

Synthesis, Characterization, Antibacterial and Thermal Studies of Cu(II) Complex of Thiophene-2-aldehyde Semicarbazone

ABSTRACT

Copper (II) complex of the ligand, thiophene-2-aldehyde semicarbazone was synthesized and characterized. Their structures were explored on the basis of CHN analysis, conductance and magnetic susceptibility measurements, spectral studies (FT-infrared and ESI-MS) and thermogravimetric analysis (TGA). It has been observed from spectral and analytical studies, the copper complex have the composition of $[\text{CuL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$ [where L is thiophene-2-aldehyde semicarbazone]. The electrospray mass spectrum of the ligand and complex exhibited ion at mass-to charge ratio (m/z) of 169.13 and 368.86 matching the calculated values for the molecular ion of the ligand and complex, respectively. One mole of the ligand behaves as bidentate chelating agents around the Cu(II) ion. From conductivity studies, we obtained that the copper complex of the ligand, thiophene-2-aldehyde semicarbazone had no ionic properties. All data confirmed a trigonal bipyramidal geometry of the complex. Antibacterial activity of the compounds against the microbe *Enterobacter Aerogenes* and *Bacillus Cereus* have been screened to reflect that the complex has higher antimicrobial activity than the free ligand.

Keywords: Schiff base; Bidentate ligand; Complexation; Thermal analysis; Antibacterial activity.

1. INTRODUCTION

Schiff base metal complexes have enrolled a noteworthy significance in coordination chemistry. Scientist are especially interested in Schiff base complexes for their possible applications in biology, medicine and photonics because of their convenient routs of synthesis. Significant variations in biological activity with structure and type are observed for these complexes [1-3]. In the Last two decades, considerable attention has been paid to the chemistry of Schiff bases metal complexes containing nitrogen, oxygen and

other donors [4-9]. These may be ascribed to their stability, bioactivity [10-12] and prospective applications in many other fields such as oxidation catalysis [13-16], electrochemistry [17] and analytical chemistry etc. [18, 19].

It is commonly known that semicarbazones have substantial biological, anticonvulsant, analgesic, anti-inflammatory and antitumoral activities [20-25]. The dependence of their bioactivity on the type of chelating with

transition metal ions have been of considerable importance [26-29].

We here report this present investigation which deals with copper complex with Schiff base because of comprehensive area of applications of the metal complexes of Schiff bases. We have synthesized and characterized the ligand, thiophene-2-aldehyde semicarbazone and its Cu(II) complex using elemental analysis, conductivity and magnetic susceptibility measurements, spectral studies (FT-IR and ESI-MS), thermogravimetric analysis (TGA) and also studied the antibacterial activity of as synthesized compounds against the microbes *Enterobacter Aerogenes* and *Bacillus Cereus*.

2. EXPERIMENTAL

2.1 Materials

All reagents, starting materials as well as solvents employed to prepare Schiff base in addition to its copper complex were obtained from Aldrich, BDH, Fluka and Merck and were used as received. Nutrient agar medium (Include-Peptone, Agar, Sugar, Marmite) was used to check anti-microbial activity.

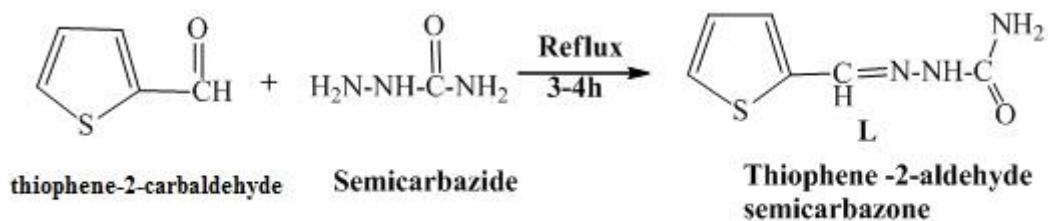
2.2 Instrumentation

The melting points of the ligand, thiophene-2-aldehyde semicarbazone and complex in degree Celsius were checked with a capillary devices and were recorded on a digital melting point apparatus, ThermoCal. Both of the compounds were routinely characterized and checked by FT-IR, ESI-Mass, CHN and molar conductance measurements. Elemental analyses for CHN were performed using a Vario EL cube [Germany elements (Elemental)

