

Synthesis and Characterization of Zinc (II) Complex of Schiff Base Derived from p-Chlorobenzaldehyde

M. Kalaimathi^{1*}, Y. Yesu Thangam², R. Ebenezer³, R. Anitha²

¹Department of Chemistry, Karpagam Academy of Higher Education (Deemed to be a University), Coimbatore, Tamil Nadu, India, ²Department of Chemistry, Jayaraj Annapackiam College for Women Affiliated to Mother Teresa Women's University, Kodaikanal, Tamil Nadu, India, ³Department of Chemistry, The American College Affiliated to Madurai Kamaraj University, Madurai, Tamil Nadu, India

ABSTRACT

Schiff base complex of Zinc (II) ion has been derived from benzoyl acetone, p-chlorobenzaldehyde, and o-anisidine. The ligand, as well as metal complex, was characterized by elemental analysis, UV-visible, magnetic moments, IR, ¹H NMR, ¹³C NMR. Non-electrolytic nature of zinc (II) complex was proved by the molar conductance data. The antimicrobial activities of the ligand (L1) and its zinc (II) complex against the bacterial strains such as *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus* and the fungus *Candida albicans*, *Aspergillus niger*, *Aspergillus flavus* have been carried out. The effect of the substituent on the biological activity of Schiff base and its complex was investigated. Antibacterial and antifungal activity of the metal complex is greater than the free ligand (L1) due to chelation and the presence of the electron releasing methoxy group as a substituent in the aromatic portion of the complex.

Key words: Schiff base ligand, Zinc (II) complex, Biological activity, Chelation, Antimicrobial activity.

1. INTRODUCTION

Zinc is the only metal ion that has the ability to reduce gastric mucosal necrosis without disturbing gastric acid secretion [1]. It is considered as an antitumor agent. Zinc is the most important transition element present in the biosphere [2]. Several enzymes also having zinc (II) ion such as carbonic anhydrases, zinc proteinases, histone deacetylases, alkaline and acid phosphatases, alcohol dehydrogenases, and aminopeptidases [3,4]. It is suggested to synthesis Schiff base metal complexes from carbonyl compounds (it may be aldehyde or ketone) and amines because of inconvenience faced on conventional methods. Due to the bulkiness of the ligand, it induces particular configuration on the metal complexes. Steric effect may support this configuration [5]. Kalaimathi *et al.* synthesized and characterized Schiff base zinc (II) complex and reported that metal complex exhibited greater activity compared to Schiff base ligand [6]. The studies on Schiff base ligand gave interesting results. The ligand acts as NN chromophore and possesses octahedral geometry. Comparative results of β -diketone-based metal complexes with Schiff base ligand also given in article written by Kalaimathi *et al.* [7].

In 2020 Mekhribon *et al.*, synthesized new metal complexes based on Ammonium vanadate and 5-phenyl-1,3,4-oxadiazole-2(3H)-thione and characterized using EDX, IR-spectroscopy and X-ray phase, elemental analysis, and thermal analysis. Metal monodentally binds to two molecules of the heterocyclic ligand, coordinated through sulfur atoms of the heterocycles [8].

In 2020 Sharmila synthesized and characterized metal (II) complexes with pyrazoline derivatives. Biological and fluorescent studies were also carried out for the synthesized metal complexes. Pyrazoline derivatives were synthesized by the condensation of 1-acetyl-2-hydroxynaphthalene and indole-3-carboxaldehyde followed by condensation of substituted phenylhydrazine. The binding behavior of

the complexes with CT-DNA has been investigated and the binding constants revealed that all the complexes are interacted with DNA through intercalation mode [9].

