

Original Research Article

Cu (II) Complex of 1- Naphthaldehyde Semicarbazone: Synthesis, Characterization, Thermal Analysis and Antibacterial Activity

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ABSTRACT

The ligand, L is the Schiff base formed by condensation of 1- naphthaldehyde with semicarbazide and its Cu(II) complex have been synthesized and characterized by elemental and thermogravimetric analysis and molar conductivity, magnetic and spectroscopic measurements. Elemental analysis of the chelate suggests the stoichiometry is 1:1 (metal-ligand). Infrared spectra of the complex agree with the coordination to the central metal atom through the nitrogen of the azomethine (-HC=N-) group and the carbonyl oxygen atom. Magnetic susceptibility data suggest a tetrahedral geometry for the complex. ESI-MS data also supports the proposed structure of the synthesized compounds. The ligand and its copper complex have been screened for their antibacterial activity against *Enterobacter aerogenes* and *Bacillus cereus*. The metal complex were shown to possess more antibacterial activity than the uncomplexed ligand.

Keywords: Semicarbazone; Complexation; Thermogravimetric analysis; Antibacterial activity.

1. INTRODUCTION

Much work has been done on the biological and industrial applications of Schiff bases and their metal complexes recently, due to their striking physical and chemical properties. Schiff bases are compounds containing an azomethine group (>C=N) and they have the general structure R—N=C—R' where R and R' are aryl, alkyl, cycloalkyl or heterocyclic groups. Schiff bases are the most common representatives of azomethine ligands capable of forming binuclear and polynuclear homo- and hetero-metallic complexes [1-10].

The Schiff's base metal complexes of semicarbazone [11, 12] have been received much consideration of scientists and researchers because of their extensive biological and pharmacological applications [13, 14]. They are the subject of significant interest for the number of chemists due to the formation of transition metal complexes having different chemical, physical and structural properties [15]. The structure of the metal complex depends upon the type and the nature of the ligand and the nature refers to the number of donor atoms, the flexibility

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between them and the ability to combine with metal ions.

The manifold biological activities of Cu(II) complexes has augmented the interest of researchers to design and synthesize these complexes [16]. Numerous Cu(II) complexes with semicarbazones have been prepared and structurally characterized by different physicochemical techniques and it was found that these complexes have increased antioxidant [17], anticancer [18], and antiproliferative [19, 20] activities. Moreover, There are several copper complexes having attractive antibacterial [21-23] and catalytic activities [24, 25].

Here, we report the synthesis, structural characterization, thermogravimetric analysis and antibacterial activities of Cu(II) complex with Schiff base ligand derived from the condensation of 1-naphthaldehyde and semicarbazide.

2. EXPERIMENTAL

2.1 Chemicals

Semicarbazide (99%, Sigma-Aldrich), naphthaldehyde (98%, Sigma-Aldrich) and copper acetate (98%, BDH Reagents & Chemicals) were used as received. Methanol (GRP), Ethanol (95%), Dichloromethane (WINLAB GRG 98%), Diethyl ether and DMSO (BDH lab, England 99%) were used as solvents without further purification. Nutrient agar medium (Include-Peptone, Agar, sugar, marmite) was used to check anti-microbial activity.

2.2 Instruments

To identify the melting points of synthesized compounds, a digital melting point apparatus (METTLER TOLEDO) was used. Microanalyses for CHN were performed using a Vario EL cube [Germany elements (Elemental) analysis system]. FT-IR spectra were obtained on a FT-IR spectrophotometer [JASCO, FT-IR/4100 Japan], using KBr pellets as the standard reference. ESI-MS spectra were recorded with an Agilent Technologies MSD SL Trap mass spectrometer with ESI source coupled with an 1100 Series HPLC system. A Sherwood Scientific MX Gouy magnetic susceptibility apparatus was used to determine the magnetic properties of the metal complexes. The thermogravimetric analysis was carried out using a thermobalance of the type Mettler Toledo STARe System.

2.3 Preparation of the Ligand, Naphthaldehyde Semicarbazone, L

A solution of 1-naphthaldehyde (0.01 mol) in ethanol (40 mL) was added to a solution of semicarbazide (0.01 mol) in hot ethanol (50 mL). The reaction mixture was then boiled under reflux for 3 h. On cooling, the solid product that crystallized was filtered and washed with ethanol. The product was recrystallized from ethanol to obtain white coloured products that were filtered and dried in vacuum over calcium chloride.

