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Synthesis, Characterization and Antioxidant Activity of a Novel Cu (II) Complex of Schiff Base Derived from N, N'-bis(benzoin)-1,4 Butane Diimine

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ABSTRACT

In this study, a new metal complex of Cu (II) with N, N'-bis(benzoin)-1,4 butane diimine was synthesized and characterized by FT-IR, ^{1}H-NMR and Scanning Electron Microscope. The antioxidant activity of this complex was studied and compared with the activity of ascorbic acid. Antioxidant study was carried out against the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH$^\bullet$) which shows the metal complex found to be good antioxidant, as comparable with ascorbic acid.

Key words: Antioxidant, Cu(II) complex, DPPH, schiff base

INTRODUCTION

Reactive Oxygen Species (ROSs) plays an important role in degenerative condition such as aging cancer, cardiovascular diseases, cataracts, neuron degenerative disorders,liver diseases and inflammations (Aruoma, 1998). These free radicals occur in the body during an imbalance between ROSs (Reactive oxygen species) and anti oxidants. Hence, the dietary intake of antioxidant is necessary and important to balance the antioxidant states that would reduce pathological conditions induced free radicals (Mohan *et al*., 2012). Metal complexes play an essential role in agriculture, pharmaceutical and industrial chemistry. The biological studies of these complexes highlighted the potential of metal (II) complex with bioactive ligand as anti-oxidant activity. The synthetic metal complexes act as antioxidants which strengthen the endogenous antioxidant defenses from ROS ravage and restore the optimal balance by neutralizing the reactive species. They are gaining immense importance by virtue of their critical role in disease prevention. In the chosen copper (II) complex, its antioxidant avtivity has not been evaluated. In our previous study the synthesized Schiff base ligand N, N'-bis(benzoin)-1,4 butane diimine was tested against the bacterial and fungal species which showed remarkable zone of inhibition with standards and have good antibacterial and antifungal activities (Balamurugan and Sankar, 2014). Hence, in the present study, an attempt has been made to evaluate an antioxidant potential of the N, N'-bis(benzoin)-1,4 butane diimine copper (II) complex. This study is focused on the antioxidant activity of Cu (II) complex, to find out if there is an increased activity with the presence of the metallic center.

MATERIALS AND METHODS

Chemicals: The chemicals and solvents used in this work were purchased from sigma chemicals (Sigma Aldrich chemical Pvt. Ltd., Bangalore, Karnataka, India). All other reagents and chemicals used in this study were of analytical grade with high purity. All the glass wares used were washed thoroughly with distilled water and dried in an oven. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wave number region 400-4000 cm^{-1}. The ^1H NMR spectrum of the complex was recorded in DMSO-d_6 solution on a Bruker-3410 Nm, 300 MHz spectrometer with chemical shifts reported in ppm relative to TMS as internal standard. SEM images were recorded in VEGA3 TESCAN SEM analyzer.

Preparation of N, N'-bis(benzoin)-1,4 butane diimine: To a methanolic solution of 2.12 g (0.01 mol) benzoin and 1.09 g (0.005 mol) 1,4 butane diimine was added anhydrous sodium acetate (4 g) and the mixture refluxed for 1 h. The hot solution was poured into ice-cold water where upon yellow precipitate of the schiff's base separated, it was filtered. Washed with water, dried and recystallised from ethanol (Mohapatra *et al*., 1978).

Preparation of N, N'-bis(benzoin)-1,4 butane diimine copper (II) complex: The ethanolic mixture of (0.01 mol) copper (II) chloride and N, N'-bis(benzoin)-1,4 butane diimine Schiff base (0.01 mol) was refluxed separately, followed by drop wise addition of ammonia. The metal chelate separated out was filtered, washed with ethanol followed by ether and dried in an oven at 50°C (Mohapatra *et al*., 1978).

In vitro antioxidant study

DPPH free radical scavenging activity: DPPH radical-scavenging activity was determined by the method of Shimada *et al*. (1992) Briefly, a 2 mL aliquot of DPPH methanol solution (25 μg mL^{-1}) was added to 0.5 mL sample solution at different concentrations. The mixture was shaken vigorously and allowed to stand at room temperature in the dark for 30 min. Then the absorbance was measured at 517 nm in a spectrophotometer:

$$\text{Radical scavenging activity (\%)} = \frac{A_C - A_S}{A_C} \times 100$$

where, A_C is control is the absorbance and A_S is sample is the absorbance of reaction mixture (in the presence of sample). All tests and analyses were performed with three replicates and the results were averaged. IC_{50} values denote the concentration of metal complex required to scavenge 50% of the DPPH radicals and were obtained from a plot of scavenging activity vs. metal complex.