analysis system. FT-IR spectra were recorded on a FT-IR spectrophotometer [JASCO, FT-IR/4100] Japan using KBr pellets as the standard reference. ESI-MS spectra were done with an Agilent Technologies MSD SL Trap mass spectrometer with ESI source coupled with an 1100 Series HPLC system. Magnetic susceptibility of the copper complex was measured using a Sherwood Scientific MX Gouy magnetic susceptibility apparatus. Molar conductance of the synthesized compounds were recorded on W.T.W conductivity Master LBR meter. Thermal analysis were done using a Perkin-Elmer Thermogravimetric Analyzer TG/DTA 6300 under a N₂ gas flow (20 mL min⁻¹) at ambient pressure. A heating rate of 20°C min⁻¹ was chosen. In the cases where the TG curve showed the possibility of stable intermediates, a heating rate of 5°C min⁻¹ was applied.

2.3 Synthesis of the Ligand L, Thiophene-2- aldehyde Semicarbazone

thiophene-2-carbaldehyde (0.93458 mL, 2.0 mmol) was mixed with ethanol (15 mL) and the mixture was brought to boil, producing a slurry. Barely sufficient additional amount of ethanol was then added to give a homogeneous solution. Semicarbazide (0.223058g, 2 mmol) was added drop-wise to the homogeneous solution of thiophene-2-carbaldehyde over 5 minutes. The reaction mixture was refluxed for 4 hours, then allowed to cool slowly and to stand overnight. Finally, it produces white solid which was filtered off and dried.



Scheme 1. Synthesis of the ligand, L, thiophene-2- aldehyde semicarbazone

2.4 Synthesis of Cu(II) Complex of the Ligand, L

To the warm ethanolic solution (10 mL) of the ligand L (2 mmol), 10 mL warm ethanolic solution (2 mmol) of Cu(II) acetate was added and the resulting mixture was refluxed for about 4 hours. The obtained precipitates were

filtered, washed with ethanol and dried under vacuum on anhydrous CaCl₂.

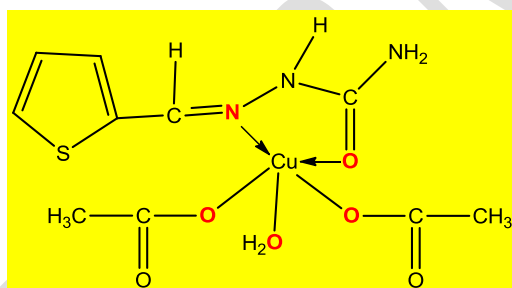


Fig. 1. Proposed structure of the synthesized Cu(II) complex

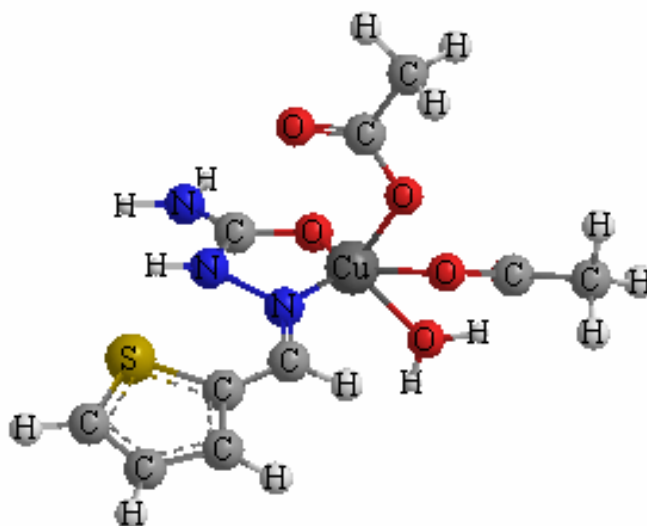


Fig. 2. 3D structure of the Cu(II) complex (Generated by Argus Lab Software)

2.5 Metal Content Estimation in the Complex

A known weight of the metal complex was taken into a conical flask and concentrated H_2SO_4 (500 μL) was added to it. It was fumed down to dryness and the process was repeated. Concentrated HNO_3 (500 μL) and HClO_4 (500 μL) were then added and the mixture was fumed to dryness. The process of adding acids and fuming down to dryness was continued until there was no black materials. 100 mL distilled water was added to dissolve the residue. Finally, the weight of the copper was estimated complexometrically using EDTA (Ethylenediamine Tetra Acetic Acid) [30].

