The Scientific Temper (2023) Vol. 14 (1): 20-28
Doi: 10.58414/SCIENTIFICTEMPER.2023.14.1.04

E-ISSN: 2231-6396, ISSN: 0976-8653
https://scientifictemper.com/

RESEARCH ARTICLE

Synthesis, spectral characterization and antimicrobial effect of Cu(II) complexes of Schiff Base Ligand, N-(3,4-dimethoxybenzylidene)-3-aminopyridine (DMBAP) Derived from 3,4-dimethoxybenzaldehyde and 3-aminopyridine

Anil Kumar*, Aditya Kumar

Abstract

The present study emphasizes strictly on the synthesis, and characterization of complex 3,4- dimethoxybenzaldehyde and 3-aminopyridine with Cu(II) using several techniques like Elemental Analysis, FTIR spectroscopy, NMR, HRMS, UV-vis spectroscopy, Magnetic Susceptibility and Conductivity Measurements. The Ligand [L] acts as bidentate and co-ordinates through Nitrogen atom of imine group [azomethine group] and Nitrogen atom of pyridine ring. Electronic data of the complexes suggest the probable geometry is octahedral in nature. All the complexes and ligand were screened for their antibacterial activity and behaved non-electrolytic in nature. The metal ligand ratio obeys 1:2 ratio. Antimicrobial studies of gram-positive bacteria (GPB)- (*Bacillus subtilis*), gram-negative bacteria (GNB)- (*E. coli*) and some antibiotic reveal the MIC value in the range of (6–20 mm) followed the order $[Cu(L)_2Cl_2]>[Cu(L)_2Br_2]>$Antibiotic>Ligand. Antimicrobial activity has been explained on the basis of Tweedy Chelation Theory (TCT) and Anil's Conceptual Model of Inhibition (ACMI).

Keywords: Anil`s conceptual model of inhibition (ACMI), Antibiotics, Antimicrobial effect, Octahedral geometry, Schiff base ligand, Schiff base metal complexes [SBMC], Spectral characterization (FTIR, NMR, HRMS, UV), Tweedy chelation theory (TCT).

Introduction

Schiff base are an important class of ligands and played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metal (Sunjuk *et al.,* 2022; Singh *et al.,* 1998; Yildirm *et al.,* 2022; Pul, 2022; Garnovski *et al.,* 1993). Schiff Base Ligand or [L] and their metal complexes have variety of application, including bactericidal (gram-negative and gram-positive bacteria), anticancerous, flame retardant, clinical, analytical, industrial fields and also in organic synthesis (Ouyang *et al.,* 2022; Raman *et al.,* 2001; Jayabalkrishnan *et al.,* 2002; Sharghi *et al.,* 2003; Gao *et al.,* 2002; Senthamilselvean *et al.,* 2022; Deepika *et al.,* 2022; Kumar *et al.,* 2022). Metal complexes of schiff base are studied extensively due to synthetic flexibility of the compounds and their selectivity as well as sensitivity towards the central metal atom.

Copper is essential to all living organisms either in a trace dietary proportion or a Co-factor of numerous exogenously administered compounds in human beings. It is a key constituent of the respiratory enzyme complex cytochrome, c-oxidase, ceruloplasmin, dopamine-β monooxygenase, galactose oxidase, and copper-zinc superoxide dismutase. Copper proteins have a significant role in biological electron and oxygen transportation that involved a brilliant test of interconversion of Cu (I) and Cu (II) and are important in facilitating iron uptake by binding to mucosal transferring (Vest *et al.,* 2013; Lippard *et al.,* 1994; Chan *et al.,* 1980; Williams *et al.,* 1976; Bala 2022).

Department of Chemistry, Sahibganj College, Sahibganj, Sido Kanhu Murmu University, Dumka, Jharkhand, India

***Corresponding Author:** Anil Kumar, Department of Chemistry, Sahibganj College, Sahibganj, Sido Kanhu Murmu University, Dumka, Jharkhand, India, E-Mail: anilkumar_ism@yahoo.com

How to cite this article: Kumar, A., Kumar, A. (2023). Synthesis, spectral characterization and antimicrobial effect of Cu(II) complexes of Schiff Base Ligand, N-(3,4-dimethoxybenzylidene)-3-aminopyridine (DMBAP) Derived from 3,4-dimethoxybenzaldehyde and 3-aminopyridine
. The Scientific Temper, **14**(1):20-28.

Doi: 10.58414/SCIENTIFICTEMPER.2023.14.1.04

Source of support: Nil

Conflict of interest: None.

Received: 11/01/2023 **Accepted:** 12/02/2023 **Published** : 25/03/2023

Considering the biological importance of copper, complexes of this metal with various ligands have received attention as models of natural enzyme, antiviral, antibacterial, antifungal, anticonvulsant, antiamoebic, anticancer, potentially therapeutic, good catalyst in many reactions (Connor *et al.,* 2012; Vilchez *et al.,* 2005;Sathisha *et al.,* 2007).

Experimental Methodology

A-R grade chemicals were directly used in the same way as it was received. Standard methods analyzed the Ligands, metal complexes and solvents (Jeffery *et al.,* 1996; Choudhary *et al.,* 1997; Choudhary *et al.,* 2020; Kumar *et al.,* 2020; Kumar *et al.,* 2019; Kumar *et al.,* 2022). FTIR spectra were recorded on Perkin Elmer- Spectrum (2) spectrophotometer using KBr –pellet method. Electronic spectra were recorded on Agilent Carry 5000 Spectrophotometer at IIT (ISM) Dhanbad. NMR Spectrum was analyzed on Bruker Ascend™ 400 Spectrophotometer at C.D.R.I., Lucknow. HRMS spectroscopy was recorded in USA Xevo Spectrophotometer, Elemental Analyser GMBTT Germany UNICUBE at (IIT) ISM Dhanbad. Magnetic susceptibility was measured on a Guoy balance using mercury tetrathiocyanate cobaltate as a calibrant. Conductivity measurement were made on systronics conducted metal model - 303 using DMSO.

