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Microwave Solid Phase Synthesis and Crystal Structure of Copper(II) Complex with 2-Hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)hydrazide

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One mononuclear copper(II) complex [CuLCl]·2H_2O has been synthesized by 2-hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)-hydrazide (L) with $CuCl_2$·2H_2O in microwave radiation assistance. It crystallizes in the monoclinic system, space group C2/c, with the cell parameters a = 14.8571(13) Å, b = 12.4560(11) Å, c = 16.5409(16) Å, α = γ = 90.00°, β = 95.5770(10)°, V = 3046.6(5) $Å^3$ and Z = 8. The Cu atom is surrounded by one O atom and two N atoms from 2-hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)-hydrazide molecule and one Cl from $CuCl_2$ to form a quadrilateral coordination environment.

Keywords: Copper complex, Crystal structure, 2-Hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)hydrazide.

INTRODUCTION

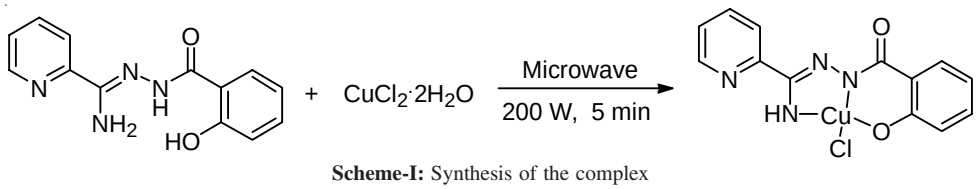
In past, chemistry of copper(II) complexes have been particularly enriched by many contributions in both synthetic and structural areas[1-7]. Copper is one of the most important metals in biological systems, mainly due to the role it plays in the binding, transport, activation of molecular oxygen and is required by creatures[8-10]. We reported here the microwave solid phase synthesis and characterization of a mononuclear Cu(II) complex with 2-hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)hydrazide and $CuCl_2$·2H_2O (**Scheme-I**).

EXPERIMENTAL

2-Hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)-hydrazide was synthesized with pyridine-2-carboximidic acid methyl ester and equimolar 2-hydroxy-benzoic acid hydrazide in ethanol and refluxed on 8 h. The other chemicals (reagent grade) used were commercially available. IR spectra were recorded on a Nexus 870 FT-IR. The crystal structure of complex was determined using SMART 1000 CCD diffractometer instrument. Melting points were measured on a XRC-1 micro melting point apparatus.

Synthesis of complex: Copper(II) chloride dihydrate salt and equivalent molar of 2-hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)hydrazide were mixed together and microwave radiated 5 min in 200 W. The brown powder was dissolved in DMF/H_2O(1/2) and stood still in air for two weeks. Large column crystals were precipitated. They were filtered and washed with ethanol for three times and dried in a vacuum desiccator containing anhydrous $CaCl_2$. The yield is 82 %, m.p.: > 300 °C. Selected IR (KBr, ν_{max}, cm^{-1}): 3420, 3230, 1628, 1567, 1455, 1296, 1135, 1101, 875, 780, 682.

X-ray crystal structure determination: A crystal with dimensions 0.38 mm × 0.24 mm × 0.20 mm was chosen and mounted on a SMART 1000 CCD diffractometer. The data were collected with graphite monochromated MoK_α radiation (λ = 071073 Å) using ω-2θ scan technique. The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model. The structures were refined on F^2 using SHELXTL-97[11]. The crystal used for the diffraction study showed no decomposition during data collection. The crystal data and refinement data are listed in Table-1. Selected bond lengths and bond angles are given in Table-2.



Scheme-I: Synthesis of the complex

TABLE-1
EXPERIMENTAL CRYSTALLOGRAPHIC DATA

Empirical formula	$C_{13}H_{14}N_4O_{3.5}CuCl$
Formula weight	381.27
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Cell dimensions	a = 14.8571(13) Å b = 12.4560(11) Å c = 16.5409(16) Å β = 95.5770(10) °
Volume	V = 3046.6(5) $Å^3$
Z	8
Density (calculated)	1.663 Mg/m^3
Absorption coefficient	1.630 mm^{-1}
F(000)	1552
Crystal size	0.38 × 0.24 × 0.20 mm
Theta range for data collection	2.40-25.02 °
Index ranges	-17 ≤ h ≤ 17, -14 ≤ k ≤ 14, -19 ≤ l ≤ 10
Reflections collected	7631
Independent reflections	2705 [R_{int} = 0.0370]
Data/restraints/parameters	2705/0/204
Goodness of fit on F^2	1.053
Final R indices [I > 2σ(I)]	R1 = 0.0348, wR2 = 0.0810
R indices (all data)	R1 = 0.0524, wR2 = 0.0933
Extinction correction	None
Largest diff. peak and hole	0.334 and -0.370 e· $Å^{-3}$
Deposition number	CCDC 1005785