2.6 Antibacterial Activity

The ligand (L) and its Cu(II) complex were screened for in vitro antimicrobial activity in DMSO against gram-negative bacteria, *Enterobacter Aerogenes* and gram-positive bacteria, *Bacillus Cereus* strains by Kirby Bauer's disc diffusion technique [31]. A uniform suspension of test organism of 24 hours old culture was prepared in a test tube containing nutrient broth media. Sterile nutrient agar was then added in each of the Petri

dishes. The dishes were related to ensuring the uniform mixing of the microorganism in the agar medium which was then allowed to solidify. Sterile Whatmann filter paper discs were dipped in the solution of each compound and placed on the labelled plates. The DMSO was used as a control of the solvent. Plates were kept in the incubator for 24 hours at 37°C . The diameter of the zone of inhibition around each disc was measured by scale and results were recorded in terms of millimeter (mm). The observed data of antimicrobial activity of both of the compounds are presented in Table 5.

3. RESULTS AND DISCUSSION

3.1 Synthesis

The ligand, L (thiophene-2- aldehyde semicarbazone) was prepared in good yield from the condensation reaction of thiophene-2- aldehyde and semicarbazide in a 1:1 stoichiometric ratio. Treatment of the Cu(II) acetate salt with the ligand, L formed the complex corresponding to 1:1 metal-ligand ratio. Physical and analytical data of studied compounds are presented in Table 1 and 2

Table 1. Physical data of the ligand, L and its Cu complex.

Compound	Empirical Formula	F.W. (g/mol)	Colour (% yield)	m. p. ($^\circ\text{C}$)
L	$\text{C}_6\text{H}_7\text{N}_3\text{SO}$	169.20	White (79%)	220-224
$[\text{CuL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$	$\text{C}_{10}\text{H}_{15}\text{CuN}_3\text{O}_6\text{S}$	368.85	Dark Brown (74%)	> 300

Table 2. Analytical data of the ligand, L and its Cu-complex

Compound	Found (Calculated) (%)				μ_{eff} (B.M.)	Conductivity (μScm^{-1})	ESI-MS
	Cu	C	H	N			
L	-	41.85 (42.59)	4.19 (4.17)	24.74 (24.83)	-	-	169.13
[CuL(CH₃COO)₂(H₂O)]	17.19 (17.23)	32.46 (32.56)	4.11 (4.10)	11.30 (11.39)	1.80	6	368.86

3.2 Elemental Analysis

The CHN analysis data of the synthesized compounds are given in Table 2. The percentage of metal content in the complex also reveal that metal to ligand ratio for the complex is 1:1. Moreover, these data also support the proposed structure of the ligand (Scheme 1) and complex [Fig. 1].

3.3 Magnetic Measurement

The magnetic moment value (1.80 BM) revealed the paramagnetic nature of the central copper atom in the complex, [CuL(CH₃COO)₂.H₂O] where the ligand, L (thiophene-2-aldehyde semicarbazone) act as bidentates [32].

3.4 Molar Conductivity Measurements

The molar conductance values of 10⁻³ M solution of the ligand, L and copper complex in DMSO are presented in Table 2. The low molar conductance value revealed that the copper complex was non-electrolyte in nature [33].

3.5 FT-IR Spectral Studies

The infrared data provide considerable sign of the formula of ligand and its Cu (II)-complex. The FT-infrared spectra gives the worthy information relating to the behavior of functional groups coordinated to the Cu (II)

ions. However, the existence of a strong and sharp peak at 1687 cm⁻¹ which is related to C=N stretching frequency and another sharp peak at 1718 cm⁻¹ assigned to C=O stretching frequency in the spectra of the ligand [34, 35]. The band at 1718 cm⁻¹ for the $\nu(\text{C}=\text{O})$ stretching vibration of the Schiff base ligand, L is shifted to downward region 1646 cm⁻¹ in the complex suggesting that the carbonyl oxygen of the ligand coordinated to the copper ion [36, 37]. The azomethine band observed at 1687 cm⁻¹ for the ligand was shifted to 1594 cm⁻¹ after complexation, confirming the participation of the azomethine nitrogen atom in the coordination with the copper ion. Furthermore, the stretching of new bands, Cu(II)-O and Cu(II)-N appeared in lower wavelength region ranging 696 and 527 cm⁻¹ respectively which also supports the coordination through nitrogen and oxygen atom from -CH=N- and carbonyl group from the Schiff base, L. In the other side, new bands observed at 1225 and 1097 cm⁻¹ in the infrared spectrum of the complex were attributed to -C-C-O and O-C-C stretching confirming the coordination of acetate group to the metal ion [36-38]. The broad band appeared at 3453 cm⁻¹ together with new band at 609 cm⁻¹ in the spectra of the complex confirmed the presence of coordinated water molecule. The important FT-IR bands for the ligand, L and its copper complex are given in Table 3.