Preparation of the Ligand, [L]- [N-(3,4-Dimethoxybenzylidene)-3-Aminopyridine]

A total of 0.01 mol of 3,4-dimethoxybenzaldehyde was dissolved in minimum ethanol, and the solution was warmed for four hours. To this an ethanolic solution of 3-aminopyridine (0.01 mol) was added and refluxed the solution for an hour. Ligand prepared was in liquid state (Kumar *et al.,* 2019). The colour of the ligand is of wine colour of yield-65%.

Preparation of the Cu-Metal Complexes

The Cu-metal complexes were prepared by refluxing ethanolic solution of metal salts with the ethanolic solution of the ligand (DMBAP) in the molar ratio (1:2) and refluxed for 4-8 hrs. The solid-colored complexes that separated on cooling were filtered, washed with cold water followed by ethanol and dried at room temperature yielding 67-69%.

Mechanistic Pathway

$C_9H_{10}O_3 + C_5H_6N_2 \rightarrow C_{14}H_{14}N_2O_2 + H_2O$ $MX_2 + 2C_9H_{10}O_3 + 2C_5H_6N_2 \rightarrow [M(C_{14}H_{14}N_2O_2)_2X_2]$, [Where M=Cu, X = Cl^-, Br]

Results And Discussion

- ***FTIR Analysis***

FTIR spectrum of the ligand [N- (3,4-dimethoxy benzylidene)-3-amino pyridine] [DMBAP](Figure 4) and the metal complexes of the type $[M(DMBAP)_2X_2]$ have been recorded in the frequency region of 4000 to 400 cm^{-1} in KBr and Nujol method. The vibrational bands of structural significance have been recorded in Table 2 (Figures 4-6).

- ***Characterization of Ligand, [DMBAP]***

Elemental analysis [Table 1] suggests that the molecular formula of [N- (3-methoxy benzylidene)-3-amino pyridine] as $C_{14}H_{14}N_2O_2$. The spectrum of 3-amino pyridine shows a sharp band at (Sharma, 2016) 3435 cm^{-1} is attributed to ν (N-H) band of $-NH_2$ group. It also shows a band at 1586 cm^{-1} due to breathing vibrations of pyridine nucleus. (Table 2, Figure 4)

The spectrum of N(3,4 dimethoxy-benzylidene)-3-amino pyridine containing a sharp band (El-Sherif *et al.,* 2011) at 1677 cm^{-1} attributed to ν (C=N) of the imine group. It also shows a band at 1269 cm^{-1} attributed to ν (C-O) of the methoxy group.

It is significant to note that ν–(N-H) bands and ν (C=O) band have disappeared in the spectra of the ligand (DMBAP) give the clear indication of the condensation of the C=O group of the aldehyde and $-NH_2$ group. A new band has appeared in the vicinity of 1677 cm^{-1} which can be assigned to the ν (C=N) [azomethine] group (Al-Resayes *et al.,* 2012; Gulcan *et al.,* 2012; Sunjuk *et al.,* 2022). The band at 2929 cm^{-1} are assigned to ν-(C-H) stretching due to presence of $-OCH_3$ group. The ν (C=N) imine band and ν (pyridine) band for the complex $[Cu(L)_2Cl_2]$ and $[Cu(L)_2Br_2]$ lies in the range of 1600-1601 cm^{-1} and 1513–1512 cm^{-1} (Figures 5, 6) respectively. The ν (C=N) shift in the complexes were about (77-76) cm^{-1} and ν (pyridine) shift in complexes by about 73–74 cm^{-1} indicates the involvement of azomethine nitrogen and pyridine nitrogen in the coordination sphere with the metal ions for all the synthesized complexes.

Proton ¹H - NMR Study

The ^1H-NMR spectral data of the ligand and its complexes were recorded in DMSO-d6 and were compared. It was observed that the signals of the protons of the different functional group of the complexes have been shifted towards the downfield region, indicating the coordination of ligand to the metal ion through N-atom of imine group and pyridine molecules.

^1H-NMR spectra of (DMBAP) ligand and $[Cu(DMBAP)_2Cl_2]$, $[Cu(DMBAP)_2Br_2]$ complexes are supported by ^1H–NMR spectral study [Figures 7-9]. The spectral comparison delivers the idea about the binding nature of the ligand to metal ions. The integral intensities of each signal in the ^1H – NMR Spectra of Ligand (DMBAP) and $[Cu(L)_2Cl_2]$ and $[Cu(L)_2Br_2]$ complexes are found to agree with the number of different types of proton. For the present study, the ^1H-NMR spectrum of DMBAP (ligand) displays the resonance signals at = 7.96 ppm, = 3.2 ppm assigned to C=N and $-OCH_3$ group respectively. However, the resonance signal assigned to imine Proton ^{H}>C=N- and methoxy group ($-OCH_3$) in free ligand is obtained. However for $[Cu(L)_2Cl_2]$ and $[Cu(L)_2Br_2]$, the resonance signals of imine proton is in the range of =[9.816-9.811 ppm] and the resonance signal for the above complexes for pyridine ring proton is in the range of =[8.293-8.378 ppm] suggesting