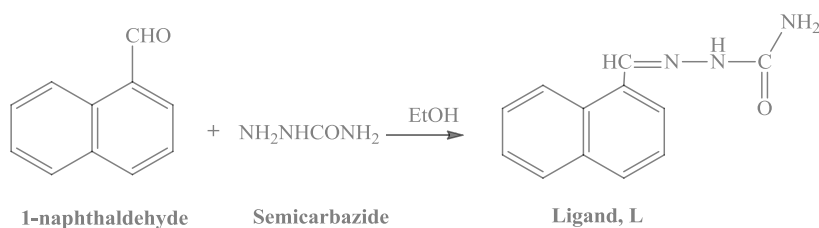
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Scheme 1. Synthesis of Schiff base ligand, L.

2.4 Preparation of the Cu(II) Complex

The complex was prepared by mixing the ethanolic solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ (2 mmol) with the ethanolic solution of the ligand, naphthaldehyde semicarbazone, L (2 mmol) in 1 : 1 molar ratio. The resulting mixture was refluxed for 4 h. A brown coloured product

appeared on standing and cooling the above solution. The complex was filtered, washed with ether and dried under reduced pressure over anhydrous CaCl_2 in a desiccator. It was further dried in an electric oven at 60°C .

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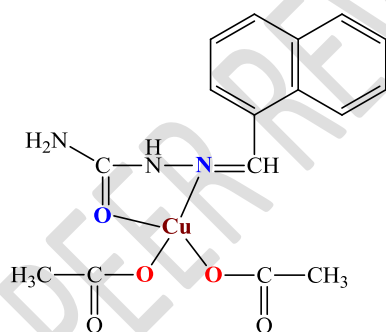


Fig. 1 Proposed structure of the Cu(II) complex.

2.5 Metal Weight Determination

A known amount of copper complex was put into a conical flask whose weight was known. Then, concentrated H_2SO_4 (500 μL) was added. It was fumed until dry and the process was repeated. Concentrated HNO_3 (500 μL) and HClO_4 (500 μL) were then added and the mixture was again fumed until dry. The process of adding acids and fuming was continued until there was no black material. 100 mL distilled water was added to dissolve the residue. Finally, the weight of the copper was estimated complexometrically using EDTA (Ethylenediamine tetraacetic acid).

2.6 Antibacterial experiments

The ligand and the metal complex were screened for their antibacterial activity against *Enterobacter aerogenes* and *Bacillus cereus* by the agar diffusion method [26]. The concentration of the synthesized compound solution in DMSO was 300 $\mu\text{g}/\text{mL}$. A hot nutrient agar solution (20 mL) was poured into sterilized petri dishes and allowed to attain room temperature. The seed layer medium consisted of peptone (1.0 g), yeast extract (0.8 g), glucose (0.2 g), sodium chloride (0.6 g) and agar (0.2 g). It was melted and cooled to about 45°C with gentle shaking. The previously grown subculture was added to the seed layer

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medium and mixed well. It was immediately raked into the petri dishes and allowed to attain room temperature. Then wells were made with a sterile cork borer and to these wells, the compound solution (0.01mL) was added and the plates were allowed to cool for an hour to facilitate diffusion. The plates were then incubated at 37^o C for 48 h. At the end of the incubation period the zones of inhibition around the wells were measured.

3. RESULTS AND DISCUSSION

The Schiff base ligand (L) was obtained as white colored product of condensation of 1-naphthaldehyde and semicarbazide in good yield. It was complexed with copper (II) acetate to obtain the corresponding Schiff base Cu (II) complex as in Fig. 1. Sharp melting /decomposition temperature indicated that the compounds are pure.

3.1 Elemental Analysis

The elemental analysis data suggest that the complex is mononuclear. The elemental analysis data also exposed that metal-to-ligand ratio for the synthesized complex was

1:1. The proposed structure of the ligand and complexes were consistent with these data.