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

Compound	Empirical Formula	ν (C=O)	ν (C=N)	ν (M-O)	ν (M-N)	ν (C-C-O)	ν (O-C-C)
Ligand (L)	$\text{C}_6\text{H}_7\text{N}_3\text{SO}$	1718	1687	-	-	-	-
$[\text{CuL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$	$\text{Cu}(\text{C}_6\text{H}_7\text{N}_3\text{SO})$	1646	1594	696	527	1225	1097

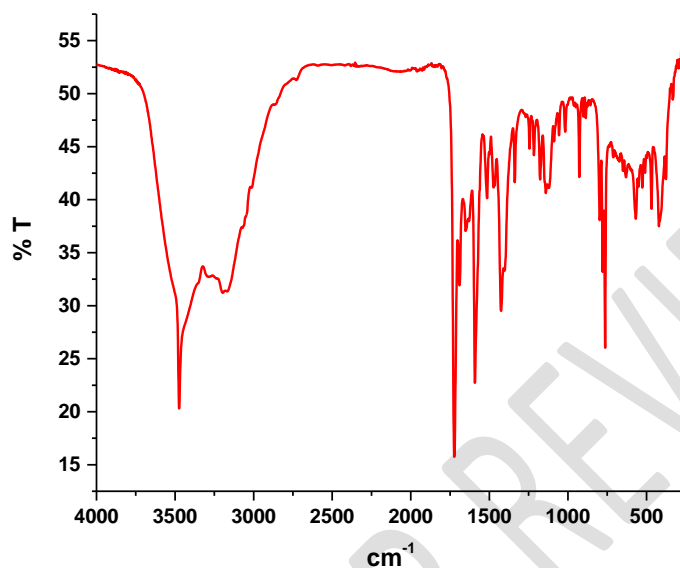


Fig. 3. IR Spectrum of L, thiophene-2-aldehyde semicarbazone

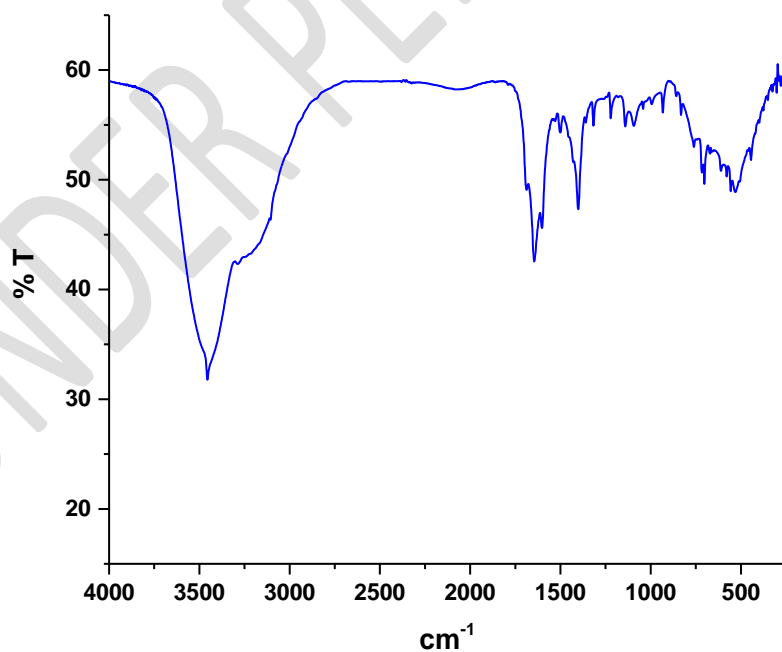


Fig. 4. IR Spectrum of the complex, $[\text{CuL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$

3.6 ESI-Mass Spectra

The ESI-Mass spectra of the ligand and complex are presented in Fig. 5. The obtained m/z values are similar to the formula weight

(Table 2) which further supports the proposed structure of the synthesized compounds.

