends of each scan. A total of 1701 reflexions were observed in a region of $(\sin \theta)/\lambda < 0.72$ Å⁻¹. Corrections were made for Lorentz and polarization factors, but not for absorption ($\mu = 21.05$ cm⁻¹) and extinction.

The positions of all the non-hydrogen atoms were determined by the combined use of Patterson and Fourier syntheses. After four cycles of least-squares refinement the R value dropped to 0.063 ($R = \sum |F_o| - |F_c| / \sum |F_o|$). A difference Fourier map computed at this stage showed the positions of all H atoms. Further refinements with anisotropic temperature factors for

Table 1. *Final positional parameters* ($\times 10^4$) *and thermal parameters* (Å² $\times 10^2$)

Estimated standard deviations are given in parentheses. The anisotropic thermal factors are of the form $T = \exp[-\frac{1}{3}(h^2 a^{*2} B_{11} + \dots + 2k lb^* c^* B_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	216 (1)	78 (1)	73 (1)	19 (1)	-5 (1)	2 (1)
C(F)	-161 (2)	2680 (2)	2342 (2)	215 (8)	138 (8)	117 (7)	40 (6)	-32 (6)	-12 (6)
C(U)	6307 (2)	468 (2)	3620 (2)	163 (7)	208 (8)	179 (7)	-15 (6)	19 (6)	-8 (6)
O(1F)	-644 (2)	2050 (1)	972 (1)	254 (6)	123 (5)	116 (5)	36 (5)	-31 (4)	-38 (4)
O(2F)	-531 (2)	4057 (1)	2758 (1)	263 (6)	95 (5)	102 (5)	18 (4)	-10 (4)	-18 (4)
O(U)	5426 (2)	-190 (2)	2430 (2)	275 (6)	227 (7)	213 (5)	-28 (6)	-76 (5)	-36 (5)
O(W)	2795 (2)	950 (2)	246 (2)	197 (6)	245 (6)	224 (6)	7 (5)	4 (5)	5 (5)
N(1)	6303 (2)	2030 (2)	3868 (2)	302 (8)	173 (7)	374 (9)	2 (7)	-121 (7)	9 (7)
N(2)	7307 (2)	-411 (2)	4662 (2)	342 (9)	172 (7)	316 (8)	24 (6)	-123 (6)	-30 (6)

Table 1 (cont.)

$$T = \exp(-B \sin^2 \theta / \lambda^2).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(N11)	7097 (22)	2413 (14)	4605 (24)	200 (42)
H(N12)	5869 (24)	2572 (24)	3235 (25)	286 (48)
H(N21)	7801 (24)	82 (27)	5435 (26)	355 (49)
H(N22)	7266 (23)	-1338 (23)	4598 (24)	239 (45)
H(1 <i>W</i>)	3486 (24)	692 (25)	1019 (25)	301 (50)
H(2 <i>W</i>)	3280 (26)	769 (25)	-534 (26)	315 (49)
H(<i>F</i>)	635 (24)	2041 (25)	3165 (25)	285 (47)

the non-hydrogen atoms and isotropic ones for the H atoms gave the final *R* value of 0.042. The final positional and thermal parameters are given in Table 1.*

The atomic scattering factors for C, N, O and Cu²⁺ and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Cu, were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for H were of Stewart, Davidson & Simpson (1965). The quantity minimized during the least-squares procedure was $\sum w(|F_o| - k|F_c|)^2$. The following weighting scheme was used: $w = 1/\sigma^2$, $\sigma = 5.0$ if $F_o = 0.0$ or if $F_o/\sigma(F) < 5.0$, $\sigma = [(I - I_m)/I_m] + \sigma(F)$ if $I > I_m$, and otherwise $\sigma = \sigma(F)$, where $\sigma(F)$ was determined from counting statistics and I_m was one sixth of the maximum intensity. All computations were performed on a NEAC 2200/700 computer at the Computer Center, Osaka University, using local modifications of *RSSFR-5*, *HBL5 IV*, *DAPH* and *RSDA-4* in the UNICS program system (1967).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31362 (7 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Copper(II) formate-urea-water (1/2/2) (hereafter abbreviated as CFUH) was first prepared and described as a derivative of CFTH by Kishita (1962). The crystal structure of CFTH is characterized by alternating layers of copper formate and of hydrogen-bonded water molecules; of two non-equivalent water molecules, only one coordinates to a copper ion (Kiryama, Ibamoto & Matsuo, 1954). The tetrahydrate has been investigated extensively in recent years as it possesses very interesting antiferroelectric (Okada, Kai, Cromer & Almodover, 1966) and antiferromagnetic properties (Kobayashi & Haseda, 1963). Our measurements on d.c. conductivities and dielectric constants showed that CFUH exhibits no antiferroelectric phase transition as does CFTH. On the other hand, magnetic properties at low temperatures (Kobayashi *et al.*, 1963) and also infrared spectra (Kuroda, Sasano & Kubo, 1966) suggested that the crystal structure of CFUH is very similar to that of CFTH. The present study was undertaken to ascertain these suggestions and to establish the structural origin of the dielectric and magnetic properties in both compounds.