RESULTS AND DISCUSSION

The crystal structure of [CuLCl]·$2H_2O$ consists of a mononuclear complex, there is a coordination environment (Fig. 1). The central copper(II) atom is four-coordinated by two nitrogen atoms and one oxygen atom from 2-hydroxy-benzoic acid(amino-pyridin-2-yl-methylene)hydrazide (L) molecule and one Cl from $CuCl_2$. The L is tridentate ligand. The Cu atom is in a distorted quadrilateral coordination environment with the N2-Cu1-O1 angle [79.92(9)°], N2-Cu1-N4 angle [80.40(11)°], O1-Cu1-N4 angle [160.15(10)°], N2-Cu1-Cl1 angle [169.92(8)°], O1-Cu1-Cl1 angle [98.50(7)°] and N4-Cu1-Cl1 angle [100.42(9)°]. The Cu1-N2 [1.926(2)Å], Cu1-O1[1.976(2) Å], Cu1-N4[2.022(3) Å] and Cu1-Cl1[2.2335(9) Å] bond lengths are in normal range[12]. The title crystal structure is indicated by the torsion angles separately being C1-N1-N2-Cu1 = 0.0(3)°, O1-Cu1-N2-C8 = 175.0(2)°, N4-Cu1-N2-C8 = -2.4(2)°, Cl1-Cu1-N2-C8 = 93.2(5)°, O1-Cu1-N2)-N1 = -0.80(19)°, N4-

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Atoms	Length	Atoms	Length
Cu1-N1	1.926(2)	Cu1-O1	1.976(2)
Cu1-N4	2.022(3)	Cu1-Cl1	2.2335(9)
N1-C1	1.326(4)	N1-N2	1.381(3)
N2-C8	1.293(4)	N3-C8	1.344(4)
N4-C13	1.332(4)	N4-C9	1.356(4)
O1-C1	1.298(4)	O2-C3	1.359(4)
C1-C2	1.483(4)	C2-C3	1.400(5)
C2-C7	1.404(5)	C3-C4	1.393(5)
C4-C5	1.381(6)	C5-C6	1.376(6)
C6-C7	1.388(5)	C8-C9	1.477(4)
C9-C10	1.380(5)	C10-C11	1.379(5)
C11-C12	1.361(6)	C12-C13	1.397(6)
Atoms	**Angles**	**Atoms**	**Angles**
N2-Cu1-O1	79.92(9)	N2-Cu1-N4	80.40(11)
O1-Cu1-N4	160.15(10)	N2-Cu1-Cl1	169.92(8)
O1-Cu1-Cl1	98.50(7)	N4-Cu1-Cl1	100.42(9)
C1-N1-N2	108.6(2)	C8-N2-N1	124.0(3)
C8-N2-Cu1	118.9(2)	N1-N2-Cu1	116.93(18)
C13-N4-C9	119.0(3)	C13-N4-Cu1	128.0(3)
C9-N4-Cu1	112.9(2)	C1-O1-Cu1	110.39(19)
O1-C1-N1	124.1(3)	O1-C1-C2	118.3(3)
N1-C1-C2	117.6(3)	C3-C2-C7	118.1(3)
C3-C2-C1	122.1(3)	C7-C2-C1	119.8(3)
O2-C3-C4	117.2(3)	O2-C3-C2	121.9(3)
C4-C3-C2	121.0(3)	C5-C4-C3	119.3(4)
C6-C5-C4	121.2(4)	C5-C6-C7	119.6(4)
C6-C7-C2	120.8(4)	N2-C8-N3	126.0(3)
N2-C8-C9	113.7(3)	N3-C8-C9	120.3(3)
N4-C9-C10	121.5(3)	N4-C9-C8	113.9(3)
C10-C9-C8	124.6(3)	C11-C10-C9	119.1(4)
C12-C11-C10	119.5(4)	C11-C12-C13	119.2(4)
N4-C13-C12	121.6(4)	–	–

