

The Crystal Structure of Cupric Formate Tetrahydrate, $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$

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The crystal structure of this compound has been determined by Patterson and Fourier syntheses and refined by F_o-F_c syntheses. Each copper atom is surrounded by four oxygen atoms of four different formate ions in an approximately square configuration and by two water molecules at a greater distance. The formate ion is nearly symmetrical with an O-C-O angle of 120° .

In the course of our investigations on paramagnetic resonance absorption, it became desirable to know the atomic arrangements of the crystals of cupric formate tetra- and di-hydrates. The present note reports the structure analysis of the former carried out by us recently. Kabraji (1931) has already given the cell dimensions, the number of formula units and the space group.

Useful X-ray data in the present experiments were obtained from oscillation photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$): The unit cell, containing two formula units, has the dimensions

$$a = 8.18 \pm 0.02, \quad b = 8.15 \pm 0.02, \quad c = 6.35 \pm 0.02 \text{ \AA}, \\ \beta = 101^\circ 5' \pm 20',$$

which almost agree with Kabraji's data, the morphological value of β being taken. From the systematic absences, the space group was found to be $P2_1/a-C_{2h}^3$ (not $C2_1/m-C_{2h}^3$ as reported by Kabraji). The intensities of the reflexions were estimated visually and corrected for Lorentz and polarization factors. In view of the small size of the crystals used, absorption and extinction corrections were neglected. Because the general point position in $P2_1/a$ is fourfold, and since the unit cell contains only two formula units, it follows that the copper atoms must occupy special positions. From the ordinary Patterson maps projected along three crystallographic axes, approximate parameters for the O_I , O_{II} , O_{III} and O_{IV} atoms could be determined, while those for the C atoms remained less certain. Next, the electron-density maps projected along the c and b axes were prepared by taking into account probable positions of the C atoms. The atomic parameters were refined by two-dimensional Fourier syntheses and structure-factor calculations

Table 1. Final atomic parameters

	x	y	z
Cu	0	0	0
O_I (f)	0.206	-0.092	-0.080
O_{II} (f)	0.117	0.210	0.086
O_{III} (w)	0.077	-0.101	0.353
O_{IV} (w)	0.086	0.349	0.483
C	0.238	0.270	0.018

until the signs of the calculated structure factors ceased to change. Furthermore, we obtained precise values by using the F_o-F_c syntheses proposed by Cochran (1951). The final values of the atomic parameters are given in Table 1. With these coordinates, structure factors were calculated, using a temperature factor $\exp[-B(\sin \theta/\lambda)^2]$, where $B = 1.35 \text{ \AA}^2$. The observed and calculated structure factors are listed in Table 2.* The R factors are 0.10, 0.12 and 0.11 for $(h k 0)$, $(h 0 l)$ and $(0 k l)$, respectively, when the absent and over-exposed spectra are excluded.

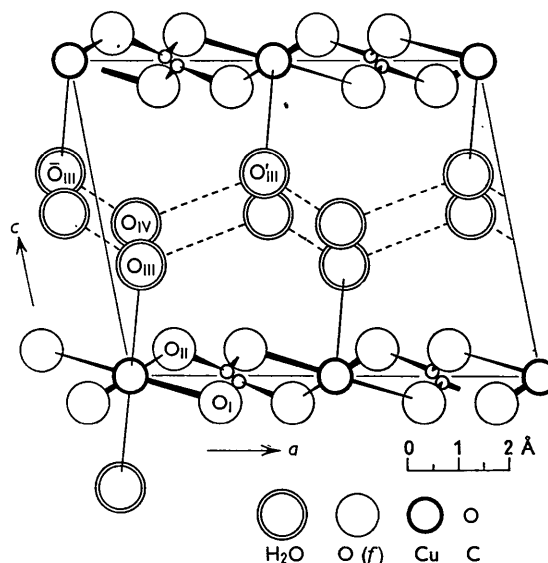


Fig. 1. Atomic arrangement of $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ projected on (010) . Broken lines show the layer of water molecules.

