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Synthesis, characterization, crystal structure determination and computational study of a new Cu(II) complex of bis [2-{(E)-[2-chloroethyl)imino]methyl}phenolato)] copper(II) Schiff base complex

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ABSTRACT

The copper (II) Schiff base complex of [Cu**L**$_2$] (**1**), H**L** = 2-{(E)-[2-chloroethyl) imino]methyl}phenol, has been synthesized and characterized by elemental (CHN) analysis, UV–Vis and FT-IR spectroscopy. The molecular structure of **1** was determined by single crystal X-ray diffraction technique. The conformational analysis and molecular structures of Cu**L$_2$** were investigated by means of density functional theory (DFT) calculations at B3LYP/6-311G* level. An excellent agreement was observed between theoretical and experimental results. The Schiff base ligand of H**L** acts as a chelating ligand and coordinates *via* one nitrogen atom and one oxygen atom to the metal center. The copper (II) center is coordinated by two nitrogen atoms and two oxygen atoms from two Schiff base ligands in an approximately square planar trans-[MN_2O_2] coordination geometry. Thermogravimetric analysis of Cu**L**$_2$ showed that it was decomposed in five stages. In addition, the Cu**L**$_2$ complex thermally decomposed in air at 660 °C and the XRD pattern of the obtained solid showed the formation of CuO nanoparticles with an average size of 34 nm.

1. Introduction

Azomethines (known as Schiff-bases), having imine groups (–C=N–), are formed by condensation reaction of primary amines with aldehydes or ketones. They are some of the most widely used organic compounds in different aspects. They played central role in development of coordination chemistry of transition metals [1,2]. In the area of bioinorganic chemistry interest in Schiff base complexes with transition and inner-transition metals has centered on the role of such complexes in providing synthetic interesting models for the metal-containing sites in metallo-proteins and -enzymes [3–14]. In the recent years many researchers have been devoted to investigate the synthesis of copper (II) complex with salicylaldehyde substituted Schiff-base ligands for their interesting structural application and properties [15–21]. In this research we describe the synthesis, characterization, crystal structure determination of a new Cu(II) Schiff base complex of [Cu**L$_2$**] (Scheme 1), and improve understanding of conformational and structural information of this complex by means of density functional theory (DFT) studies. The calculated conformational and geometrical analysis are compared with those observed experimentally. In addition, comparison between the geometrical and conformational analysis of Cu**L$_2$** in this research with the results of our recent publication about the Ni**L**$_2$ [22] gives a clear understanding of electronic configuration of metal ion on conformation, structure, and the M–O bond length.

2. Experimental

2.1. Physical techniques and materials

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus

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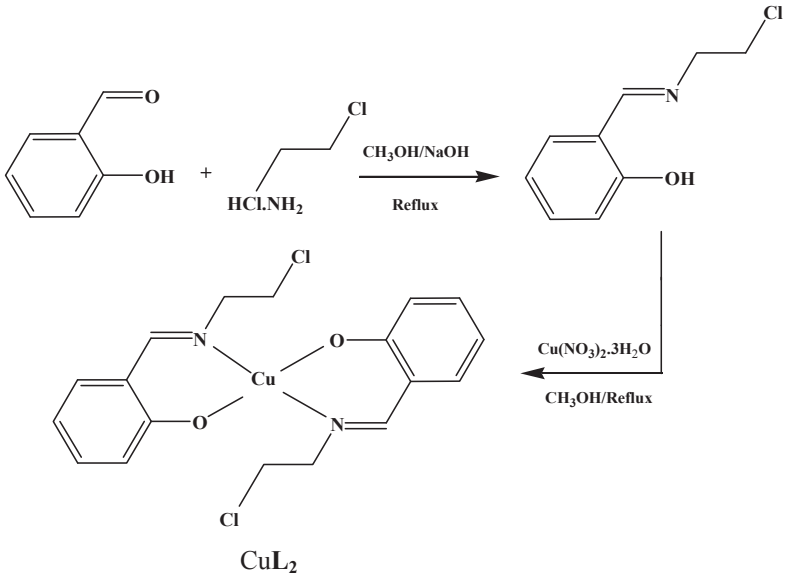

Scheme 1. The preparation procedures of the [Cu**L**$_2$] Schiff base complex.

