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Copper(II) Carboxylate Containing Paddle Wheel Structure: Synthesis and Crystal Structure

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ABSTRACT

A dinuclear copper(II) complex of the type $[Cu_2(2\text{-nb})_4(MeOH)_2]$ (2-nb = 2-nitrobenzoate) has been synthesized and characterized by single crystal X-ray diffraction method.The compound belongs to monoclinic space group $P2_1/c$ with a = 19.9374(10), b = 21.1404(11),c = 7.6533(4) Å, α = 90, β= 96.817(3), $\gamma = 90^0$, V = 3246.8(3)Å^3 Z = 4, F(000) = 1736.0.0, D_c = 1.774Mg/m^3, μ = 1.422 mm^{-1}. The Cu(II) complex is a cocrystal containing two inorganic units. Each Cu(II) adopted square pyramidal geometry.

Keywords: Paddle wheel, Nickel, Synthesis, Carboxylate.

INTRODUCTION

Generally, most copper(II) carboxylates display the dinuclear paddle-wheel cage structure which consists of two copper centers bridged by four carboxylate molecules and each copper(II) is attached to a neutral ligand .The dimeric copper (II) carboxylates with the formula $[Cu_2(RCOO)_4 L_2]$ are known to contain two or more antiferromagnetically coupled metal centers [1-4].Dinuclear copper(II) compounds with four *syn-syn* bridging carboxylato ligands areof special interest due to their fungicidal activity which should arisefrom the unique coordination sphere around central copper(II) ions[5]. Apaddle-wheelstructure type was first reported in 1953 for the case of cupric acetate dehydrate [6]. Carboxylate ligands can coordinate to metal center in monodenate, bidentate or bridging mode[7]. Copper is a significant transition metal in biology and coordination chemistry [8,9].Dinuclear copper centres are present in the oxygen breathing protein hemocyanin and in a number of enzymes which have oxidase or oxygenase function[10]. Different members of metalloproteins of the type-3 with binuclear copper sites are known: hemocyanins, tyrosinase, catechol oxidase with bridging oxygen atoms and cytochrome *c*oxidase with bridging sulfur atoms. In most of these,copper is ligated by histidine and cysteine amino acids[11,12].In this work, we report synthesis and crystal structure of binuclear Cu(II) complex containing 2-nitrobenzoic acid.The complex exhibited a paddlewheel structure.

EXPERIMENTAL

Synthesis

A mixture of 2-nitrobenzoic acid (0.302 g, 2 mmol) and K_2CO_3(0.138 g, 1 mmol) in H_2O (10ml) was added to $Cu(NO_3)_2$ (0.188 g, 1 mmol) in H_2O (10ml). The mixture was stirred for 30 minutes. The precipitate formed was filtered and recrystallized from MeOH.

Crystal structure determination

Single crystal of the title compound with dimensions of 0.44 mm × 0.42 mm × 0.12 mm was mounted on Bruker APEX-II CCD diffractometer equipped with a graphite-monochromated MoKα radiation (λ = 0.71073Å) at 100.0(2) K. The compound crystallizes in monoclinic space group $P2_1/c$ with a = 19.9374(10), b = 21.1404(11), c = 7.6533(4) Å α =90, β = 96.817(3) γ = 90º V = 3246.8(3) Å^3 Z = 4, F(000) = 1736.0.0, D_c = 1.774Mg/m^3, μ = 1.422 mm^{-1}.The structure was solved by direct method using XS solution program and refined by least-squares techniques using XL [13] refinement package. Empirical absorptions were applied to all intensity data. All hydrogen atoms were placed in geometrically calculated positions and allowed to ride on the parent carbon atoms.The full final matrix least square refinement gave R= 0.0356 and wR= 0.0805.

Table 2: Selected Bond Lengths (Å) and Angles (°) For The Complex

	Bond length (Å)		
Cu1-O1	1.9671(10)	Cu1'-O1'	1.9622(10)
Cu1-O2	1.9722(10)	Cu1'-O2'	1.9658(10)
Cu1-O3	1.9670(10)	Cu1'-O3'	1.9586(11)
Cu1-O4	1.9638(10)	Cu1'-O4'	1.9798(10)
Cu1-O5	2.1451(10)	Cu1'-O5'	2.1898(11)
Cu1-Cu1^1	2.6210(4)	Cu1'-Cu1'^{2}	2.6134(4)
	Bond angle (°)		
O5-Cu1-O1	97.15(4)	O5'-Cu1'-O1'	88.06(4)
O5-Cu1-O2	93.19(4)	O5'-Cu1'-O2'	93.63(4)
O5-Cu1-O3	93.60(4)	O5'-Cu1'-O3'	102.69(4)
O5-Cu1-O4	97.78(4)	O5'-Cu1'-O4'	96.84(4)
O1-Cu1-O3	169.18(4)	O1'-Cu1'-O3'	168.88(4)
O2-Cu1-O4	169.02(4)	O2'-Cu1'-O4'	169.51(4)