3.2 Molar Conductivity and Magnetic Measurements

Molar conductance value of the synthesized compounds were determined at a concentration of 10⁻³ M in DMSO at room temperature. The conductance value revealed that the complex is non-electrolyte in nature [27]. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_A T)^{1/2}$ where χ_A is the magnetic susceptibility per copper. Room temperature magnetic susceptibility measurements (Gouy method, powdered sample) show that the Cu(II) complex has magnetic moment close to 1.73 BM as expected for discrete magnetically non-coupled copper(II) ion [28]. Magnetic moment of the copper complex lie within the range reported for tetrahedral structure [29-31]. The complex exhibits magnetic moments 1.55 BM, which is less than the spin only value (1.73 BM). Low magnetic value can be expected for complexes having antiferromagnetic effect, with spin-orbital coupling in the ground state for spin doublet species [30].

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Table 1 Microanalysis data of the ligand and Cu(II) complex.

| Compound | Found (Calculated) (%) | | | |
|----------|------------------------|------------------|----------------|------------------|
| | Cu | C | H | N |
| Ligand | - | 67.44 (67.59) | 5.10 (5.20) | 19.70 (19.76) |
| Complex | 15.75 (16.09) | 48.42 (48.67) | 4.24 (4.34) | 10.42 (10.64) |

Table 2 Physical data of the Ligand, L, and its Cu(II) complex.

| Compound | Empirical Formula | Formula Weight (g/mol) | M.P (°C) | Color |
|----------|---|------------------------|----------|-------|
| Ligand | C ₁₂ H ₁₂ N ₃ O | 213.24 | 202 | White |
| Complex | C ₁₆ H ₁₇ CuN ₃ O ₅ | 410.93 | 261 | Brown |

3.3 IR Spectral Studies

IR spectral data of the ligand, L and its copper (II) complex are given in Table 3. The IR spectra of the synthesized compounds are shown in Fig. 2-3. The IR spectrum of ligand, L exhibits a band at 1718 cm⁻¹ which may be assigned due to C=O stretching of semicarbazone moiety [32]. This band is shifted to lower frequency region at 1610 cm⁻¹ in the complex indicating the participation of carbonyl oxygen of semicarbazone in the coordination confirmed by the appearance of a band in the far IR region at 511 cm⁻¹ which may be assigned to Cu-O stretching [33]. On coordination of the Schiff base ligand, the C=N stretching frequency are slightly displaced to

lower frequency indicating a decrease in the C=N bond order due to the coordinate bond of the copper ion with the azomethine nitrogen lone pair [34]. The coordination of the azomethine nitrogen atom to the central copper atom on complexation is further confirmed by the appearance of a new band in the IR spectrum of the complex at 444 cm⁻¹ due to Cu-N stretching. In the copper (II) complex, derived from copper acetate, presence of acetate group is noticed. For the coordinated unidentate acetate ion, the asymmetric stretching for COO⁻ occurs at 1451 cm⁻¹ and the symmetric stretching for COO⁻ is observed 1389 cm⁻¹ [35]

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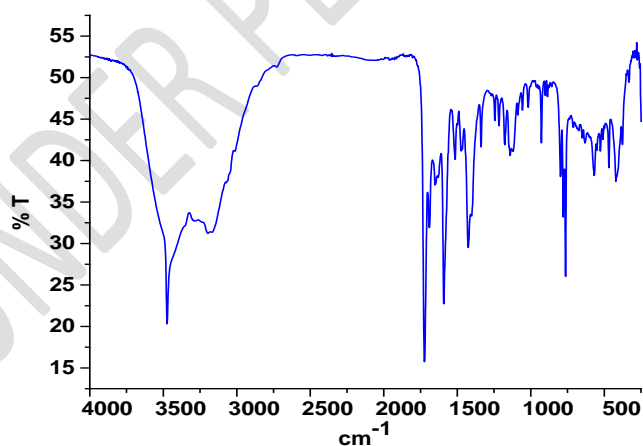


Fig. 2 IR Spectrum of the ligand, L

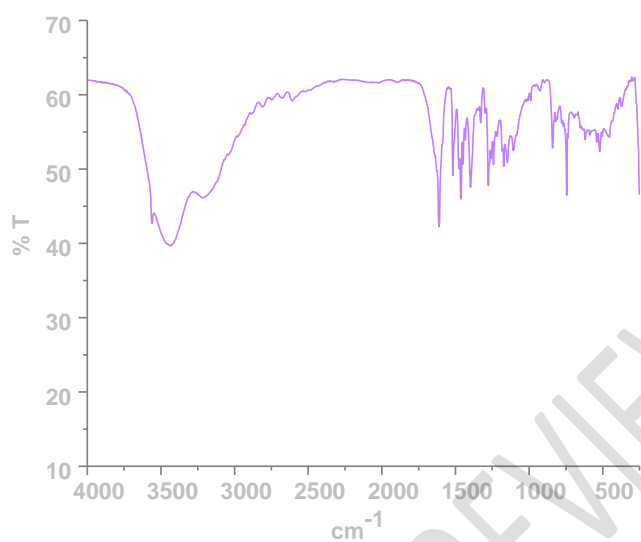


Fig. 3 IR Spectrum of the complex.