Table 1: Micro Analytical Data of Ligands and Metal Complexes

S. No.	*Compound*	*Color*	*Elemental Analysis Data % Found(Calculated)*						
			Metal [Cu]	*C*	*H*	*N*	*O*	*Halogen*	*Yield*
1.	Ligand [L], (DMBAP)	Wine	-	69.42 (69.40)	5.78 (5.69)	11.57 (10.98)	13.22 (12.97)	-	65%
2.	$[Cu(DMBAP)_2Cl_2]$	Dark Grey	10.27 (10.21)	54.32 (54.30)	4.52 (4.50)	9.05 (9.02)	10.34 (10.30)	11.47 (11.43)	67%
3.	$[Cu(DMBAP)_2Br_2]$	Dark Greyish Green	8.98 (8.90)	47.50 (47.45)	3.95 (3.92)	7.91 (7.90)	9.04 (9.02)	22.59 (22.54)	69%

Table 2: FTIR Spectral Analysis of Ligand and Complexes

S. No.	*Compound*	*v (C=N)*	*v (Pyridine)*	*v - (C-H)*	*v - (OCH_3)*	*v (M-N)*
1.	Ligand [L], (DMBAP)	1677(s)	1586(s)	2929(b)	1269(s)	-
2.	$[Cu(DMBAP)_2\ Cl_2]$	1600(s)	1513(s)	2926(m)	1240(w)	438(w)
3.	$[Cu(DMBAP)_2\ Br_2]$	1601(s)	1512(s)	2853(m)	1244(s)	457(w)

Table 3: Electronic Absorption Spectral Data of DMBAP and its Metal Complexes

S. No.	*Compound*	*Peak (nm/cm⁻¹)*	*Assignments (Transition)*	*Magnetic Moment (B.M.)*	*Geometry*	*Hybridization*
1.	DMBAP	398 nm or 25126 cm^{-1}	$n \longrightarrow \pi^*$	0	-	-
2.	$[Cu(DMBAP)_2Cl_2]$	595 nm or 16807 cm^{-1}	$^2E_g \to {}^2T_{2g}$	2.04	Octahedral	sp^3d^2
3.	$[Cu(DMBAP)_2Br_2]$	560 nm or 17857 cm^{-1}	$^2E_g \to {}^2T_{2g}$	1.92	Octahedral	**sp^3d^2**

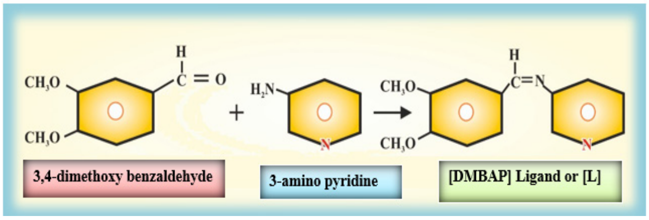

Figure 1: Preparation of Ligand [L], [DMBAP].

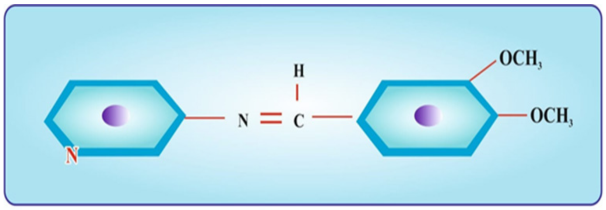

Figure 2: Proposed Structure of Ligand [L], [N-(3,4-dimethoxybenzlidene)-3-amino pyridine]

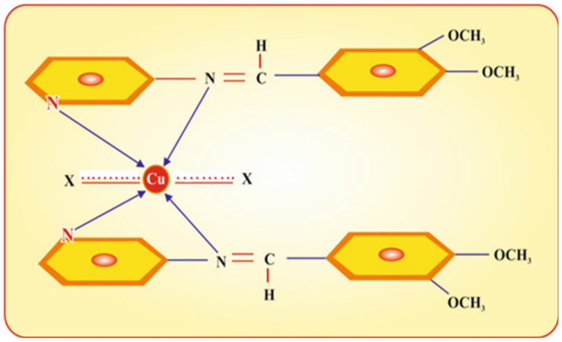

Figure 3: Proposed structure of $[Cu(DMBAP)_2X_2]$; X = Cl, Br ; Hybridization sp^3d^2.

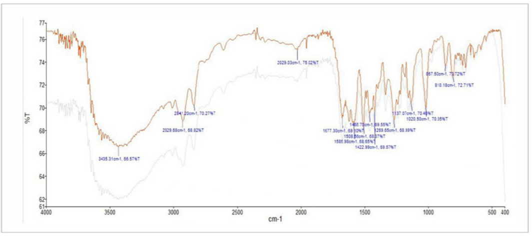

Figure 4 : FTIR of Ligand (DMBAP).

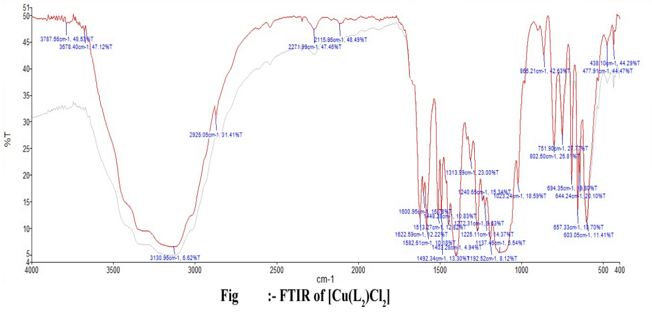

Figure 5: FTIR of $[Cu(DMBAP)_2Cl_2]$.

the coordination of azomethine nitrogen to Cu(II) ion and pyridine nitrogen to Cu(II) ion. The other resonance signal of methoxy appeared in the range of =[3.297- 3.309 ppm] (Figures 7-9). This is in accordance with what the IR data has revealed (Silversteins *et al.,* 1991; Sharma 2016; Nakamoto, 2009; Lever, 1984; Bellamy, 1975; Dyer, 1965; Shriner et al 2004: Kadhim *et al.,* 2017).