CHN-O-Rapid analyzer, and the results agreed with calculated values. UV–Vis spectra were recorded by Perkin Elmer Spectrometer Lambda 25.

2.2. Preparation of Schiff base ligand (H*L*)

The ligand 2-{(E)-[(2-chloroethyl)imino]methyl}phenol *(HL)*, was prepared and characterized as described earlier [23]. *Anal.* Calc. for $C_9H_{10}ClNO$: C, 58.85; H, 5.45; N, 7.63%. Found: C, 58.51; H, 5.37; N, 7.48%. FT- IR (KBr pellet, cm^{-1}):*v* (C=N) 1640 cm^{-1}.

2.3. Preparation of Cu*L*$_2$

To a stirred solution of H**L** (2 mmol) in 60 ml of methanol was added 1 mmol of $Cu(NO_3)_2.3H_2O$ and the mixture was refluxed for 4 h. After cooling to room temperature, the content filtered off and washed with 50 ml of methanol in 5 times and the obtained precipitate was dried in air. The suitable crystals were obtained in 1:1 mixture of methanol and chloroform by recrystallization. *Anal.* Calc. for $C_{18}H_{18}Cl_2N_2CuO_2$: C, 50.40; H, 4.20; N, 6.53. Found, %: C, 50.48**;** H, 4.10; N, 6.54. FT-IR (KBr pellet, cm^{-1}):*v* (C=N) 1620 cm^{-1}.

2.4. X-ray crystallography

A Single crystal of the dimension 0.56 mm × 0.09 mm × 0.06 mm of Cu**L**$_2$ was chosen for X-ray diffraction study. Diffraction data were measured on a Bruker–Nonius X8 ApexII diffractometer equipped with a CCD area detector by using graphite-monochromated Mo Ka radiation (k = 0.71073 Å) generated from a sealed tube source. Data were collected and reduced by smart and saint software [24] in the Bruker package. The structure was solved by direct methods [25] and then developed by least squares refinement on F^2 [26,27]. All non-H atoms were placed in calculated positions and refined as isotropic with the "riding-model technique". Crystallographic data and details of the data collection, structure solution and refinements are listed in Table 1.

2.5. Method of analysis

In this study, the conformational analysis and molecular structure of Cu**L**$_2$ complex were computed with the Gaussian 09W software system [28]. The stability of four conformers (formed from different directions of the ethyl chloride pendant groups with respect to the plane of the complex) and the relative stability and geometry of the stable conformers were calculated at the B3LYP/6-311G* level [29,30], as an excellent level for similar compounds [31,32].

Acetonitrile and carbon tetrachloride, as solvents with different polarities, were selected for studying the relative energy of two C_i and C_2 conformers of Cu**L**$_2$ complex, as the most stable conformers, in solution following the SCRF/PCM method [33].

Table 1
Crystallographic data and experimental details for Cu**L**$_2$.

	Cu**L**$_2$
Chemical formula	$C_{18}H_{18}Cl_2CuN_2O_2$
Formula weight	428.78
Crystal system	Monoclinic
Space group	$P2_1/c$
T, K	296
a, Å	5.23780 (10)
b, Å	9.2791 (2)
c, Å	18.5655 (4)
β, deg	97.9470 (10)
V, Å^3	893.66 (3)
Z	2
μ, mm^{-1}	1.54
Measured reflections	32,471
Independent reflections	2263
R_{int}	0.048
GOF on F^2	1.01
Number of parameters	115
F(000)	438
Theta range for data collection	3.1–28.6 deg
Limiting indices	$-7 \le h \le 7$ $-12 \le k \le 12$ $-24 \le l \le 24$
Goodness-of-fit on F^2	
$R[F^2 > 2\sigma(F^2)]$	0.031
$wR(F^2)$	0.085