Schiff base metal complexes with nitrogen and oxygen co-coordinating chromophores are extensively studied because of the relative easiness of preparation. β -diketone ligands are enolisable whereas Knoevenagel β -diketone condensate are not enolisable Schiff base ligands derived from β -diketone condensate (benzoyl acetone and p-chlorobenzaldehyde) and aromatic amines are able to form stable and structurally well-characterized metal complexes. The transition metal ions are preferred than the non-transition metal ions because of the larger chelate effect. The characterizations of these complexes lead to design and synthesis of more stable condensate and thereby new Schiff base ligands. Steric and inductive effects introduced by the substituent in the aromatic portion of the Schiff base influence the properties of new ligands and the nature of the complexes is affected. Minute electronic variations in the aromatic portion of the Schiff base ligand may enhance or suppress the antimicrobial activity of the metal complexes.

2. EXPERIMENTAL

The synthesis and characterization of ligand L1 and its zinc (II) complex were carried out according to the procedures for analytical

***Corresponding author:**

E-mail: m.kalaimathi15@gmail.com

ISSN NO: 2320-0898 (p); 2320-0928 (e)

DOI: 10.22607/IJACS.2021.903009

Received: 24th June 2021;

Revised: 14th July 2021;

Accepted: 23rd July 2021

and spectral viz. IR, UV-vis., ^1H NMR, and ^{13}C NMR techniques, antimicrobial studies.

2.1. Synthesis of Knoevenagel Condensate 2-(4-Chlorobenzylidene)-1-Phenylbutane-1,3-Dione

To a 30 mmol (4.20g) of p-chlorobenzaldehyde dissolved in 40 ml ethanol, 30 mmol (4.86g) benzoyl acetone in 40 ml of ethanol was added and the mixture was kept stirring for about 6 hours with the addition of piperidine in drops. A bright yellow-colored precipitate was obtained. It was filtered, washed with petroleum ether and recrystallized from ethanol and kept in a vacuum desiccator.

2.2. Synthesis of N-(3-((2-Methoxyphenylimino) (Phenyl) Methyl)-4-(4-chlorophenyl) But-3-en-2-ylidene)-2-methoxybenzenamine (L1)

To 4 mmol (0.49g), 20 ml ethanolic solution of o-anisidine, 2 mmol (0.56g) of Knoevenagel condensate 2-(4-chlorobenzylidene)-1-phenylbutane-1,3-dione dissolved in 20 ml of ethanol was added with the constant stirring. The mixture was kept stirring for about 5 h at room temperature. The addition of the catalytic amount of piperidine was also added in drops. The crude product thus formed was separated by filtration and washed several times with petroleum ether. Yellow-colored product obtained was dried over anhydrous CaCl_2 in vacuum desiccator. Finally, the crude sample was recrystallized from hot ethanol.

Figure 1 gives the synthetic step involved in the synthesis of ligand (L1).

2.3. Synthesis of Zinc (II) Complex of L1

4 mmol (1.98g) of ligand (L1) was dissolved separately in 20 ml of ethanol. It was added to a solution containing 2 mmol of ZnCl_2 (0.27g) in ethanol (20 ml) with the addition of few drops of piperidine as catalyst. The mixture was refluxed at $70\text{--}80^\circ\text{C}$ with the constant stirring for about 5 h. The precipitated solid metal complex of L1 was cooled to room temperature. It was filtered off followed by washing with petroleum ether and dried over calcium chloride in vacuum desiccators. The dried complex was recrystallized from hot ethanol. Synthesis of metal (II) complex of L1 is given in Figure 2.

3. RESULTS AND DISCUSSION

The Schiff base ligand L1 and its Zn (II) complex have been synthesized and characterized by elemental, analytical, and spectral data. They are found to be stable in air. The ligand is soluble in common organic solvents, and the complex is freely soluble in CHCl_3 , DMF, and DMSO.

The ligand L1 is yellow in color, amorphous in nature, and melts at 145°C . Zn (II) complex is yellow in color and its melting point is 246°C .