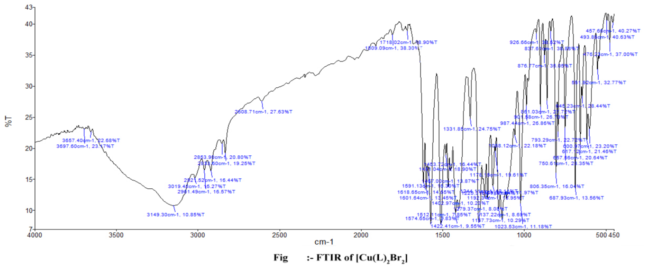

Figure 6: FTIR of [Cu(DMBAP)$_2$Br$_2$].

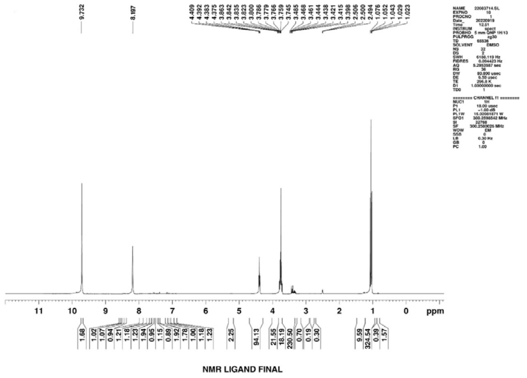

Figure 7: Proton NMR of Ligand.

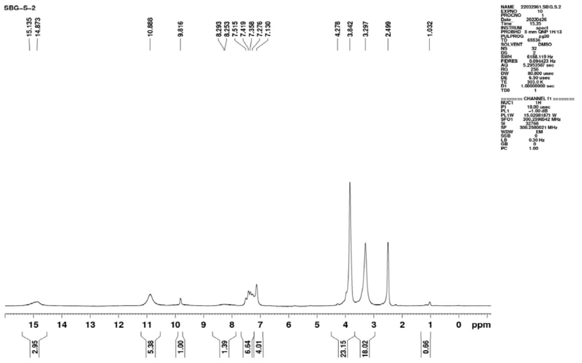

Figure 8: NMR of [Cu(DMBAP)$_2$Cl$_2$].

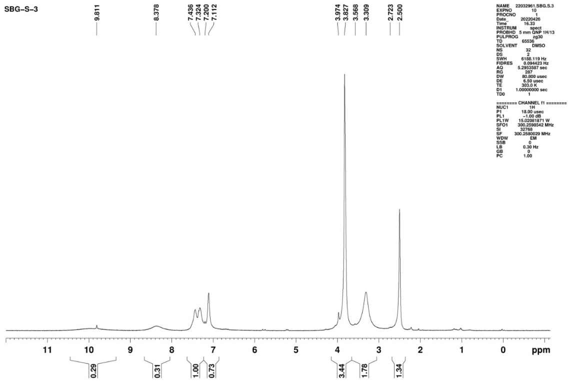

Figure 9: NMR of [Cu(DMBAP)$_2$Br$_2$]

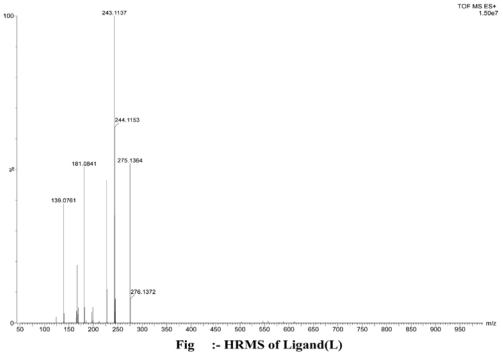

Figure 10: HRMS of Ligand (DMBAP)

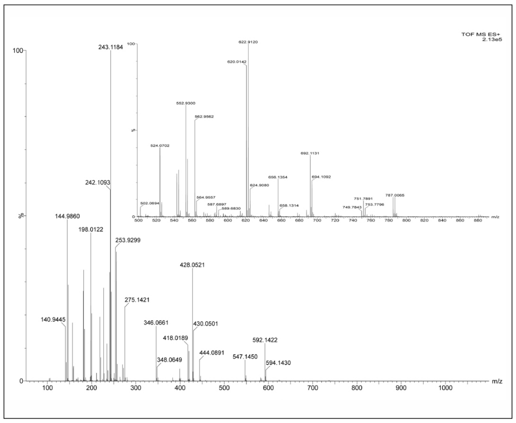

Figure 11: HRMS of [Cu(DMBAP)$_2$Cl$_2$].

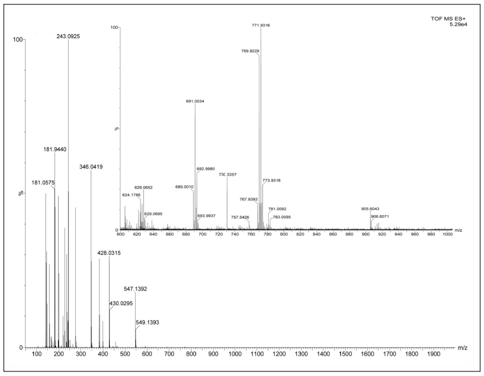

Figure 12: HRMS of [Cu(DMBAP)$_2$Br$_2$].

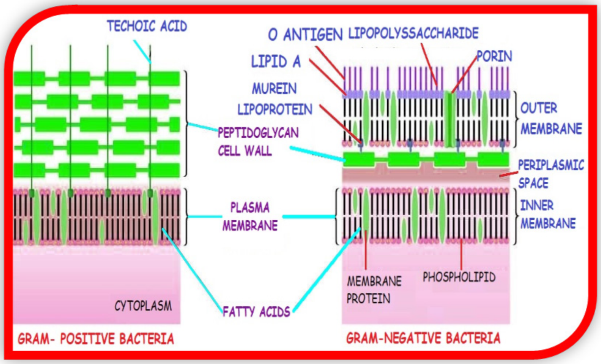

Figure 13: Modified Cell wall Structure of GPB and GNB.

