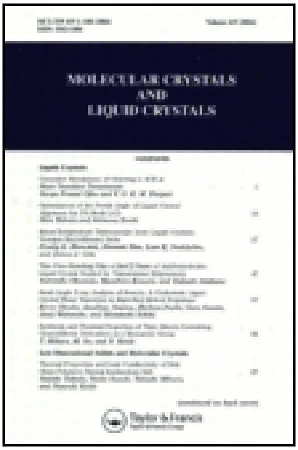

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Hydrogen-Bond Network of Dimeric Copper Complex of Vanillic Acid (HVA), $[Cu(VA)_2(H_2O)]_2$

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Hydrogen-Bond Network of Dimeric Copper Complex of Vanillic Acid (HVA), $[Cu(VA)_2(H_2O)]_2$

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The crystal structure of the title complex was first determined, showing a dimeric copper form with the four carboxylate groups. The Cu···Cu distance is short, associated with the hydrogen bond link of the apically coordinated water molecules with the nearest neighbor vanillic hydroxyl group. The hydrogen bond links afford an infinite 3-D network.

Keywords: crystal structure; vanillic acid; hydrogen bond; dimer

INTRODUCTION

Dimeric copper complexes with carboxylato bridges have been extensively investigated due to their structural characteristics of short Cu···Cu distance and magnetic properties. It is of significance to understand the coordination behaviors of complexes of carboxylate with copper. Many compounds having a constitution of $[Cu(RCOO)_2(H_2O)]_2$

have been reported, however, crystal structures only for $[Cu(CH_3COO)_2(H_2O)]_2$ and $[Cu(CH_3CH_2COO)_2(H_2O)]_2$ have been determined, indicating that the target of crystallization is quite limited[1]. Vanillic acid (3–methoxy–4–hydroxybenzoic acid, HVA) is widely used in pharmacology, starting material of some polymer rubbers and a component of polymeric soil organic matter[2]. It has three functional groups, which are potentially coordinating sites to any transition metal ions. The functional groups of carboxylic acid are important to the structural characteristics of copper dimer complexes. To our knowledge, no any crystal structure of binary or ternary complexes of vanillic acid with metal was reported. Therefore, the dimeric copper complex was synthesized and X–ray crystallographically characterized.

EXPERIMENTALSECTION

Preparation

Crystals were obtained using three–layer solutions in a tube with 0.8 cm diameter. The upper layer solution was 1ml methanol containing 0.2mol/l vanilate potassium. The bottom layer aqueous solution was 3 ml 0.03mol/l $CuCl_2$. The middle layer was 1 ml water/methanol mixed solvents with volume ration 1:1. After several days, green needle crystals were filtered. Analysis calculated for $[Cu(VA)_2(H_2O)]_2$: C 46.21%, H 3.88%; found: C 45.87% , H 3.78%.

Determination of Crystal Structure

All measurements were made on the Rigaku Mercury CCD and graphite monochromated Mo Kα (λ = 0.71069 Å) at room temperature (293K). The total reflections 14751 were collected. The structure determination was based on 2715 reflections with $I \geq 3\sigma(I)$. The crystal data of the title complex with the formula $C_{16}H_{16}O_9Cu$ is as follows: monoclinic, space group $P2_1/n$, a = 8.35(3) ,b = 19.7(2), c = 10.12(2) Å, β= 103.46(2)°, V = 1617(11) $Å^3$, Z = 4, D_X = 1.707g/cm^3, μ (MoKα) = 14.01cm^{-1}, R = 0.040 and R_w = 0.055.

RESULTS AND DISCUSSION

The crystal structure is shown in Fig.1. The title complex consists of a centrosymmetric dimer unit in which the four carboxylate groups bridge two copper atoms. Coordination sphere around each copper atom is a distorted tetragonal bipyramidal with the four oxygen atoms of the carboxylates at the equatorial sites and a water molecule and a copper atom in the axial positions. All the carboxylate groups are coordinated in a syn–syn configuration, perpendicular to each other. The Cu···Cu distance is 2.614(7) Å. The basal plane consists of four oxygen atoms at