A stereoscopic view of the crystal structure is presented in Fig. 1 (*ORTEP*, Johnson, 1965). The interatomic distances and angles uncorrected for thermal motions are listed in Table 2. Each copper ion is located at the site of a centre of symmetry and is surrounded by four square-planar oxygens of four different formate ions and by two water oxygens to form an elongated octahedral arrangement. The formate ion bridges two copper ions 5.79 Å apart in a so-called *anti-anti* bridging arrangement, thus forming the copper formate sheets, $[\text{Cu}(\text{HCO}_2)_2]_\infty$ parallel to (100). Such a two-dimensional network as well as the environment about the copper ion are essentially the same as in CFTH, except for elongation

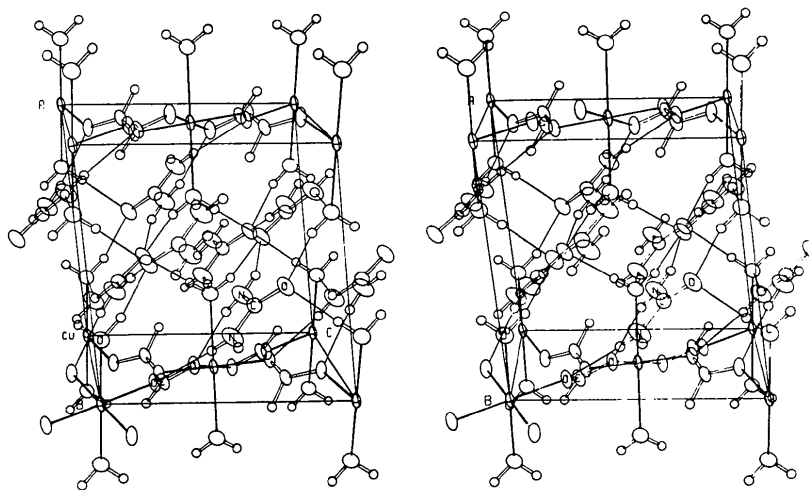


Fig. 1. A stereoscopic view of the molecular packing seen along [010]. The *a* axis is vertical and the *c* axis points to the right. The thermal ellipsoids of the non-hydrogen atoms are 50% probability surfaces.

of the Cu—O(*W*) distance and only a small difference in the nearest Cu...Cu distance. Between these layers, urea molecules are sandwiched instead of the second type of water molecules found in CFTH.

The structure of this compound can be described in another way as hydrogen-bonded networks parallel to (10 $\bar{1}$). All the atoms other than Cu and H(2*W*) lie on the planes expressed in the form of $4x - 4z = 2n + 1$,