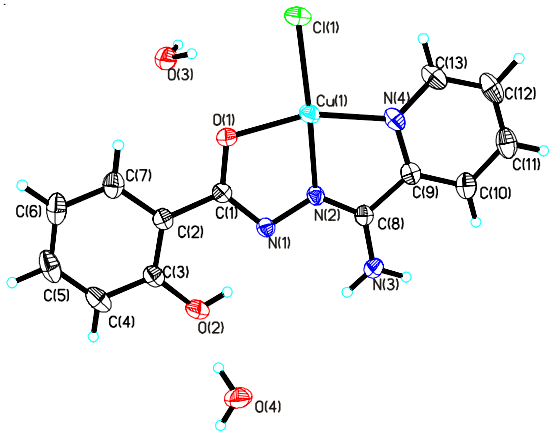


Fig. 1. A view of complex, showing 30 % probability displacement ellipsoids (arbitrary spheres for the H atoms)

TABLE-3
HYDROGEN BOND LENGTHS (Å) AND ANGLES (°)

D-H...A	ARU	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O2-H2...N1		0.82	1.84	2.5684	148
N3-H3A...O3		0.86	2.17	2.8834	140
N3-H3B...O3	[3655.02]	0.86	2.37	3.1900	159
O3- H3E...Cl1	[7555.01]	0.85	2. 73	3.5251	156
O3- H3E...O1	[7555.01]	0.85	2. 35	2.8508	118
O3-H3F...O4		0.85	2.30	3.0876	155
O4-H4...O2		0.85	2. 01	2.8162	158
C7-H7...O1		0.93	2.48	2.7976	100
C10-H10...O3	[3655.02]	0.93	2.53	3.3717	151

[7555] = 1/2-x, 1/2-y, -z; [3655] = 1-x, -y, -z

Cu1-N2-N1 = -178.2(2)°, Cl1-Cu1-N2-N1 = -82.7(5)°, N2-Cu1-N4-C13 = -176.5(3)°, O1-Cu1-N4-C13 = 175.8(3)°, Cl1-Cu1-N4-C13 = 13.7(3)°, N2-Cu1-N4-C9 = -0.8(2)°, O1-Cu1-N4-C9 = -8.5(4)°, Cl1-Cu1-N4-C9 = -170.6(2)°, N2-Cu1-O1-C1 = 1.43(19)°, N4-Cu1-O1-C1 = 9.1(4)°, Cl1-Cu1-O1-C1 = 171.35(18)°, Cu1-O1-C1-N1 = -2.1(4)° and Cu1-O1-C1-C2 = 177.5(2)°. The atoms of phenylring plane A(C2-C7) and heterocyclic plane B(N4, C9-C13) are compared the dihedral angle is A/B = 6.7°. X-ray analysis reveals that intermolecular hydrogen bonding parameters are shown in Table-3. The molecules participate to form weak intermolecular interactions, which join the constituents into a three-dimensional network structure (Fig. 2).

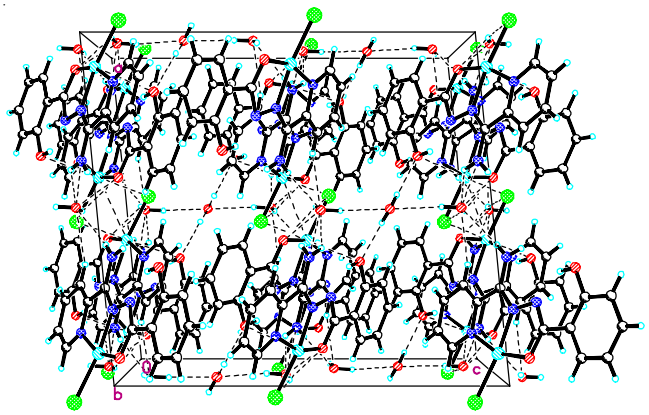


Fig. 2. Packing structure of complex along the b-axis, showing the formation of column by weak intermolecular interactions

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