High-Resolution Mass Spectrum (Hrms) of Ligand And Metal Complexes

The mass spectra of Ligand and its metal complexes were recorded and are used to compare their stoichiometric compositions. The mass spectrum of the ligand shows a molecular ion $[M+H]^+$ Peak at m/z 243.11, corresponding to formula weight 242 (Figure 10).

In addition, other peaks for the ligand are observed at m/z 276.13, 275.13, 244.11, 181.08 and 139.07 with significant intensity and they correspond to its fragment ion peaks.

The molecular ion $[M+H]^+$ peaks for metal complex appear at m/z for $[Cu(L)_2Cl_2]$ is 620.91 and complex which confirmed their formula weight 618.5 for $[Cu(L)_2Cl_2]$; the various peaks at m/z 622.91, 656.13, 692.11, 787.00 correlate fragment peak (Figure 11).

The molecular ion $[M+ Na]^+$ peaks for metal complex appear at m/z for $[Cu(L)_2Br_2]$ is 730.33 and different Cu-metals fragment peaks are 691.0034, 771.93,905.60 (Figure 12).

Electronic Complex Spectra, Magnetic Moment Conductivity Measurement of Cu- Complex

Two bands are in the region of 595 nm [16807 cm^{-1}] and 560 nm [17857 cm^{-1}] of electronic spectra of Cu(II) complexes may be due to $^2E_g \rightarrow {}^2T_{2g}$ transitions, respectively, indicating octahedral geometry (Lever, 1984; Choudhary *et al.,* 2020; Silversteins *et al.,* 1976) for Cu-complex. Further supported (Reddy *et al.,* 2013) by high μ_{eff} value in the range of 2.04 and 1.92, respectively, (Hermle *et al.,* 2011) show paramagnetic nature. Molar conductance of the complexes were measured in solvent DMSO and all the complexes were found to be non-electrolytic in nature (Ahmed *et al.,* 2011) and the conductivity are in the range of 24 and 20 mho cm^2 mol^{-1} or S cm^2 mol^{-1} (Table 3).

Antimicrobial Studies

Antibacterial activity of ligand [DMBAP] and the metal complexes were tested *in-vitro* against respective gram-positive bacteria (GPB) species like *Lactobacillus* and gram-negative bacteria [GNB] species like *E. coli* by agar well diffusion method. Compound inhibiting growths of one or both microorganisms were further tested by their minimum inhibitory concentration (MIC) of the compound. DMBAP ligands are inactive against all bacteria, amikacin, ceftriaxone, gentamycin, levofloxacin were used as reference drugs. The result of the antimicrobial activity of ligand and its metal complexes against all bacteria are shown in Table 4. All compounds inhibited to growth of bacterial (gram-negative and gram-positive) with MIC value in the range of 6–18 mm and 6–20 mm, respectively with reference to the drug and higher MIC value may be due to nature of metal ion of the ligand and orientation of the ligand around the metal ion (Table 4) (Figures 16, 17).

Biological Activity

The tested complexes were more active against GPB than GNB bacteria. It may be concluded that the compounds' antimicrobial activity is related to the bacteria's cell wall structure. It is possible because the cell wall is essential for the survival of bacteria and some antibiotics are able to kill bacteria by inhibiting a step in the synthesis of peptidoglycan. GPB possess a thick cell wall containing many layers of peptidoglycan and teichoic acids but in contrast, GNB has a relatively thin cell wall consisting of a few layers of peptidoglycan and surrounded by a second lipid membrane containing lipopolysaccharides and lipoproteins (Carcelli *et al.,* 1995; El-sherif *et al.,* 2011) (Figure 13). These differences in cell wall structure can produce differences in antibacterial susceptibility and some antibiotics can kill only gram-positive bacteria and is ineffective against gram-negative pathogen (Koch, 2003).

The result of antimicrobial activity show that the metal complexes exhibit antimicrobial properties and it is important to note that they show enhanced inhibitory activity compared to parent ligand under identical experimental conditions and the same is indicated from the result (Table 4) and morphology (Figure 15). The higher activity in the antimicrobial activity of the complex $[Cu(L)_2Cl_2]$ and $[Cu(L)_2Br_2]$ over the ligand (DMBAP) can be explained on the basis of Tweedy Chelation Theory (TCT), Overton's Concept (OC) (Tweedy *et al.,* 1964; Chohanetal; 2006; Nagesh *et al.,* 2015; Saghatforoush *et al.,* 2009; Chew *et al.,* 2004) and Anil's Conceptual Model of Inhibition (ACMI) (Kumar *et al.,* 2022). The enhancement in the antimicrobial activity may be rationalized on the basis of the complex mainly possessing azomethine (>C=N) bond confirmed by FTIR (Table 2, Figures 4, 5) [>C=N = 1600(s) and 1601(s)] for the complex 1 and complex 2. The 1-H NMR value for complex 1 and complex 2 were =[9.816-9.811 ppm] (Figures 8-9).