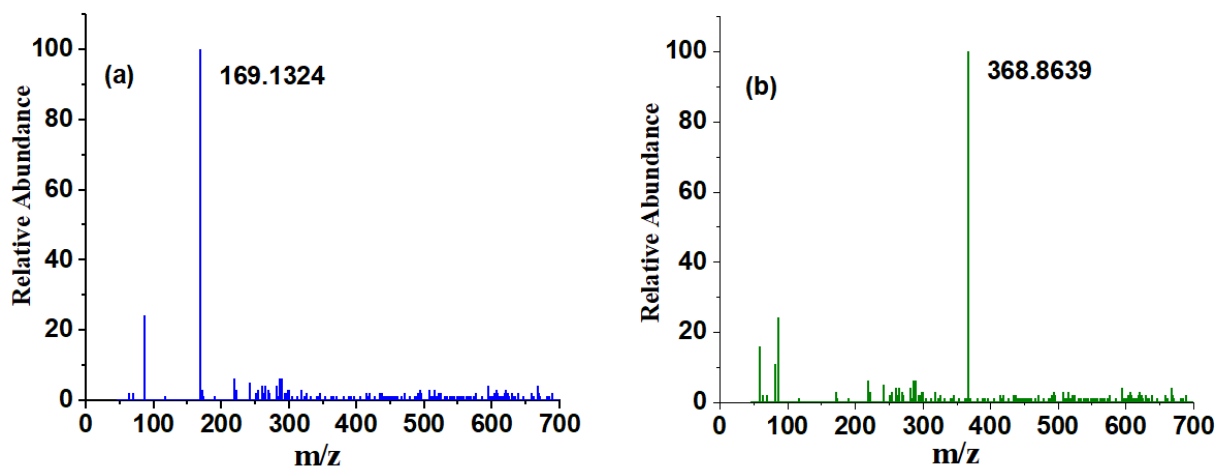


Fig. 5. ESI-Mass spectra of the (a) ligand, L and (b) $[\text{CuL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$

3.7 Thermogravimetric Analysis (TGA)

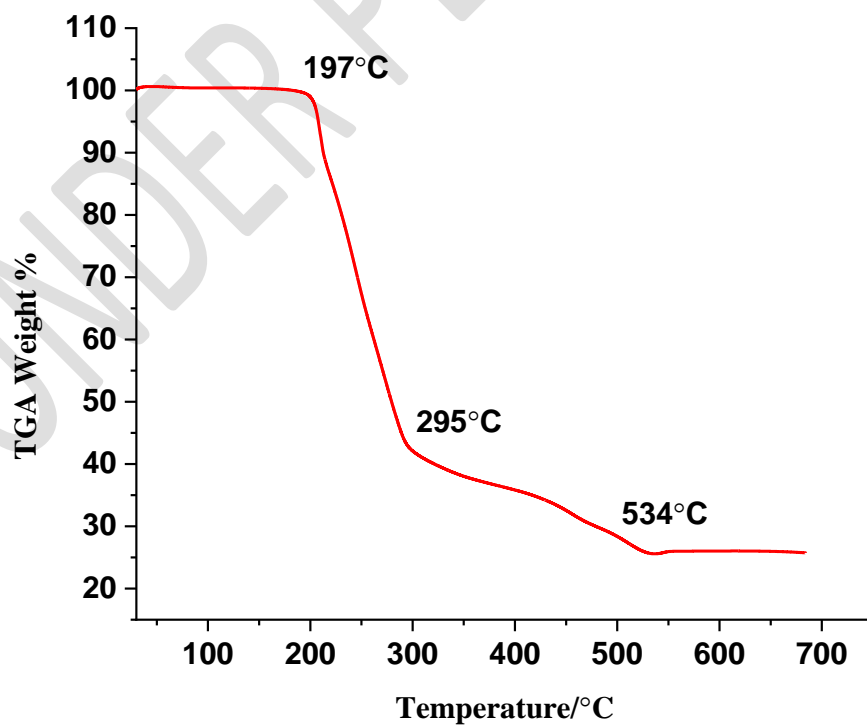


Fig. 6. Thermogravimetric (TG) curve for the complex, $[\text{CuL}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$

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

Compound	Step	Decomposition Range (° C)	TG Weight Loss (%) Calc. (Found)	Evolved Product	Residue
[CuL(CH ₃ COO) ₂ (H ₂ O)] (C ₁₀ H ₁₅ CuN ₃ O ₆ S)	1 st	197-295	57.29 (57.13)	C ₁₀ H ₁₅ NO ₄	CuO & Gaseous product
	2 nd	295 - 534	16.79 (16.71)	N ₂ O ₂	

The thermogravimetric analyses of the complex have been studied from ambient temperature up to 700°C under a N₂ atmosphere. The thermal properties of Cu(II)-complex was investigated by thermogram. The TGA curve for the complex displays two stages of mass loss within the temperature range of 197–534 °C. The first stage is at 197–295 °C, and exhibits a mass loss of 57.13%, corresponding to the loss of C₁₀H₁₅NO₄ (calc. 57.29%). The second stage occurs at 295–534 °C, with a mass loss of 16.71%, corresponding to the loss of N₂O₂ (calc. 16.79%). The decompositions of the copper complex ended with formation of CuO and gaseous products [39]. The thermogravimetric analysis data for the copper (II) complex are presented in Table 4.