The conductivity measurements were done using 1×10^{-3} M DMSO Digisun Electronics Digital conductivity meter-model: D1-909; cell constant - 1.007 as the complex is fairly soluble in DMSO. The measured molar conductance value is $5 \text{ S cm}^2 \text{ mol}^{-1}$ for DMSO solution of zinc (II) complex. Molar conductance value suggests that complex is non-electrolytic in nature. Hence, the chloride ion present in the metal complex must be inside the coordinating sphere [10]. The analytical data of the complex is in good agreement with the general formula (ZnL_2X_2). The UV-visible spectra of the ligand L1 and its metal complex recorded in DMSO solution. The bands appearing at low energy side are assignable to $n\text{-}\pi^*$ transitions which are associated with the azomethine chromophore. The bands at higher energy may be assigned to $\pi\text{-}\pi^*$ transitions within the phenyl rings [11].

The absence of bands at $3218\text{--}3237 \text{ cm}^{-1}$ and above 1641 cm^{-1} characteristic of $\nu(\text{-NH}_2)$, $\nu(\text{-C=O})$ suggests the formation of the azomethine group.

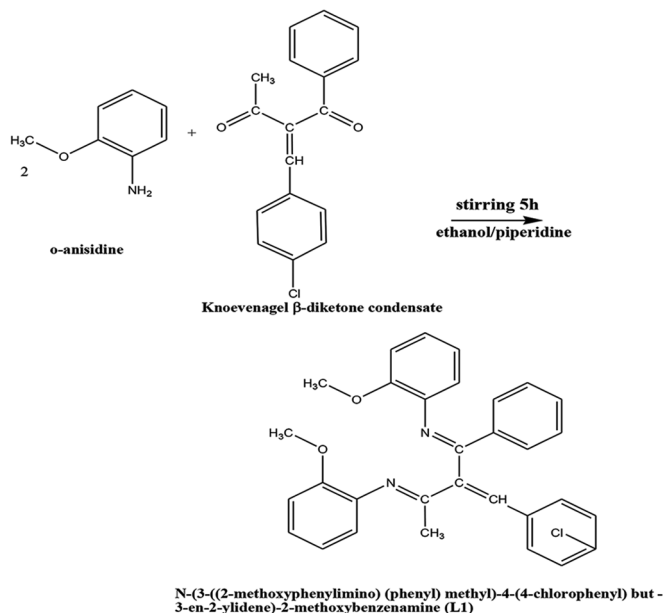


Figure 1: Synthesis of L1.

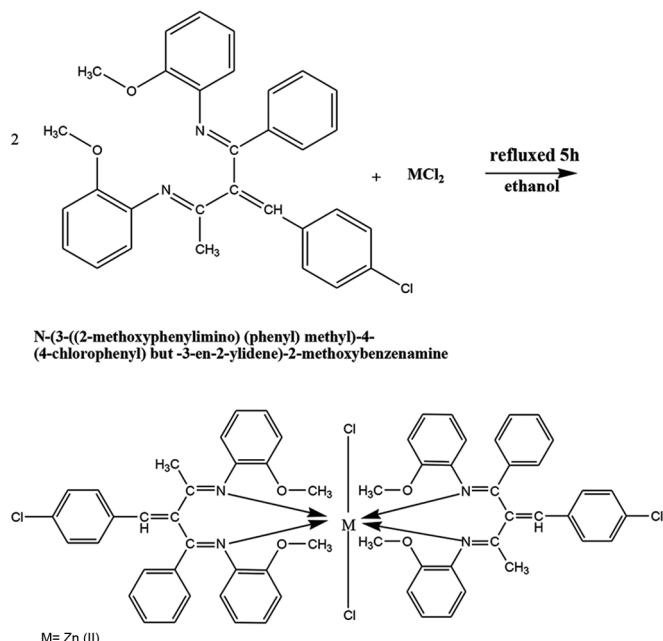


Figure 2: Synthesis of zinc (II) complex of L1.