Also in the metal complexes, the positive charge (+ve) of the metal ion is partially shared with the hetero atom[N] present in the ligand (Figure 2) and there may be π – electron

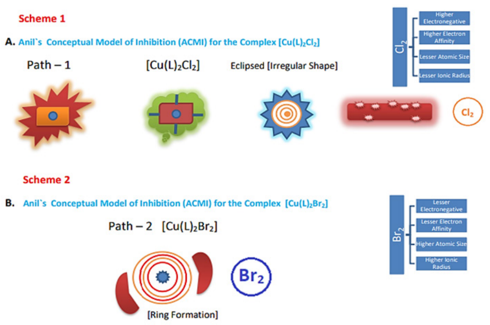

Figure 14: Anil`s Conceptual Model of Inhibition (ACMI)

Table 4: Microbial Study (MIC value in mm) of the Ligand and Complexes [Cu(DMBAP)$_2$Cl$_2$] and [Cu(DMBAP)$_2$Br$_2$]

S. No.	*Compounds*	*Gram-positive Bacteria [Bacillus Subtilis]*	*Gram-negative Bacteria [E – coli]*
	Ligand [L] { DMBAP}	6 [Resist] [W]	6 [Resist] [W]
	[Cu(DMBAP)$_2$Cl$_2$]	18 [S]	18 [S]
	[Cu(DMBAP)$_2$Br$_2$]	19 [S]	18 [S]
	Amikacin	16 [S]	15 [S]
	Ceftrixone	17 [S]	16 [S]
	Gentamycin	6 [Resist] [W]	6 [Resist]
	Levofloxacin	14 [M]	13 [M]

Note :- 10 < Weak [W] ; >10 Moderate [M] ; >16 Significant [S].

Photo 1: *E-coli* **Photo 2:** [Cu(DMBAP)$_2$Cl$_2$] **Photo 3:** [Cu(DMBAP)$_2$Br$_2$]

Figure 15: Morphology of Synthesized Complex and Bacteria

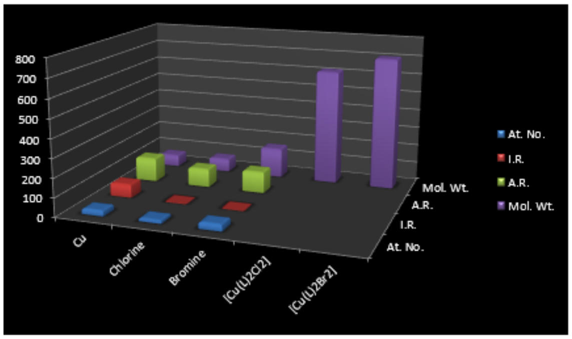

Figure 16: At. No., I.R., A.R., Mol. Wt. of metal complexes.

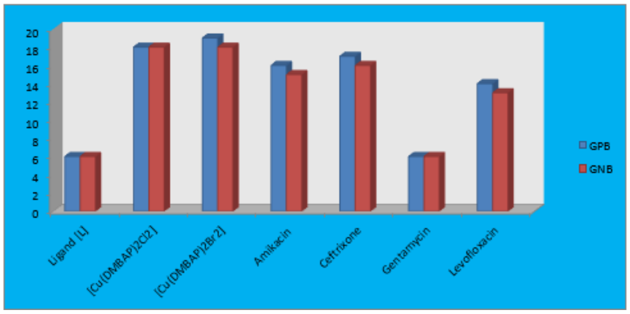

Figure 17: Inhibition Zone of Compound Vs GPB and GNB.

delocalization over the whole chelate ring system (Wahab *et al.,* 2004). Hence the increase in the lipophilic character of the metal chelates favor its permeation through the lipid layer of the bacterial membrane and blocking the metal binding site in the enzyme of microorganism.

The present investigation clearly depicts that the metal complexes may serve as a vehicle for activation of ligands as the principal cytotoxic species (Sigel *et al.,* 1995). The MIC values of the compound against the respective bacteria (GPB and GNB) are summarized in Table 4.

Anil's Conceptual Model of Inhibition (Acmi)

The mechanism of inhibition may be explained on the basis of Anil's Conceptual Model of Inhibition (ACMI). IN GPB, the metal complex protects as a pocket via Scheme 1 (Figure 14) and covers the whole surface in an irregular manner/ eclipsed form in case of [Cu(L)$_2$Cl$_2$] while the inhibition effect of [Cu(L)$_2$Br$_2$] takes place via Scheme – 2 (Figure 15) in a concentric circular meniscus shaped (Figure 16). The order of inhibition of the synthesized complexes may be due to higher electronegativity, lesser atomic size, higher electron affinity and lesser ionic radius of Cl atom than Br atom (Figures 14-17). Although, mol. wt. (707.346) The synthesized compound 3 is higher than compound 2 (618.446). Apart from the greater size, high mol. wt. [Cu(L)$_2$Br$_2$] , the effect of MIC is just reverse due to small size and low mol. wt. (Figure 16) of [Cu(L)$_2$Cl$_2$] (Kumar *et al.,* 2022), so the complex 2 will easily enter in the bacterial cell wall (Figure 13) and thus the MIC value is greater and followed the increasing order: [Cu(L)$_2$Cl$_2$] > [Cu(L)$_2$Br$_2$] > Antibiotic (Except Gentamycin) > Ligand.

The antibacterial activity has been explained on the basis of Tweedy Chelation Theory and Anil`s Conceptual Model of Inhibition (ACMI) (Figure 14). The investigation showed that complexes were more active against GPB than GNB. From the structure of bacteria it can be concluded that the antibacterial activity of the compounds can be related to cell wall structure of bacteria. It is possible because the cell wall is essential for the survival of many bacteria and some antibiotics are able to kill bacteria by inhibiting a step in the synthesis of peptidoglycan.

Table 4 clearly indicate that $[Cu(DMBAP)_2Cl_2]$ and $[Cu(DMBAP)_2Br_2]$ has significant impact on GPB and GNB. All tested antibiotics have significantly impacted GPB and GNB except Gentamycin (Resist).

The MIC value of inhibition follows the order:

$[Cu(L)_2Cl_2] > [Cu(L)_2Br_2] >$ Antibiotic $>$ Ligand.

Since the electronegativity of chlorine is higher than bromine so delocalization of electron of metal ion will increase, so the MIC value will be greater for $[Cu(L)_2Cl_2]$. Lesser is the size (Compact pocket), greater is the tendency to inject foreign particle in the cell wall of the bacteria. Thus the inhibition is higher. This can be clear by the Anil`s Conceptual Model of Inhibition (Figure 14).

