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Molecular and Crystal Structure of Cu(HCOO)(OH)

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Introduction

Basic copper(II) formate, Cu(HCOO)(OH), has been recently prepared and subjected to the PMR spectrum and magnetic susceptibility [1]. Ferromagnetic interaction dominates in the compound, while a phase transition to an antiferromagnetic ordered state takes place at 21.3 K due to additional antiferromagnetic interaction. This magnetic behavior suggests the existence of infinite Cu–O–C–O–Cu and Cu–OH–Cu bondings.

We have determined the structure of this copper(II) compound by single crystal X-ray analysis, in order to investigate the relation between the molecular structure and the magnetic behavior.

Experimental

Blue prismatic crystals of Cu(HCOO)(OH) were prepared according to the previously reported procedure [1]. Space group and preliminary cell constants were determined by oscillation and Weissenberg photographs. Accurate unit cell constants were determined by least-squares refinement of the θ values of 20 reflections measured on a diffractometer. Intensity data were measured by the θ–2θ scan technique on a Rigaku four-circle diffractometer with graphite-monochromated MoKα radiation. The size of the crystal used was 0.20 × 0.11 × 0.09 mm. The scan speed and scan width in ω were 2° min^{-1} and $(1.2 + 0.35 \tan\theta)°$, respectively. Of 350 independent reflections collected up to $\sin\theta/\lambda = 1.15$ Å^{-1}, 336 reflections with $|F_o| \geqslant 3\sigma(|F_o|)$ were used in the subsequent calculation. The corrections were made for Lorentz and polarization effects, but not for absorption. *Crystal data*: CH_2O_3Cu, F.W. = 125.6, monoclinic, space group $P2_1$, a = 7.316(1), b = 5.958(1), c = 3.279(1) Å, β = 103.83(1)°, V = 138.8 Å^3, D_m = 2.96, D_x = 3.01 g cm^{-3}, Z = 2, μ = 79.1 cm^{-1} (MoKα).

Structure Determination

The systematic absence 0k0, k = 2n + 1 indicated the space group, $P2_1/m$ or $P2_1$. The space group,

TABLE I. Atomic Coordinates and Anisotropic Thermal Parameters of the Form: $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$, and Their Standard Deviations.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.0011(6)	0.0	0.0018(11)	0.0059(2)	0.0015(3)	0.0356(12)	0.0006(6)	0.0055(8)	−0.0053(12)
O(1)	0.2674(17)	0.0732(21)	0.1585(38)	0.0084(22)	0.0069(30)	0.0426(106)	0.0023(46)	0.0084(78)	−0.0060(98)
O(2)	0.2719(17)	0.4446(18)	0.2131(40)	0.0084(21)	0.0022(32)	0.0641(126)	0.0014(42)	0.0056(83)	−0.0060(95)
O(3)	−0.0582(12)	0.2550(47)	0.3297(27)	0.0079(16)	0.0034(21)	0.0327(78)	0.0005(117)	0.0130(59)	0.0020(212)
C	0.3470(18)	0.2538(78)	0.2551(48)	0.0068(22)	0.0101(37)	0.0503(137)	−0.0011(156)	−0.0000(91)	−0.0325(275)

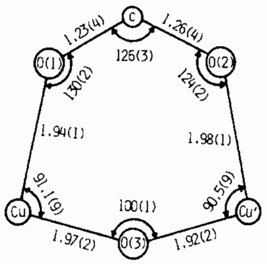

Fig. 1. Bond lengths (Å) and bond angles.

$P2_1/m$ was excluded, since there are two dissymmetric molecules in the unit cell. The crystal structure was solved by the heavy-atom technique. As the space group is $P2_1$, the y-coordinate of the copper atom can be fixed at an arbitrary position. The coordinates of the copper atom were found from a three-dimensional Patterson synthesis and those of all other non-hydrogen atoms were from the subsequent Fourier synthesis. Several cycles of block-diagonal least-squares refinement, using isotropic thermal parameters, brought the R value to 0.130. After further several cycles of blick-diagonal least-squares refinement with anisotropic temperature factors was carried out, R dropped to 0.052. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with w = 1.0 for all reflections. All the atomic scattering factors were taken from the International Tables for X-Ray Crystallography [2]. The computations were carried out on an ACOS-S700 computer at the Crystallographic Research Center, Institute for