Table 2. *Interatomic distances (Å) and angles (°)*

(a) Copper octahedron			
Cu—O(1 <i>F</i>)	1.977 (1) (2×)		
Cu—O(2 <i>F</i> , V)	1.967 (1) (2×)		
Cu—O(<i>W</i>)	2.433 (1) (2×)		
O(1 <i>F</i>)—Cu—O(2 <i>F</i> , V)		91.7 (2)	
O(1 <i>F</i>)—Cu—O(<i>W</i>)		88.9 (2)	
O(2 <i>F</i> , V)—Cu—O(<i>W</i>)		86.7 (2)	
(b) Formate ion			
C(<i>F</i>)—O(1 <i>F</i>)	1.243 (2)		
C(<i>F</i>)—O(2 <i>F</i>)	1.244 (2)		
C(<i>F</i>)—H(<i>F</i>)	1.029 (21)		
O(1 <i>F</i>)—C(<i>F</i>)—O(2 <i>F</i>)		124.3 (2)	
O(1 <i>F</i>)—C(<i>F</i>)—H(<i>F</i>)		117.9 (12)	
O(2 <i>F</i>)—C(<i>F</i>)—H(<i>F</i>)		117.7 (12)	
(c) Urea molecule			
C(<i>U</i>)—O(<i>U</i>)	1.260 (2)		
C(<i>U</i>)—N(1)	1.319 (3)		
C(<i>U</i>)—N(2)	1.329 (3)		
N(1)—H(N11)	0.893 (19)		
N(1)—H(N12)	0.743 (20)		
N(2)—H(N21)	0.815 (22)		
N(2)—H(N22)	0.776 (19)		
O(<i>U</i>)—C(<i>U</i>)—N(1)		122.3 (2)	
O(<i>U</i>)—C(<i>U</i>)—N(2)		120.2 (2)	
N(1)—C(<i>U</i>)—N(2)		117.5 (2)	
C(<i>U</i>)—N(1)—H(N11)		116.1 (13)	
C(<i>U</i>)—N(1)—H(N12)		120.6 (16)	
H(N11)—N(1)—H(N12)		119.9 (20)	
C(<i>U</i>)—N(2)—H(N21)		115.1 (16)	
C(<i>U</i>)—N(2)—H(N22)		119.3 (15)	
H(N21)—N(2)—H(N22)		124.6 (21)	
(d) Water molecule			
O(<i>W</i>)—H(1 <i>W</i>)	0.824 (21)		
O(<i>W</i>)—H(2 <i>W</i>)	0.794 (21)		
H(1 <i>W</i>)—O(<i>W</i>)—H(2 <i>W</i>)		100.0 (20)	
O(<i>U</i>)—O(<i>W</i>)—O(<i>U</i> , IV)		87.9 (2)	
(e) Hydrogen bonds			
N(1)···O(1 <i>F</i> , I)	2.979 (2)		
N(1)···O(<i>U</i> , II)	2.861 (2)		
N(2)···O(2 <i>F</i> , I)	3.108 (2)		
N(2)···O(<i>W</i> , III)	3.040 (2)		
O(<i>W</i>)···O(<i>U</i>)	2.805 (2)		
O(<i>W</i>)···O(<i>U</i> , IV)	2.805 (2)		
N(1)—H(N11)···O(1 <i>F</i> , I)		164.9 (20)	
N(1)—H(N12)···O(<i>U</i> , II)		150.9 (20)	
N(2)—H(N21)···O(2 <i>F</i> , I)		167.5 (22)	
N(2)—H(N22)···O(<i>W</i> , III)		173.1 (19)	
O(<i>W</i>)—H(1 <i>W</i>)···O(<i>U</i>)		165.6 (20)	
O(<i>W</i>)—H(2 <i>W</i>)···O(<i>U</i> , IV)		176.3 (20)	

Symmetry code

None	<i>x</i>	<i>y</i>	<i>z</i>	III	1− <i>x</i>	−½+ <i>y</i>	½− <i>z</i>
I	1+ <i>x</i>	½− <i>y</i>	½+ <i>z</i>	IV	1− <i>x</i>	− <i>y</i>	− <i>z</i>
II	1− <i>x</i>	½+ <i>y</i>	½− <i>z</i>	V	− <i>x</i>	−½+ <i>y</i>	½− <i>z</i>

where *x* and *z* refer to their fractional coordinates and *n* is an integer. The projection on to one of these planes is shown in Fig. 2. Both the water and urea molecules play important roles in connecting the [Cu(HCO₂)₂]_∞ layers. The water oxygen O(*W*) has a nearly tetrahedral coordination of type *H* (Chidambaram, Sequeira & Sikka, 1964). That is, one of the lone pairs of O(*W*) points towards one copper ion and the other towards one amino group of urea, whereas two hydrogens, H(1*W*) and H(2*W*), are incorporated in hydrogen bonding to two adjacent carbonyl O atoms. On the other side the urea molecule

Table 3. *Equations of least-squares planes and displacement of atoms (Å) from planes*