The structure is best described by reference to Fig. 1. The interatomic distances and bond angle are given

* Table 2 has been withdrawn and deposited as Document No. 4233 with the ADI Auxiliary, Publications Project, Photoduplication Service, Library of Congress, Washington, 25, D.C., U.S.A. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm. Advance payment is required. Make cheques or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 3. *Interatomic distances and bond angle*

Cu-O _I = 2.00 Å	O _{IV} -O _{II} = 2.82 Å	C-O _I = 1.26 Å
Cu-O _{II} = 2.01	O _{IV} -O _{III} = 2.78	C-O _{II} = 1.25
Cu-O _{III} = 2.36	O _{IV} -O _{III} = 2.74	
∠ O-C-O = 120°		

in Table 3. Each copper atom is surrounded by four oxygen atoms of four different formate ions in an approximately square configuration with Cu-O distances 2.00 Å and 2.01 Å and, above and below this plane, by two equivalent water molecules (O_{III}) with a far longer Cu-O distance (2.36 Å). Such facts suggest that there is a considerable difference between the nature of these Cu-O bindings, and this also accounts for the strong pleochroism. Another water molecule (O_{IV}) is not linked to the copper atom, but to one O_{II} and two O_{III}'s with hydrogen-bond distances 2.82, 2.74 and 2.78 Å. The formate ion has a nearly symmetrical configuration with the C-O distances 1.25 and 1.26 Å and the bond angle ∠ O-C-O about 120°.

As shown in Fig. 1, there is formed a distinct layer structure in which one formate ion is coordinated to two copper atoms. Such layers are parallel to (001) and both kinds of water molecules are sandwiched between these layers.

Owing to this predominant layer structure, this crystal shows highly perfect cleavage parallel to (001) and also large anisotropy in its dielectric behaviour and paramagnetic properties. Besides these, the very efflorescent nature of this tetrahydrate may be explained reasonably on the basis of this crystal structure.

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References

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Generalisation du Principe de Focalisation de Bragg-de Broglie

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On the basis of the Bragg-de Broglie principle of focusing the author has studied the focusing of a pencil of X-rays diffracted by lattice planes inclined to the reflecting face of the crystal. A discussion is given of applications to emission spectroscopy and to the formation of radiographic images of thin crystal plates.

Introduction

Bragg & Bragg (1914) et de Broglie (1914) ont montré que les faisceaux diffractés par les plans réticulaires parallèles à la surface plane d'une lame monocristalline tournant autour d'une droite de sa face, sont focalisés sur un cercle, section droite du cylindre de révolution, contenant la source ponctuelle de rayons X et ayant pour axe, l'axe de rotation du cristal.

D'autre part, Tellez-Plasencia (1943) a montré que d'autres conditions de focalisation peuvent être obtenues si la source et le film sont animés de mouvements convenables.

Dans cette note, on poursuit, sur les bases expérimentales de Bragg-de Broglie, l'étude géométrique des faisceaux diffractés par les plans réticulaires inclinés sur la face de réflexion; on envisage le cas des plans dont l'intersection avec la face de réflexion est parallèle à l'axe de rotation et on recherche les lieux de focalisation.

Schéma expérimental

Soient (Fig. 1(a) et (b)):

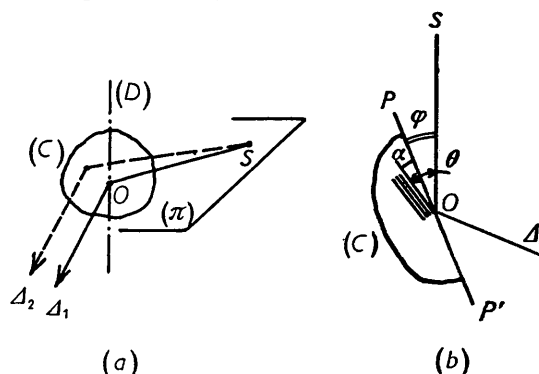


Fig. 1. Schéma expérimental. *S*, source de rayons X; (*D*) axe de rotation du cristal; (*Δ*) direction des faisceaux diffractés. (a) Cas général. (b) Cas des plans réticulaires ayant (*D*) comme axe de zone. Réflexion du rayon *SO* dans le plan (*π*) perpendiculaire à (*D*).