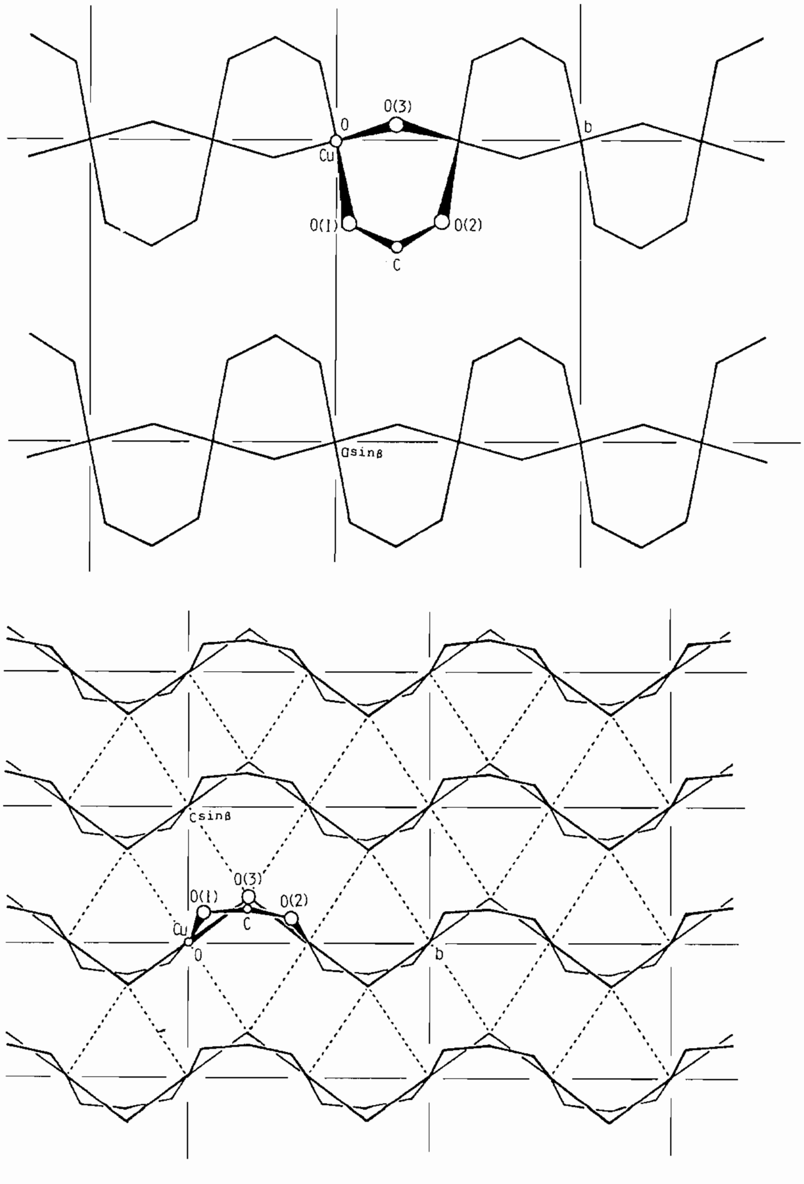

Fig. 2. Crystal structures: (a) *c* axis projection; (b) *a* axis projection. Broken lines denote the axial Cu–O Bonds.

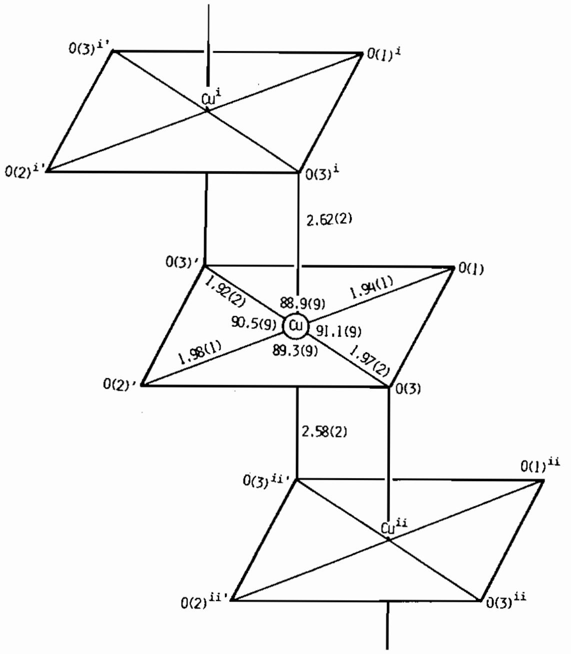

Fig. 3. Environment of the copper atoms. The symmetry code is the following: ', $\bar{x}$, −½ + y, $\bar{z}$; i, x, y −1 + z; i', $\bar{x}$, −½ + y, −1 − z; ii, x, y, 1 + z; ii', $\bar{x}$, −½ + y, 1 − z.