3.8 Antimicrobial Screening Results

The Schiff-base ligand, L and its copper complex reported here were evaluated for antibacterial activity against *Enterobacter Aerogenes* and *Bacillus cereus*. The values of inhibition zone were measured in millimeter (mm). The data of antibacterial activities of the ligand and its complex are given in Table 5. The inhibitory zone data reveals that the ligand, as well as its copper complex shows good antibacterial activity. The biological activity of Schiff base ligand arises from the presence of imine group which imports in elucidating the mechanism of transformation reaction in biological systems. However, its copper complex showed remarkable antibacterial activity as a result of chelation of metal with organic ligand synergistically increasing its effect. The DMSO control did not show any antimicrobial activity against the tested bacterial strains whereas considering with respect to the standard, both the tested compounds were found to be moderately active.

Table 5. Antibacterial screening results of ligand L and its complex

Diameter of inhibition zone of bacteria (mm)		
Compound	Gram Negative	Gram Positive
	<i>Enterobacter Aerogenes</i>	<i>Bacillus Cereus</i>
L	7	6
[CuL(CH ₃ COO) ₂ (H ₂ O)]	11	13

Control (DMSO): No activity (There was no inhibition zone)

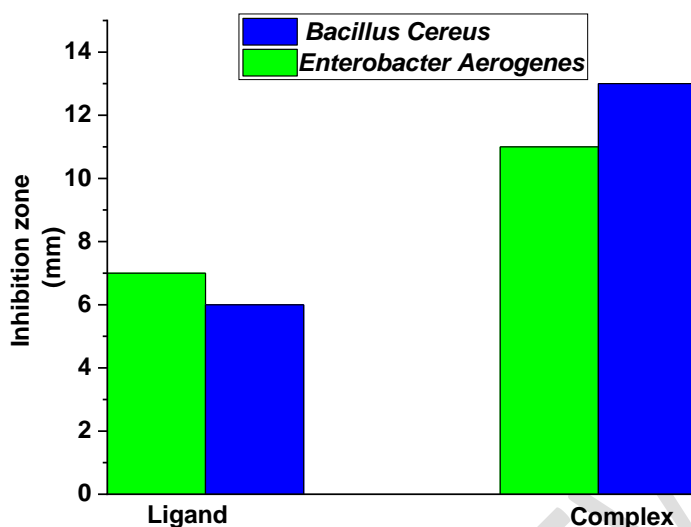


Fig.7 Statistical representation for antibacterial activity for the ligand, L and its Cu (II) comple

4. CONCLUSION

In this paper we have reported the preparation, isolation and characterization of a bidentate Schiff base derived from thiophene-2-aldehyde and semicarbazide and its copper complex. It is tentatively proposed that the Schiff base ligand coordinates through the nitrogen of the azomethine group and the oxygen of the carbonyl group. Another three coordination sites of the Cu(II) have been occupied with two acetate group and water molecule forming a stable trigonal bipyramidal structure. The synthesized copper 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 the metal ion.

REFERENCES

1. Islam, M.A., M.R. Karim, and M.K.-E. Zahan, Studies on Synthesis, characterization and Biological Activity of Mn(II), Cu(II), Fe(II) and Al(III) Metal Complexes of Schiff Base Ligand Derived from Semicarbazide and Anisaldehyde. M. Sc. (Thesis), Dept. of Chemistry, Rajshahi University, Bangladesh, 2017.
2. Koh, L., et al., Complexes of salicylaldehyde acylhydrazones: cytotoxicity, QSAR and crystal structure of the sterically hindered t-butyl dimer. *Journal of Inorganic Biochemistry*, 1998. **72**(3-4): p. 155-162.
3. Ainscough, E.W., et al., Cytotoxicity of salicylaldehyde benzoylhydrazone analogs and their transition metal complexes: quantitative structure–activity relationships. *Journal of Inorganic Biochemistry*, 1999. **77**(3-4): p. 125-133.
4. Djebbar-Sid, S., O. Benali-Baitich, and J. Deloume, Synthesis, characterization and electrochemical behaviour of some copper (II) complexes with linear and tripodal tetradentate ligands derived from Schiff bases. *Polyhedron*, 1997. **16**(13): p. 2175-2182.