The importance of such work lies in the possibility that new compounds might be more effective drug against bacteria for which a thorough investigation regarding the structure activity relationship, toxicity and their biological effects need to be done which could be helpful in desiring more potent antibacterial agents for therapeutic use.

Based on the elemental analysis, FTIR, HRMS, NMR, UV spectra of the ligand (DMBAP) i.e; N-(3,4-dimethoxy-benzylidene)-3-amino pyridine may be suggested to have following structure below (Figure 2).

It is vivid from the structure of ligand that there are four donor atoms two are on one side and other two are on the other side. Pyridine nitrogen and azomethine nitrogen have potential donor properties while the other two oxygen atoms of methoxy groups have comparatively low donor capacity (Figure 2). On the arrangement of donor atoms it is clear that two donor sites are available in one condition mainly ligand may coordinate through pyridine Nitrogen and azomethine nitrogen (imine group) so ligand may behave as bidentate.

FTIR, NMR, HRMS, UV, magnetic moment elemental analysis electronic spectrum data revealed that the ligand behaves as bidentate coordinating through the imine group and pyridine nitrogen having proposed octahedral geometry (Figure 3) with sp^3d^2 hybridization as shown below.

Conclusion

Metal complexes of Cu(II) and DMBAP ligand have been characterized structurally. The microanalytical data shows that the metal-ligand stoichiometry in complex is 1:2. All complexes are non-electrolytic in nature. The ligand(L) behaves as bidentate and coordinates through N-atom of imine or azomethine group and N-atom of the pyridine ring. Cu(II) complexes show octahedral geometry with sp^3d^2 hybridization. High value of MIC may be due to the nature of the ligand and orientation of the ligand with the central metal ion. The order of MIC is $[Cu(L)_2Cl_2]>[Cu(L)_2Br_2]>$Antibiotic$>$Ligand.

Acknowledgement

Author provides deep gratitude to Director, IIT (ISM) Dhanbad, SAIF C.D.R.I, Lucknow for providing facilities of FTIR, UV, HRMS, NMR, Elemental Compositions and Molar conductivity etc. Thanks to V.C. S.K.M.U Dumka for providing research facility at Sahibganj College, Sahibganj. We are also very thankful to Dr. Abdul Sattar, Dean, Faculty of Science, and Dr. Hasmat Ali, P.G. Head of University Dept. of Chemistry for his timely valuable suggestions and moral support through out the research work. Author also admires the valuable advices presented by Dr. D. K. Yadav, Asst. Prof, Sahibganj College, Sahibganj. I am also greatful to Dr. R C Pandit(MBBS), Ankur Chatterjee and Shoaib Akhtar, Lab Technician(Bio Chem. Lab Sahibganj). I deeply convey my love to Prateek Mohan Mishra and Wasim Akhtar (Ph.D Scholar), Sudhanshu Jha(P.G. Sem-III), Abhishek Anand, Ashwaraya Prakash, Aman Khurshid (U.G. Sem – 2) , Mukhtar, Suraj, Manash Ojha for typing, drawing, sketching and literature review.

References

Sunjuk, M., Al-Najjar, L., Shtaiwi, M., Al-Noaimi, M., Al-Essa, L., & Sweidan, Kamal. (2022). Transition metal complexes of schiff base ligand, prepared from reaction of amino benzo thiazole with benzaldehyde. Inorganics, 10(4), 43.

Singh, V. K., Sinha, R., Kant, R., & Sinha, B. K. (1998). Nickel(II) complexes of schiff bases derived from substituted 1,2,4-triazole. Asian J. Chem, 10, 532.

Yildirm, L. T., & Atakol, O. (2002). Crystal structure analysis of bis {(N,N′-dimethylformamide-)-[μ-bis-N,N′-(2-oxybenzyl)-1,3-propanediaminato](μ-asetato) nickel (II)}nickel (II). Cryst. Res. Technol, 37, 13.

Pul, A. (2002). Binding of molecules dioxygen to the cobalt (II) complexes in nonaqueous solution. Croatica Chemica Acta, 75, 165.

Garnovski, A. D., & Nivorozhkin, A. L. (1993). Ligand environment and the structure of schiff base adducts and teracoordinated metal – chelates. Coord. Chem. Rev, 126, 1.

Ouyang, X. M., Feri, B. L., Okamuro, T. A., Sun, W. Y., Tang, W. X., & Ueyama, N. (2002). Synthesis, crystal structure and superoxide dismutase (SOD) activity of novel seven – coordinated manganese (II) complex with multidentate di-schiff base ligands. Chem Lett, 31(3), 362.

Raman, N., Raja, Y. P., & Kutandatsmy, A. (2001). Synthesis and characterization of Cu(II),Ni(II),Mn(II), Zn(II) and VO(II) schiff base complexes derived from O-phenylenediamine and acetoacetanilide. Proc. Indian Acad. Sci, (Chem. Sci), 113, 183-189.

Jayabalkrishnan, C., & Natarajan, K. (2002). Ruthenium (II) carbonyl complexes with tridentate schiff base and their antibacterial activity. Transition. Metal Chemistry, 27, 75-79.

Sharghi, H., & Nasser, M.A. (2003). Schiff base metal (II) complexes as new catalysts in the efficient, mild and regioselective conversion of 1, 2- epoxyethanes to 2-hydroxyethyl thiocyanates with ammonium thiocyanate. Bull. Of Chem. Soc. (JPN), 76, 137-142.

Gao, W. T., & Zheng, Z. (2002). Synthetic studies on optically active schiff-base ligands derived from condensation of 2 –hydroxyacetophenone and chiral diammines. Molecules, 7(7), 511-516.