Protein Research Laboratory, Osaka University, with 'The Universal Crystallographic Computing System-Osaka' [3]. Table I lists the final positional and thermal parameters with their estimated standard deviations. The bond distances and angles are shown in Fig. 1.

Results and Discussion

The arrangement of atoms in the unit cell is illustrated in Fig. 2. There are no discrete molecules or ions in the crystal. The HCOO group coordinates to the two copper ions in syn–syn bridging arrangement [4]. The HCOO and OH group bridge the neighboring copper ions, and in this way infinite zigzag chains are formed along the *b* axis. The chains are connected together by the bonds of copper ions and hydroxy groups, and the layers parallel to (100) are formed. There are no shorter contacts than 4.30 Å between the layers. Owing to this layer structure, this crystal shows cleavage parallel to (100).

Each copper(II) ion is surrounded by four square-planar oxygen atoms of formate and hydroxy groups in the chain and perpendicularly surrounded by two oxygen atoms of hydroxy groups in the neighboring chains, and thus an octahedral arrangement is formed (Fig. 3). The Cu–O bond distances in the equatorial plane range from 1.92 to 1.98 Å. The axial Cu–O bond distances, 2.58 and 2.62 Å, are longer than the corresponding distances of Cu-$(HCOO)_2 \cdot 2H_2O$ [5], $Cu(HCOO)_2 \cdot 4H_2O$ [6] and copper(II) formate–urea–water (1/2/2) [7]. The O(1), O(3), O(3)', O(2) atoms on the equatorial plane deviate from their least-squares plane in the range of ±0.04 Å. The axial bonds, Cu–O(3)^{i}, Cu–O(3)^{ii}, make angles of 83° and 81° with the equatorial plane, respectively. The C–O bond distances of 1.23 and 1.26 Å are comparable to those in Royal blue form of $Cu(HCOO)_2$ [8], $Cu(HCOO)_2 \cdot 2H_2O$, $Cu(HCOO)_2 \cdot 4H_2O$ and $[(CH_3)_4N]_2[Cu(HCOO)_2(NCS)]_2$ [9]. The six-membered ring composed of Cu, O(1), C(1), O(2), Cu' and O(3) atoms has a conformation as shown in Fig. 4. The Cu, Cu' and C(1) atoms deviate from the plane through the O(1), C(1), O(3) atoms by +0.78 Å, +1.02 Å and −0.31 Å, respectively. The angle Cu–O(3)–Cu' is 100°.

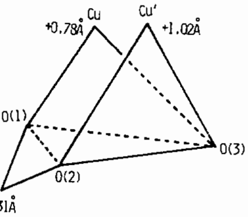

Fig. 4. Conformation of the six-membered ring composed of Cu, O(1), C(1), O(2), Cu' and O(3) atoms.

Among the derivatives of copper(II) formate such as the Royal blue form of $Cu(HCOO)_2$, $Cu(HCOO)_2 \cdot 2H_2O$, $Cu(HCOO)_2 \cdot 4H_2O$, copper(II) formate monourea [10] and $[(CH_3)_4N]_2[Cu(HCOO)_2(NCS)]_2$, the last two compounds were found in the syn–syn bridging arrangement. They adopt a dimeric structure, while the present compound has a layer structure in the syn–syn Cu–O–C–O–Cu arrangement as noted above. The Cu···Cu' distance, 2.979 Å, of Cu(HCOO)(OH) is significantly different from those (2.643–2.716 Å) of the formate compounds which adopt the dimeric structure.

As reported previously, ferromagnetic interaction operating between copper(II) ions dominates in the present compound. Therefore, it may be deduced that the copper(II) ions interact ferromagnetically through hydroxy and/or formate bridgings.

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