5. Ross, A. and A.Z. Slawin, First synthesis of a unique dilead Schiff base complex. *Journal of the Chemical Society, Dalton Transactions*, 1998(19): p. 3149-3150.
6. He, L., et al., The formation of a Schiff base intermediate: a nickel (II) complex of an asymmetric tripodal ligand. *Journal of Chemical Crystallography*, 1999. **29**(2): p. 207-210.
7. Wu, J.C., et al., Intramolecular hydrogen bond self-template synthesis of some new Robson-type macrocyclic ligands. *Chinese Chemical Letters*, 2001.
8. Asraf, M.A., et al., Structural Elucidation, 3D Molecular Modeling and Antibacterial Activity of Ni (II), Co (II), Cu (II) and Mn (II) Complexes Containing Salophen Ligand. *Asian Journal of Applied Chemistry Research*, 2019: p. 1-15.
9. Sarker, D., et al., Copper (II) Complex of Salicylaldehyde Semicarbazone: Synthesis, Characterization and Antibacterial Activity. *Asian Journal of Chemical Sciences*, 2019: p. 1-8.
10. Al-Allaf, T.A. and A.Z. Sheet, Platinum group metal Schiff base complexes—I. Platinum complexes. *Polyhedron*, 1995. **14**(2): p. 239-248.
11. Highfield, J.A., et al., Synthesis, hydroxyl radical production and cytotoxicity of analogues of bleomycin. *Bioorganic & Medicinal Chemistry*, 2000. **8**(5): p. 1065-1073.
12. Das, A., et al., Inhibition of herpes simplex virus type 1 and adenovirus type 5 by heterocyclic Schiff bases of aminohydroxyguanidine tosylate. *Antiviral Research*, 1999. **44**(3): p. 201-208.
13. Djebbar-Sid, S., O. Benali-Baitich, and J.P. Deloume, Synthesis, characterization, electrochemical behaviour and catalytic activity of manganese (II) complexes with linear and tripodal tetradentate ligands derived from Schiff bases. *Transition Metal Chemistry*, 1998. **23**(4): p. 443-447.
14. Asraf, M.A., et al., Earth-abundant metal complexes as catalysts for water oxidation; is it homogeneous or heterogeneous? *Catalysis Science & Technology*, 2015. **5**(11): p. 4901-4925.
15. Asraf, M.A., et al., Homogeneous photochemical water oxidation with metal salophen complexes in neutral media. *Photochemical & Photobiological Sciences*, 2019.
16. Asraf, M.A., et al., Homogeneous photochemical water oxidation with metal salophen complexes in neutral media. *Photochemical & Photobiological Sciences*, 2019. **18**(11): p. 2782-2791.
17. Hamada, Y., The development of chelate metal complexes as an organic electroluminescent material. *IEEE Transactions on Electron Devices*, 1997. **44**(8): p. 1208-1217.
18. Patel, P., B. Thaker, and S. Zele, Preparation and characterisation of some lanthanide complexes involving a heterocyclic β -diketone. *Indian Journal of Chemistry*, 1999(38A): p. 563-567.
19. Mohammed, A.A., Synthesis and Spectroscopic Studies of Some Furfuraldehyde Schiff Bases Complexes. *Iraqi National Journal of Chemistry*, 2005(17): p. 103-111.
20. Rollas, S. and S.G. Küçükgüzel, Biological activities of hydrazone derivatives. *Molecules*, 2007. **12**(8): p. 1910-1939.
21. Aurbach, D., et al., Design of electrolyte solutions for Li and Li-ion batteries: a review. *Electrochimica Acta*, 2004. **50**(2-3): p. 247-254.
22. Bottari, B., et al., Isoniazid-related copper (II) and nickel (II) complexes with antimycobacterial in vitro activity. Part 9. *Bioorganic & Medicinal Chemistry letters*, 2000. **10**(7): p. 657-660.
23. Sridhar, S.K., M. Saravanan, and A. Ramesh, Synthesis and antibacterial screening of hydrazones, Schiff and Mannich bases of isatin derivatives. *European Journal of Medicinal Chemistry*, 2001. **36**(7-8): p. 615-625.
24. Kaymakçioğlu, B.K. and S. Rollas, Synthesis, characterization and evaluation of antituberculosis activity of some hydrazones. *Il Farmaco*, 2002. **57**(7): p. 595-599.
25. Agarwal, R.K., L. Singh, and D.K. Sharma, Synthesis, spectral, and biological properties of copper (II) complexes of thiosemicarbazones of Schiff bases derived from 4-aminoantipyrine and aromatic aldehydes. *Bioinorganic Chemistry and Applications*, 2006. **2006**.
26. Singh, N., et al., Antitumor activity studies of newly synthesized N-