Table 3 Key Infrared bands (cm^{-1}) of the ligand, L and its Cu(II) complex.

| Compound | Empirical Formula | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{N}-\text{H})$ | $\nu(\text{Cu}-\text{O})$ | $\nu(\text{Cu}-\text{N})$ | $\nu(\text{COO}^{\ominus})_{\text{asym}}$ & $\nu(\text{COO}^{\ominus})_{\text{sym}}$ | ESI-MS |
|----------|--|--------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---|----------|
| Ligand | $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}$ | 1718 | 1594 | 3474 | - | - | - | 213.1435 |
| Complex | $\text{C}_{16}\text{H}_{17}\text{CuN}_3\text{O}_5$ | 1610 | 1523 | 3474 | 511 | 444 | 1451 & 1389 | 410.934 |

3.4 ESI-MS Spectra

The obtained m/z values in the ESI-MS spectra for the ligand and complex (Fig. 4) are

almost similar to their formula weight (Table 2) which further supports the proposed structure of the synthesized compounds.

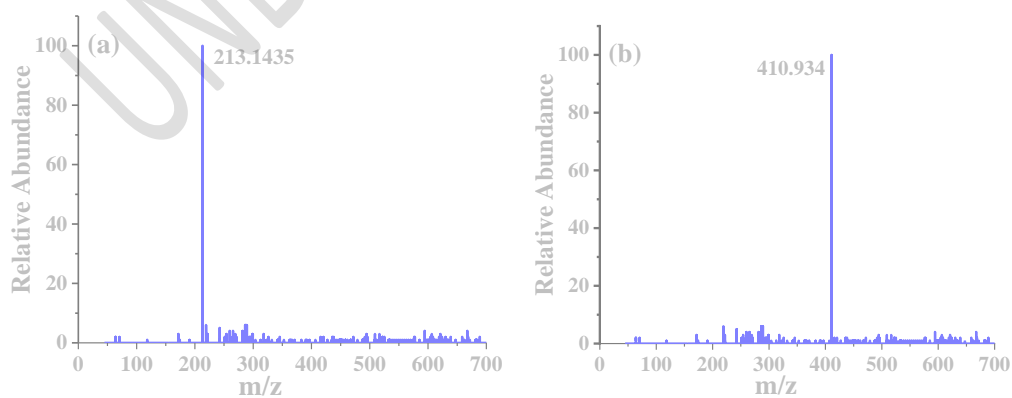


Fig. 4 ESI-MS spectrum of (a) Ligand and (b) Complex.

3.5 Thermogravimetric Analysis

The thermogravimetric analysis of the complex has been studied from ambient temperature up to 800°C under a N_2 atmosphere. The thermogravimetric analysis curve for the complex is represented in Fig. 5. Thermal behaviors of the complex has been summarized in Table 4. The results show the presence of a ligand molecule per metal ion and confirm the formula suggested from the analytical data. The absence of weight loss up to 198 °C indicates that there is no hydrated

water molecule in the crystalline solid in the complex. The complex experience a weight loss between 198-444°C in the first step which can be interpreted as loss of the greatest part of the ligand which attributes to the decomposition of the ligand and the removal of the $C_{11}H_{16}N_2O$. In the second and final step, the complex shows decomposition between 444-559°C corresponds to the loss of C_5HNO_3 . At the end of the decomposition, the residues are acknowledged as CuO [36]. In general, the complex exhibits good thermal stability

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Table 4 Thermogravimetric analysis (TGA) data for the copper (II) complex.

| Compound | Step | Decomposition Range (° C) | TG weight Loss (%) | | Evolved Product | Final Product |
|------------------------|-----------------|---------------------------|--------------------|---------|--------------------|---------------|
| | | | Calc. | (Found) | | |
| $C_{16}H_{17}CuN_3O_5$ | 1 st | 198–444 | 48.75 | (49.04) | $C_{11}H_{16}N_2O$ | CuO |
| | 2 nd | 444-559 | 31.23 | (31.86) | C_5HNO_3 | |