The spectrum of the free ligand L1 shows a peak in the region 1610 cm^{-1} , a characteristic feature of the $\nu(\text{C=N})$ (azomethine) stretching mode indicating the formation of the Schiff base. Its shift toward lower frequencies in the spectrum of its metal complex (1600 cm^{-1}) indicates the involvement of the azomethine nitrogen in coordination with the metal ion. The observation of a new peak around 511 cm^{-1} , characteristic of the $\nu(\text{M-N})$ stretching vibration, which is not observed in the spectrum of free ligand (L1) is due to the coordination of azomethine nitrogen to metal. The characteristic peak appearing at 2802 cm^{-1} in the spectrum of the ligand (L1) is assignable to the methoxy group. No remarkable shift in the stretching frequencies of -OCH_3 showed that the oxygen atoms of -OCH_3 have no involvement in coordination with the metal ion. The absence of peaks around $450\text{--}500 \text{ cm}^{-1}$ corresponding to $\nu(\text{M-O})$ support the above non-coordination of oxygen atoms with the metal ion. Further,

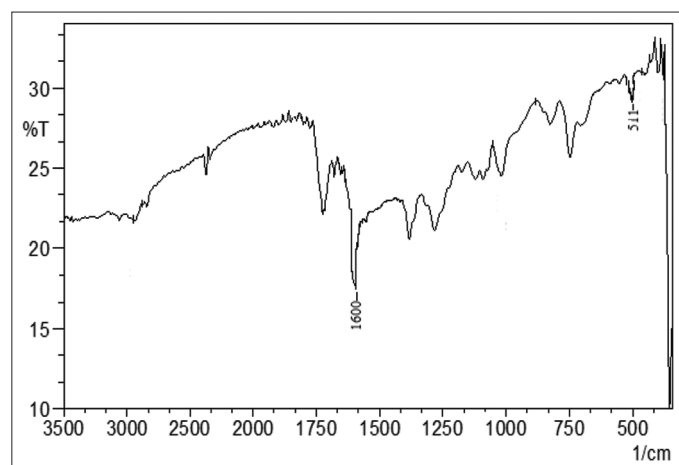


Figure 3: IR spectrum of Zinc (II) complex.

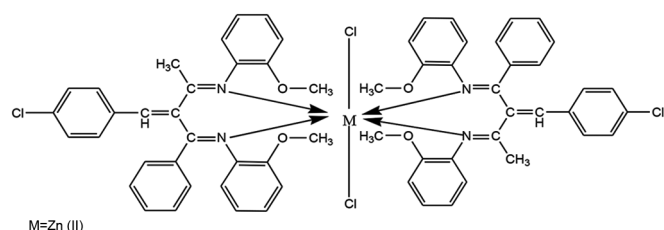


Figure 4: Zn (II) complex of L1.

IR spectrum of zinc complex of the L1 shows another peak at 350 cm^{-1} , which may be due to $\nu(\text{M-Cl})$ [12] vibration. Figure 3 represents the IR spectrum of Zinc (II) complex.

The ^1H NMR spectrum of the Schiff base was recorded at room temperature in CDCl_3 . The ligand (L1) shows a peak at 3.90 ppm (δ) as singlet (s) due to $-\text{OCH}_3$ (6H) protons. The peak at 0.90 ppm (δ) is attributable to $-\text{CH}_3$ as singlet(s) for methyl protons (3H) and $-\text{C}=\text{CH}-$ proton was obtained at 6.50 ppm (δ) as singlet (s). Signals at 7.20 and 7.22 ppm (δ) as a doublet (d) for chlorine substituted aromatic ring protons. The aromatic ring protons were obtained as multiplets (m) at 6.74–7.60 ppm (δ). In this spectrum, the absence of resonance at 5.50 ppm of NH_2 protons confirms the formation of $\text{C}=\text{N}$. ^{13}C NMR spectrum of free ligand (L1) displayed a single resonance at δ 165 ($^{13}\text{C}=\text{N}$) and δ 175 ($^{13}\text{C}=\text{N}$) are due to azomethine carbon atoms. The signals at 123–152 ppm corresponding to aromatic carbon atoms. The signals that appeared at 14 ppm, 53 ppm, and 136 ppm denote the presence of methyl (1C), methoxy (2C), and ($\text{C}=\text{CH}$) (1C) carbon atoms, respectively. The signal at 112 ppm for ($^{13}\text{C}=\text{CH}$) carbon atom.