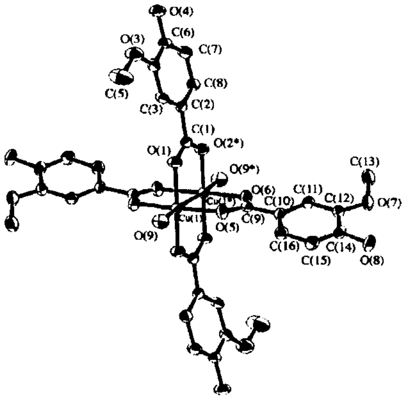

FIGURE 1. ORTEP drawing of title complex. Cu(1)–Cu(1*) 2.614(7), Cu(1)–O(1) 1.982(3), Cu(1)–O(2) 1.972(2), Cu(1)–O(5) 1.958(3), Cu(1)–O(6) 1.960(2), Cu(1)–O(9) 2.183(6) Å, Cu(1)–Cu(1*)–O(1*) 79.9(2), Cu(1)–Cu(1*)–O(2*) 89.4(2), Cu(1)–Cu(1*)–O(5*) 83.92(9), Cu(1)–Cu(1*)–O(6*) 85.22(9), Cu(1)–Cu(1*)–O(9*) 172.62(8) °(symmetry code: –*x*, –*y*, –*z*).

the Cu–O distances of 1.958(3), 1.960(2), 1.972(2) and 1.982(3) Å. The apical Cu–O bond length is 2.183(6) Å. The distances of intramolecular hydrogen bonds are 2.695(7) and 2.678(5) Å for O(3)–O(4) and O(7)–O(8), respectively. The title complex has a short Cu···Cu distance, large Cu–Cu–O (carboxylate) angle and long Cu–O(water) bond length. The Cu···Cu distance is usually associated with axial ligands, which cause a displacement of copper(II) ion from the basal plane towards the ligand[3]. A good relationship with the Cu–Cu–O (carboxylate) angles is also recognized[4], and the acidity of RCOOH (p*Ka*) is a factor influencing changes in Cu···Cu distances[5]. Several dimers with formula

$[Cu(RCOO)_2(H_2O)]_2$ are listed in Table 1. There are two factors to influence the Cu···Cu distances. One is a factor regarding the basal plane,

TABLE 1. Structural Parameters of Some Dimer $[Cu(RCOO)_2(H_2O)]_2$.

Compound	Cu···Cu	Cu–O	Cu–Cu–O	Cu–O(H_2O)	Ref.
$[Cu(MeCOO)_2 \cdot H_2O]_2$	2.616(1)	1.969	none	2.156(4)	1(a)
$[Cu(Et_2COO)_2 \cdot H_2O]_2$	2.620(3)	1.945	84.58	2.15(1)	1(b)
$[Cu(VA)_2 \cdot H_2O]_2$	2.614(7)	1.968	84.61	2.183(6)	
$[Cu(DMB)_2 \cdot H_2O]_2$	2.620(1)	1.969	84.3	2.131(4)	3
$[Cu(BBz)_2 \cdot H_2O]_2$	2.624(7)	1.99	84.28	2.17(2)	6(a)
$[Cu(DClB)_2 \cdot H_2O]_2$	2.605(1)	1.966	84.45	2.166(2)	6(b)

DMB = 2,6–dimethoxybenzoate; Bbz = 2–bromobenzoate; Acetu = N–acetylglcinate; DClB=2,6–dichlorobenzoate

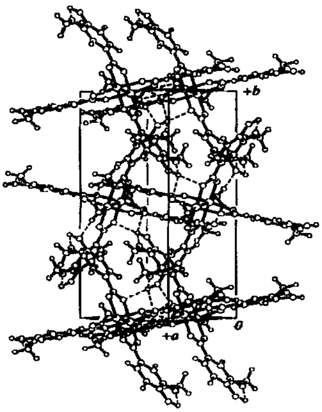

FIGURE 2. 3–D hydrogen–bond network of title complex

another is one regarding apical position. Cu–Cu–O (carbox) angle and p*Ka* belong to the basal plane parameters. The functional groups of benzoate in the title complex are different from those of compounds, $[Cu(DMB)_2(H_2O)]_2$, $[Cu(BBz)_2(H_2O)]_2$ and $[Cu(DClB)_2(H_2O)]_2$, there is a intermolecular hydrogen bond between the hydroxyl group of benzoate and the water located in axial position of the nearest neighbor molecule (see Fig. 2). The molecules are hold together by inter-molecular hydrogen bonds and extended into a 3-D network. So the intermolecular hydrogen bonds can effect the Cu–O(H_2O) and Cu···Cu distances.

Acknowledgments

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