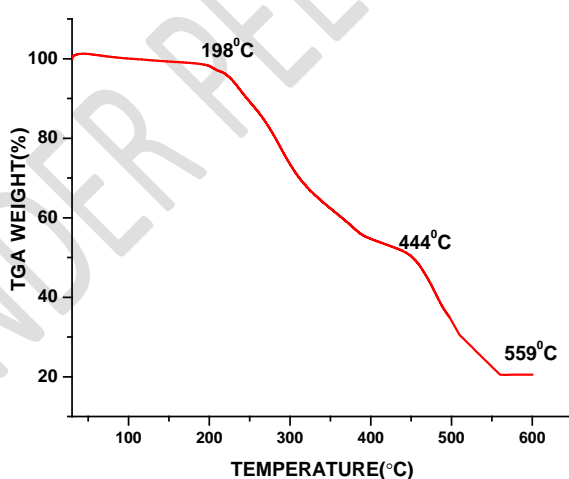


Fig. 5 TGA curve of the complex.

3.6 Antibacterial screening

The ligand, L and the metal complex were screened for their antibacterial activity and the results attained are presented in the Table 5. It is found that the metal complex is more effective bactericides than the ligand. The observed activity of the complex is comparable with those reported for complexes synthesized using Schiff bases, hydrazones, thiosemicarbazones etc. as ligands [37, 38]. This improvement in activity can be explained on the basis of chelation theory [39, 40]. Chelation reduces the polarity of the metal ion considerably, mainly because of the partial sharing of its positive charge with donor groups and possible π -electron delocalization on the whole chelate ring. Chelation can reduce not only the polarity of the metal ion, but it increases the lipophilic character of the chelate, and the interaction between metal ion and the lipid is favored. This may lead to the breakdown of the permeability barrier of the cell, resulting in interference with the normal cellular processes. If the geometry and charge distribution around the molecule are incompatible with the geometry and charge distribution around the pores of the bacterial cell wall, penetration through the wall by the toxic agent cannot take place and this will prevent the toxic reaction within the pores.

Chelation is not the only criterion for antibacterial activity. Some important factors such as the nature of the metal ion, nature of the ligand, coordinating sites, geometry of the complex, concentration, hydrophilicity, lipophilicity and presence of co-ligands have considerable influence on antibacterial activity. Undoubtedly, steric and pharmacokinetic factors also play a decisive role in deciding the potency of an antimicrobial agent. Apart from this, the mode of action of these compounds may also invoke hydrogen bonding though the $>C=N-N=CH-$ group with the active centers of biomolecules and thus interfere with normal cell processes. Presence of lyophilic and polar substituents is expected to enhance antibacterial activity. Moreover, enhancement in antibacterial activity on coordination with metal ion is probably due to the presence of donor systems in the uncoordinated compound or the coordinately unsaturated species formed may inhibit enzyme production since the enzymes which require these groups for their activity, appear to be more susceptible to deactivation upon coordination [41]. Thus antibacterial property of metal complexes cannot be ascribed to chelation alone but it is an intricate blend of all the above contributions

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Table 5 Antibacterial screening results of the ligand, L and its Cu(II) complex.

| Compounds | Antibacterial Zone of Inhibition (mm) | |
|-----------|---------------------------------------|------------------------|
| | Gram Negative | Gram Positive |
| | <i>Enterobacter aerogenes</i> | <i>Bacillus cereus</i> |
| Ligand | 7 | 5 |
| Complex | 10 | 11 |

4. CONCLUSION

In this paper we reported the synthesis, isolation, and characterization of a bidentate Schiff base derived from 1- naphthaldehyde and semicarbazide, and its complex with Cu(II). It is tentatively proposed that the Schiff base ligand coordinates to the copper ion through the nitrogen of the azomethine group and the carbonyl oxygen. Other two coordination sites of the metal occupies by the two unidentate acetate groups. Thermogravimetric analysis shows the metal complex has excellent thermal stability. The synthesized metal complex, in comparison to the uncomplexed Schiff base ligand, were screened for their antibacterial activity against pathogenic bacterial species (*Enterobacter aerogenes* and *Bacillus cereus*). The activity of the Schiff base complex became more pronounced when coordinated with copper ion.

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