- salicyloyl-N'-(p-hydroxybenzthioyl) hydrazine and its copper (II) complex both in vivo and in vitro. *Bioorganic & Medicinal Chemistry*, 1997. **5**(2): p. 245-251.
27. Agarwala, B., S. Hingorani, and G.N. Gowda, Synthetic and physicochemical studies of uranium complexes with semicarbazone and hydrazone. *Inorganica Chimica Acta*, 1990. **176**(1): p. 149-154.
28. Singh, N.K., et al., Synthesis, characterization and antitumour studies on N-salicyl-N'-thiobenzohydrazide and its copper (II) complex. *Transition Metal Chemistry*, 1996. **21**(6): p. 556-559.
29. Maurya, R., R. Verma, and T. Singh, Synthesis, magnetic, and spectral studies of some mono-and binuclear dioxomolybdenum (vi) complexes with chelating hydrazones derived from acid hydrazides and furfural or thiophene-2-aldehyde. *Synthesis and Reactivity in Inorganic and Metal-organic Chemistry*, 2003. **33**(2): p. 309-325.
30. Raoot, K., S. Raoot, and V. Vaidya, A Selective Complexometric Determination of Palladium. *Indian Journal of Chemistry*, 1979(18A): p. 90.
31. Drew, W.L., et al., Reliability of the Kirby-Bauer disc diffusion method for detecting methicillin-resistant strains of *Staphylococcus aureus*. *Appl. Environ. Microbiol.*, 1972. **24**(2): p. 240-247.
32. Raman, N., et al., Synthesis, structural characterisation and electrochemical and antibacterial studies of Schiff base copper complexes. *Transition Metal Chemistry*, 2004. **29**(2): p. 129-135.
33. Osman, A.H., Synthesis and characterization of cobalt (II) and nickel (II) complexes of some Schiff bases derived from 3-hydrazino-6-methyl [1, 2, 4] triazin-5 (4H) one. *Transition Metal Chemistry*, 2006. **31**(1): p. 35-41.
34. Ahmed, A., S. BenGuzzi, and A. El-Hadi, Synthesis and characterization of Divalent Transition Metals Complexes of Schiff bases derived from O-Phenylenediamine and Benzoylacetone and Related species. *Journal of Science and its Applications*, 2007. **1**(1): p. 79-90.
35. Payne, K. and A. Veis, Fourier transform IR spectroscopy of collagen and gelatin solutions: deconvolution of the amide I band for conformational studies. *Biopolymers: Original Research on Biomolecules*, 1988. **27**(11): p. 1749-1760.
36. Jellouli, N.K., et al., Founder effect confirmation of c. 241A> G mutation in the L2HGDH gene and characterization of oxidative stress parameters in six Tunisian families with L-2-hydroxyglutaric aciduria. *Journal of Human Genetics*, 2014. **59**(4): p. 216.
37. Vogt, R.L. and L. Dippold, *Escherichia coli* O157: H7 outbreak associated with consumption of ground beef, June–July 2002. *Public Health Reports*, 2005. **120**(2): p. 174-178.
38. Ejidike, I. and P. Ajibade, Synthesis, characterization and biological studies of metal (II) complexes of (3E)-3-[(2-((E)-[1-(2, 4-dihydroxyphenyl) ethylidene] amino) ethyl) imino]-1-phenylbutan-1-one Schiff base. *Molecules*, 2015. **20**(6): p. 9788-9802.
39. Aziz, A.A.A., et al., Synthesis, structural characterization, thermal studies, catalytic efficiency and antimicrobial activity of some M (II) complexes with ONO tridentate Schiff base N-salicylidene-o-aminophenol (saphH2). *Journal of Molecular Structure*, 2012. **1010**: p. 130-138.