The compounds synthesized have been evaluated for their antibacterial and antifungal actions. The antibacterial and antifungal tests were carried out using the well diffusion method. *Amikacin* and *Ketoconazole* were used as standard reference compounds for antibacterial and antifungal activities, respectively. Antibacterial and antifungal activities of the ligand L1 and its zinc (II) complex showed lesser activities than the standards. The results revealed that metal complex was more effective than the free ligand L1 against the same microorganisms under similar experimental conditions. When complexed with the metal ion, the activity of Schiff base becomes more pronounced [13].

The rise in the antimicrobial activity of the metal complex of L1 is due to azomethine ($>\text{C}=\text{N}-$) linkage which leads to increased lipophilicity on chelation. In addition, the presence of the electron releasing methoxy group as substituent in the ortho position of the phenyl ring increases the lipid solubility to a certain extent. Inductive effect introduced by $-\text{OCH}_3$ substituent in the aromatic portion of the

Table 1: Antibacterial activities of L1 and its metal (II) complexes

Compounds	<i>Escherichia coli</i> (mm)	<i>Staphylococcus aureus</i> (mm)	<i>Bacillus subtilis</i> (mm)
$\text{C}_{31}\text{H}_{27}\text{ClN}_2\text{O}_2$ (L1)	14	13	14
$(\text{ZnL}_1)_2(\text{Cl}_2)$	20	18	16

Table 2: Antifungal activities of L1 and its metal (II) complexes

Compounds	<i>Candida albicans</i> (mm)	<i>Aspergillus Flavus</i> (mm)	<i>Aspergillus Niger</i> (mm)
$\text{C}_{31}\text{H}_{27}\text{ClN}_2\text{O}_2$ (L1)	12	11	11
$(\text{ZnL}_1)_2(\text{Cl}_2)$	15	16	14

Schiff base influences the properties of the ligand. The presence of the structural-functional group affects the nature of the metal (II) complex. Since the electron releasing methoxy group is in the ortho position, the enhancement in the activity of the complex is not that much as we expected. Antimicrobial activities are tabulated in Tables 1 and 2.

4. CONCLUSION

The Schiff base ligand L1 and its Zn (II) complex were synthesized and structurally characterized by spectral and analytical data. The analytical data of the complex show the ratio of Metal to Ligand is 1:2 and the general formula as ML_2 , where M represents Zn (II) ions, while L1 represents the Schiff base. The spectral studies show that the ligand (L1) is coordinated to the metal ions in a bidentate manner. The IR, electronic transition, and NMR data lead to the conclusion that Zn (II) complex has octahedral geometry as proposed in the following structure (Figure 4).

The results of antimicrobial activities showed that most of the metal complexes had enhanced inhibitory activity than the Schiff base ligand (L1) due to chelation. The presence of the $-\text{C}=\text{N}$ group and the electron-donating methoxy substituent at ortho position is responsible for their enhanced activity.

5. ACKNOWLEDGMENT

I thank my teacher and well wisher Dr. K. Southamani for her support throughout my work.

6. REFERENCES

- D. K. Demertzi, A. Alexandratos, A. Papageorgiou, P. N. Yadav, P. Dalezis, M. A. Demertzis, (2008) Synthesis, characterization, crystal structures, *in vitro* and *in vivo* antitumor activity of palladium (II) and zinc (II) complexes with 2-formyl and 2-acetyl pyridine N (4)-1-(2-pyridyl)-piperazinyl thiosemicarbazone, *Polyhedron*, **27**: 2731-2738.
- R. R. Chrichton, (2012) *Biological Inorganic Chemistry a New Introduction to Molecular Structure and Function*, Amsterdam, Netherlands: Elsevier.
- G. Schenk, I. Mateen, T. K. Ng, N. Mitic, M. Jr. Jafelicci, R. F. C. Marques, L. R. Gahan, D. L. Ollis, (2016) Organophosphate-degrading metallohydrolases: Structure and function of potent catalysts for applications in bioremediation, *Coordination Chemistry Reviews*, **317**: 122-131.