RESULTS AND DISCUSSION

The interaction between copper (II) ion and N, N'-bis(benzoin)-1,4 butane diimine, yielded the desired crystalline, pale green metal (II) complex compound. This complex is insoluble in water and common organic solvents but readily soluble in acetone, chloroform and DMSO.

The IR spectra (Fig. 1) of the copper (II) complex compound shows bands in the region 1689-1471 cm^{-1} which shows the ν(C = N) stretching vibration, a fundamental feature of

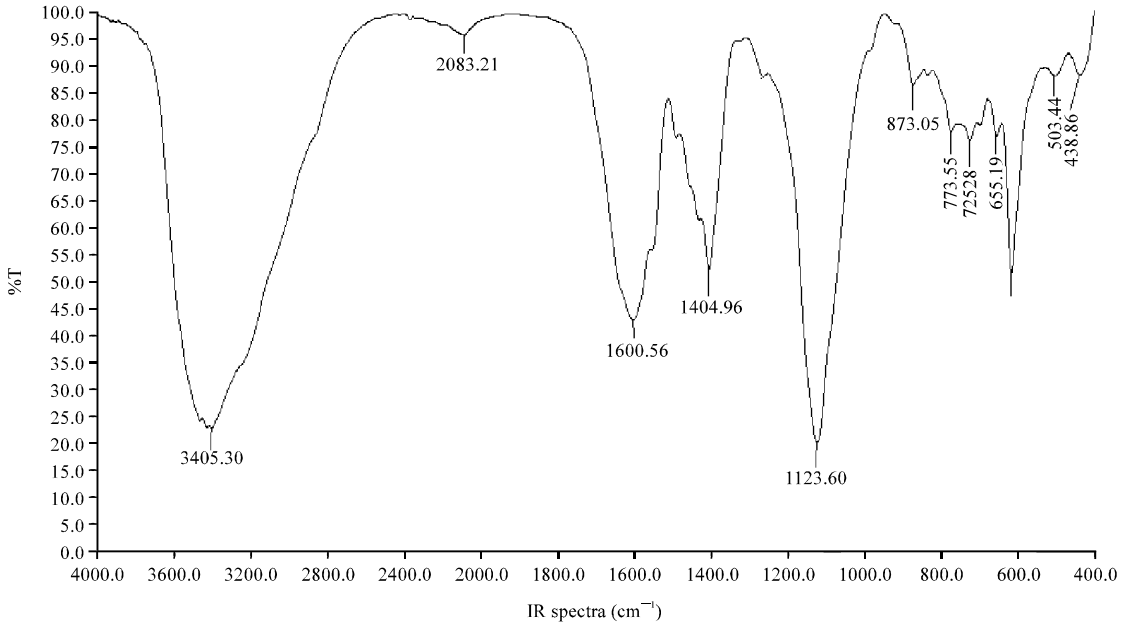

Fig. 1: IR spectrum of the Cu(II) complex

Table 1: Infrared spectral data of the copper (II) complex

Compound	H_2O	v(C-C) (cm^{-1})	v(C = N) (cm^{-1})	v(M-O) (cm^{-1})	v(M-N) (cm^{-1})
(Cu L')	3405	1123	1600	503	438

azomethine group (Silverstein *et al.*, 1991). The coordination of water molecule is indicated by the appearance of broad band in the region of 3405 cm^{-1} (Temel *et al.*, 2001). The coordination of the phenolic oxygen and azomethine further confirmed by the appearance of tow non-ligand bands at 503 and 438 cm^{-1} due to v(M-O) and v(M-N), respectively (Viswanathamurthi *et al.*, 2000; Ferraro, 1971; Zaki *et al.*, 1998). Out-of-plane NH wagging is responsible for a broad band of medium intensity in the 900-600 cm^{-1} region (Silverstein *et al.*, 1991). These bands confirmed the coordination of the Schiff base to the metal (II) ion. The IR data of the metal complex summarized in Table 1. The ^1H NMR spectrum of the metal complex (Fig. 2) exhibits a singlet signal at 7.26 d (s, H) and a multiple at 7.68-7.61 (m, Ar-H). The metal (II) complex compound revealed 1:1 metal to ligand ratio, resulting in a four coordinate complex compound and the proposed molecular structure showed in Fig. 3.