Table 1: Crystallographic Data and Refinement for cu (ii) Complex

Crystal data	
Chemical formula	$C_{30}H_{24}Cu_2N_4O_{18}$
Formula weight	855.61
Cell system, space group	monoclinic, $P2_1/c$
a (Å)	19.9374(10)
b (Å)	21.1404(11)
c (Å)	7.6533(4)
α(°)	90
β(°)	96.817(3)
γ(°)	90
Volume (Å^3)	3246.8(3)
Z	4
Dc(Mg m^{-3})	1.774
μ (mm^{-1})	1.422
Crystal size (mm)	0.44 × 0.42 × 0.12
2Θ range for data collection	5.638 to 69.496
Index ranges	$-27 \le h \le 31$, $-33 \le k \le 33$, $-12 \le l \le 10$
Reflection collected	75054
Independent reflections	12506 [R_{int} = 0.0470, R_{sigma} = 0.0465]
Data/restraints/parameters	12506/6/495
F (000)	1736.0
Goodness-of-fit on F^2	1.054
R1 [I > 2σ(I)]	R1 = 0.0356
wR2 [I > 2σ(I)]	wR_2 = 0.0805
R1 (all data)	R_1 = 0.0626
wR2 (all data)	wR_2 = 0.0897
Min. and max. resd. dens. [e/Å^3],	0.46/-0.81

RESULTS AND DISCUSSIONS

Crystal structure

Crystal structure of the Cu(II) complex is depicted in Fig. 1. Crystallographic data and refinement are given in Table-1. Selected bond lengths and angles are given in Table-2.

The title compound belongs to monoclinic $P2_1/c$ space group with four molecules in the unit cell. The Cu(II) complex is cocrystal with two neutral inorganic components (**1** and **1'**). In both components, two Cu(II) centers are bridged by four carboxylate groups of the four ligands.

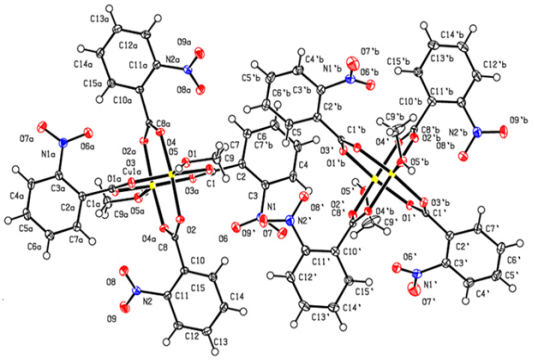

Fig. 1: Molecular structure for the complex

In compound **1,** Cu1 has distorted square-pyramidal geometry coordinated by O1,O2,O3 and O4 from four carboxylate molecules in the basal plan and O5 from MeOH molecule in the apical position. The angular and structural parameter (τ) is 0.16. The bond lengths Cu1-O1,Cu1-O2, Cu1-O3 and Cu1-O4 are 1.9671(10), 1.9722(10), 1.9670(10) and 1.9638(10)Å, respectively, while the apical bond length Cu1-O5 is 2.1451(10)Å. The values are in agreement with bond distances for other binuclear Cu(II) complex. The bond angles O5-Cu1-$O_{carboxylate}$ range from 93.19(4)to 97.78(4)°.The Cu1-Cu1^{1}bond distance is 2.6210 (4)Å in the dinuclear unit.

In compound **1',** Cu1' has almost regular square-pyramidal geometry (τ =0.0105) coordinated by O1',O2',O3' and O4' from four carboxylate ligands in the basal plan and O5' from MeOH molecule in the apical position. TheCu1'-$O_{carboxylate}$ bond lengths range 1.9586(11)from to 1.9798(10)Å, while the apical bond length Cu1'-O5'is 2.1898(11)Å.The bond angles O5'-Cu1'-O1',O5'-Cu1'-O2', O5'-Cu1'-O3' and O5'-Cu1'-O4'are 88.06(4), 93.63(4), 102.69(4) and 96.84(4)°, respectively.The Cu1'-Cu1'^{2} bond distance is 2.6210 (4)Å.

Supplementary material

CCDC 1420202 contains the supplementary crystallographicdata for this paper. These data can be obtained free ofcharge at www.ccdc.cam.ac.uk/conts/retrieving.html or fromthe Cambridge Crystallographic Data Centre (CCDC), 12 UnionRoad, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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