An asterisk indicates an atom not included in the least-squares calculation. Coordinates *XYZ* are defined as follows:

$$X = ax + cz \cos \beta, Y = by, Z = cz \sin \beta.$$

(a) Plane of the urea molecule

$$0.7955X + 0.1116Y - 0.5956Z = 2.227 \text{ \AA}$$

C(<i>U</i>)	0.006	O(<i>U</i>)	−0.002
N(1)	−0.002	N(2)	−0.002
*H(N11)	−0.16	*H(N12)	−0.11
*H(N21)	0.05	*H(N22)	0.08
*O(1 <i>F</i> , I)	−0.950	*O(2 <i>F</i> , I)	0.137
*O(<i>W</i> , III)	0.454	*O(<i>U</i> , II)	0.170

(b) Plane of the formate ion

$$-0.8450X - 0.3650Y + 0.3910Z = 0.202 \text{ \AA}$$

*H(<i>F</i>)	0.04	*Cu	0.202
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The angle between (b) and (100) is 32.3°

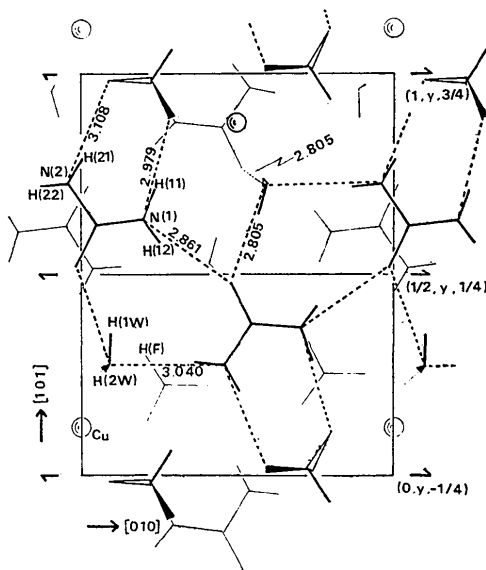


Fig. 2. Hydrogen-bonded network in CFUH as projected onto (10 $\bar{1}$). Broken lines indicate hydrogen bonds between atoms in this layer; dotted lines hydrogen bonds to atoms above or below this layer.

acts also as a hydrogen-bond donor, forming four NH...O bonds with two O atoms of a formate ion, one carbonyl O and one water O.

The formate ion and the urea molecule are nearly planar. The equations of these planes and deviations of atoms from them are given in Table 3. The average C-N distance of 1.324 Å is somewhat shorter than the corresponding distance, 1.352 Å, in tetragonal urea (Pryor & Sanger, 1970). Although the urea oxygen O(U) is involved in three hydrogen bonds, the six angles around this oxygen atom depart considerably from the tetrahedral angle, ranging from 74 to 148°.

All the hydrogen atoms of the water and urea molecules are ordered in the unique system of hydrogen bonds, in contrast to CFTH. The difference in dielectric behaviour between both compounds seems to be ascribable to the different schemes of hydrogen bonds. It was also confirmed that the magnetic properties described above are governed by the interaction between Cu²⁺ ions *via* bridging formate ions within each copper formate layer. The difference in hydrogen-bonding schemes, however, may cause a significant difference in the interlayer magnetic interaction between CFTH and CFUH.

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International Union of Crystallography

Commission on Journals

The Commission on Journals held an extensive series of meetings in connexion with the Tenth General Assembly of the International Union of Crystallography, and makes the following announcements.

Composition of the Editorial Boards

Professor L. H. Jensen and Professor D. Mootz have retired as co-editors of *Acta Crystallographica*, and Professor M. M. Woolfson as book-review editor. The Commission is deeply grateful to them for their services to the crystallographic community. The Executive Committee has approved the appointments of Dr F. R. Ahmed, Professor G. Allegra, Professor H. Bärnighausen and Professor E. C.

Lingafelter as co-editors of *Acta Crystallographica*, and of Dr J. H. Robertson as book-review editor.

Four other co-editors have given notice of their intention to retire as soon as replacements can be found.

Notes for Authors

The Commission has decided to undertake a revision of *Notes for Authors*. Deposition of structure-factor tables will become the normal practice, and publication will take place only when the nature of the paper is such that immediate reference to the tables is necessary. Any suggestions for other changes in *Notes for Authors* would be welcome and should be sent to the Chairman of the Commission, Professor A. J. C. Wilson, Department of Physics, The University of Birmingham, Birmingham B15 2TT, England.