4. G. Schenk, N. Mitić, L. R. Gahan, D. L. Ollis, R. P. McGeary, L. W. Guddat, (2012) Binuclear metallohydrolases: Complex mechanistic strategies for a simple chemical reaction, *Accounts of Chemical Research*, **45**: 1593-1603.
5. M. Kalaimathi, K. Southamani, R. Anitha, Y. Yesuthangam, (2017), Synthesis and Characterization of Schiffbase Metal (II) complexes Derived From Benzoylacetone, *International Journal of Universal Pharmacy and Biosciences*, **6**: 178-192.
6. M. Kalaimathi, K. Southamani, R. Anitha, Y. Yesuthangam, (2017) Synthesis and Characterization of Schiffbase Metal (II) Complexes Derived from Benzoylacetone and P-anisidine, *International Journal of Universal Pharmacy and Biosciences*, **6**: 83-92.
7. M. Kalaimathi, K. Southamani, R. Anitha, Y. Yesuthangam, (2017) Synthesis and Characterization of Metal (II) Complexes of n-(3-((4-methoxyphenylimino) (phenyl) methyl)-4-(4-chlorophenyl) but -3-en-2-ylidene)-4-methoxybenzenamine, *Journal of Chemistry and Chemical Sciences*, **7**: 847-853.
8. P. Mekhribon, K. Shaxnoza, Z. Abdukhakim, P. Nusrat, (2020) Synthesis and research of new mixed metal complexes Co(II), Ni(II), Cu(II) and Mn(II) based on ammonium vanadate and 5-phenyl-1, 3, 4-oxadiazole-2 (3H)-thione. *Journal of Critical Reviews*, **7(11)**: 464-471.
9. T. M. Sharmila, (2020) synthesis, characterization, biological and fluorescent behaviour of metal (ii) complexes with pyrazoline derivatives, *International Journal of Pharmaceutical Sciences and Research*, **11(2)**: 947-954.
10. N. Kumar, M. Nethaji, K. Patil, (1991) Preparation, characterization, spectral and thermal analyses of (N₂H₅)₂MCl₄·2H₂O (M=Fe, Co, Ni and Cu); crystal structure of the iron complex, *Polyhedron*, **10**: 365-371.
11. J. M. Gottesfeld, L. Neely, J. W. Trauger, E. E. Baird, P. B. Dervan, (1997) Regulation of gene expression by small molecules, *Nature*, **387**: 202-205.
12. N. Arshad, N. Abbas, M. H. Bhatti, N. Rashid, M. N. Tahir, S. Saleem, B. Mirza, (2012) Synthesis, crystal structure, DNA binding and *in vitro* biological studies of Ni(II), Cu(II) and Zn(II) complexes of N-phthaloylglycine, *Journal of Photochemistry and Photobiology B: Biology*, **117**: 228-239.
13. P. R. Reddy, A. Shilpa, N. Raju, P. Raghavaiah, (2011) Synthesis, structure, DNA binding and cleavage properties of ternary amino acid Schiff base-phen/bipy Cu(II) complexes, *Journal of Inorganic Biochemistry*, **105**: 1603-1612.

*Bibliographical Sketch

M. Kalaimathi, M.Sc., Ph. D, working as Assistant Professor in Chemistry Karpagam Academy of Higher Education, Coimbatore, India. She had UG and PG Degrees in Jayaraj Annapackiam College for Women, Autonomous, Periyakulam affiliated to Mother Teresa Women's University, Kodaikanal. She did Research work under the Guidance of Dr. Sr. Y. Yesuthangam, in Coordination Chemistry (Metal Complexes) and Published Ten Papers in well reputed journals. She has attended and Presented research works in National and International conferences and seminars. She has 8 Years teaching experience in College Level. At Present am guiding my students in Nanotechnology, Material Science. With the help of my guide Dr. Sr. Y. Yesuthangam and Co-Authors Dr. R. Ebenezer, Assistant Professor in Chemistry, The American College, Madurai, Dr. R. Anitha, Assistant Professor in Chemistry, Jayaraj Annapackiam College for Women, Periyakulam, I have done this work.