Scanning electron microscope: The SEM micrograph of the Cu(II) complex is shown in Fig. 4. It is seen from the figure that Cu(II) complex exhibit the cauliflower-like structure, the particle size of the complex was in the diameter range of few microns. However, particles with size less than 100 nm were observed.

DPPH-scavenging activity: In the DPPH assay, the ability of the Cu(II) complex to effectively scavenge DPPH radical is displayed in Fig. 5 and Table 2, where it is compared with that of ascorbic acid as standard. Lower absorbance of the reaction mixture indicated higher free-radical scavenging activity (Kumar *et al.*, 2011). The IC_{50} value of the copper complex was found to be more than the standard, ascorbic acid.

Table 2: DPPH radical scavenging capacity copper complex at different concentrations

DPPH	Cu(II) complex	Ascorbic acid
20 (μLmL^{-1})	12.5±0.87	25.60±1.79
40 (μL mL^{-1})	37.5±2.62	61.26±4.28
60 (μL mL^{-1})	62.5±4.37	88.98±6.22
80 (μL mL^{-1})	87.5±6.12	99.34±6.95
IC_{50} value	50.0±3.50	34.91±2.44

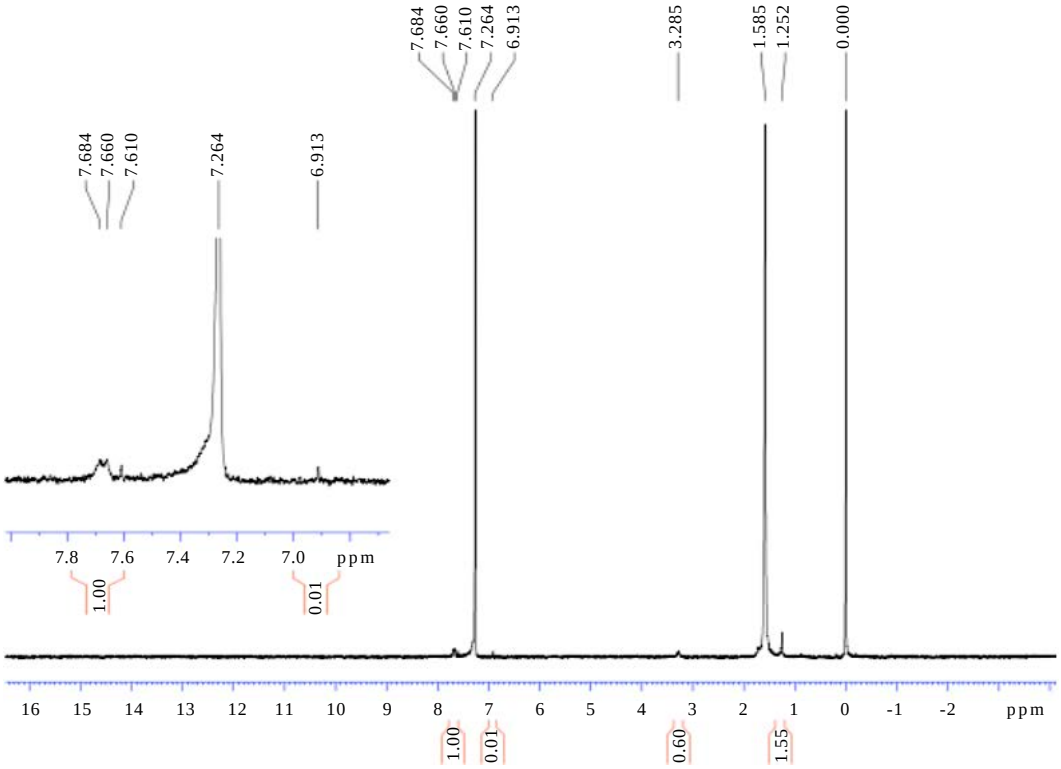

Fig. 2: ^{1}H NMR spectrum of the Cu(II) complex

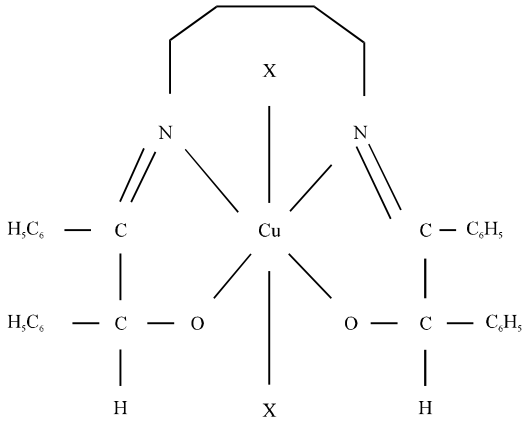

Fig. 3: Molecular structure of bis(benzoin)-1,4 butane diimine copper (II) complex compound (where X= H_2O)

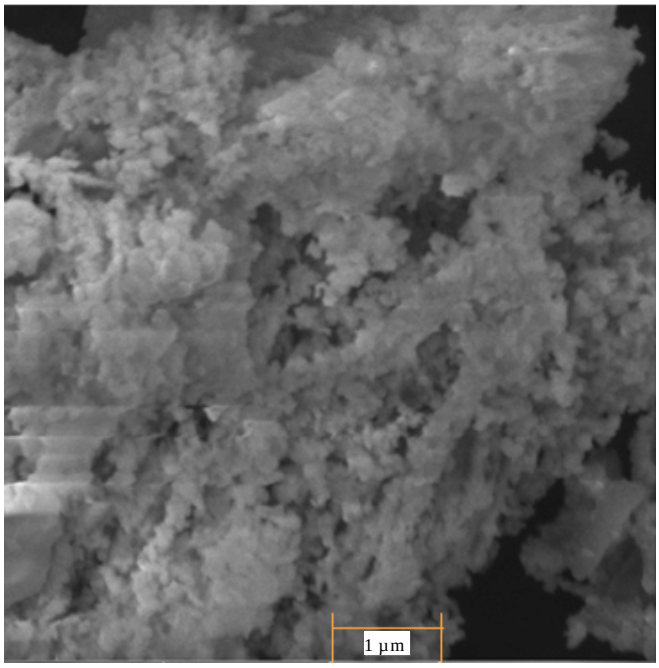

Fig. 4: SEM image of copper (II) complex

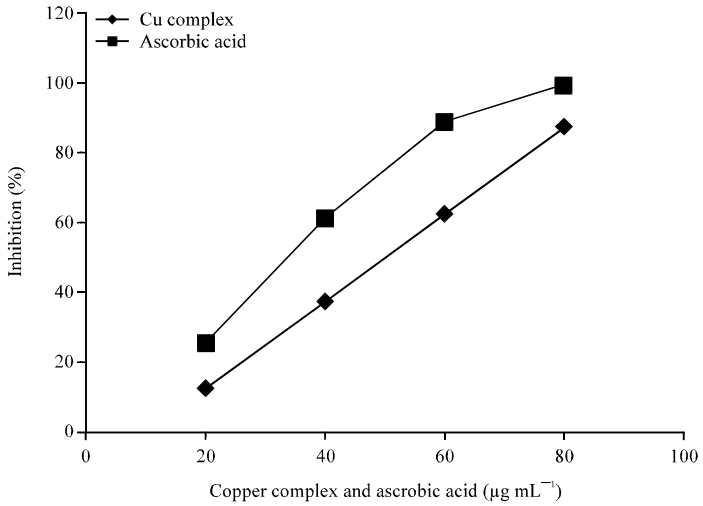

Fig. 5: DPPH radical scavenging capacity copper complex at different concentrations. Each value is the average of triplicates, representing ±SD

CONCLUSION

The Schiff base ligand and its Cu(II) complex were prepared. Cu(II) complex was characterized by IR, NMR spectra and SEM. The proposed structure of metal complex has been illustrated in Fig. 3. The surface morphology using SEM showed that the particles were polycrystalline with nano sized grains. The synthesized metal complex was screened for reduction of DPPH. Based on the results obtained, the metal complex found to be good antioxidant, as comparable with ascorbic acid.

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