Senthamilselvan, G., Asma, B., Dhanalakshmi, A., & Cyril, A. (2022). Potentially active metal of cobalt, copper and zinc complexes derived from schiff base ligand of 3-ethoxy-2-hydroxy-benzaldehyde and aniline for their anticancer activity. Journal of Advanced Scientific Research, 13(2), 76-84.

Deepika, P., Vinusha, H. M., Begum, M., Ramu, R., Shirahatti, P. S., & Prasad M. N. N. (2022). 2-Methoxy-4-(((5-nitropyridin-2-yl) imino)methyl)phenol Schiff base ligand and its Cu(II) and zinc(II) complexes: Synthesis, characterization and biological investigations. Heliyon, 8, 1-10.

Kumar, A., Ali, H., & Kumar, A. (2022). Synthesis, spectroscopic characterization, antibiotical study of Hg(II) complexes with gram-positive bacteria (GPB) and gram-negative bacteria (GNB). Asian Journal of Organic and Medicinal Chemistry, 7(2), 71-81

Vest, K. E., Hashemi, H. F., & Cobine, P. A. (2013). The Copper mettallome in eukaryotic cells, In L. Banci (Ed.), mettallomics and the cell. Metal Ions in Life Science, 12, 451. Springer, doi: http://dx.doi.org/10.1007/978-94-007-5561-10.

Lippard, S. J., & Berg, J. M. (1994). Principles of bioinorganic chemistry. University Science Books, Mill Valley, 1-411.

Chan, W.Y., & Rennert, O.M. (1980). The role of copper in iron molecules. Annals of Clinical and Laboratory Science, 10, 338-344.

Williams, D. M., Loukopoulos, D., & Lee, G. R. (1976). Cartwright, G.E. Role of copper in mitochondrial iron metabolism. Blood, 48, 77-85.

Bala, U. (2022). Synthesis, characterization and antimicrobial activities of schiff base complexes of Co(II) and Cu(II) derived from salicyldehyde and diphenylamine. Scholars International Journal of Chemistry and Material Sciences, 5(1), 6-10.

Connor, M., Kellett, A., Mc. Cann, M., Rosair, G., Namara, M., Howe, O., Creaven, B. S., Clean, M C., & Faltyn-Arfa Kih, A. (2012). Copper (II) complexes of salicylic acid combining superoxide dismutase mimetic properties, with DNA binding and cleaning capacities display promising chemothepeutic potential with fast acting in vitro cytotoxicity against cisplatin sensitive and resistant cancer cell likes. Journal of Medicinal. Chemistry, 55, 1957.

Vilchez, F.G., & Vilaplana, R. (2005). 2,4 Cu-chemotherapeutic compounds in mettalo-therapeutic drugs and metal based diagonostic agents, gledin, M E.R.T, Tiekink (Eds). John-Willey and Sons, New York, NY Chapter, 12, 219-236.

Sathisha, M. P., Revankar, V. K., & Pai, K. S. R. (2007). Synthesis, structure, electrochemistry, and spectral characterization of bis-isatin thiocarbohydrazone metal complexes and their antitumor activity against ehrlich ascites carcinoma in swiss albino mice. Metal Based Drugs, 2008, 1-11

Jeffery, G. H., Bassett, J., Mendham, J., & Vogel, R.C. (1996). Text book of quantitative chemical analysis, 5th ed.

Choudhary, G. L., Prasad S. R., & Rahman, A. R. (1997). Transition metal complexion studies on hetrocyclic ligands. J. Indian Chem.Soc, 74, 683.

Choudhary, G. L., Kumar, A., Kumari, S., Kumar, A., & Mishra, P. M. (2020). Synthesis and spectral characterization of Co(II), Ni(II), and Cu(II) complexes of quinoline based schiff bases (QBSB) . International Journal in Physical and Applied science, 07, 70-75.

Kumar, A., Choudhary, G. L., Kumari , S., Kumar, A., & Prabha, S. (2020). Synthesis, spectral and microbial activity of Cr(II), Mn(II), and Cu(II) complexes of quinazoline based schiff base (QSB). International Research Journal of Natural and Applied science, 7, 25-30.

Kumar, A., Choudhry, G. L., Ali, H., Kumar, A., & Yadav, D. K. (2019). Synthesis, spectral characterization and microbial activity of Ni(II) complex with DBAP schiff's base ligand. Research Review International Journal of Multidisciplinary, 04, 2465-2472.

Kumar, A., & Kumar, A. (2022). In vitro microbial study of metal complexes Cu(II) with reference to schiff base ligand and antibiotics. International Journal of Research in Pharmacy and Pharmaceutical Sciences, 07, 14-19.

Kumar, A., Choudhry, G. L., Ali, H., Kumar, A., & Yadav, D. K. (2019). Synthesis, spectral characterization and microbial activity of Ni(II) complex with DBAP schiff's base ligand. Research Review International Journal of Multidisciplinary, 04, 2465-2472.

Sharma, Y. R. (2016). Elementary organic spectroscopy principles and chemical applications.

El-Sherif, A. A., & Eldebss, T. M. A. (2011). Synthesis, spectral characterization, solution equilibria, In vitro antibacterial and cytotoxic activities of Cu(II), Ni(II), Mn(II), Co(II) and Zn(II) complexes with schiff base derived from 5-bromosalicylaldehye and 2- aminomethylthiophene. Spectrochimica Acta Part A, 79, 1803-1814.

Al-Resayes, S. I., Shakir, M., Abbasi, A., Amin, K. M. Y., & Lateef, A. (2012). Synthesis, spectroscopic characterization and biological activities of N4O2 schiff base ligand and its metal complexes of Co(II), Ni(II), Cu(II), and Zn(II). Spectrochimica Acta Part A, 93, 86-94.

Gulcan, M., Sonmez, M., & Berber, I. (2012). Synthesis characterization and antimicrobial activity of a new pyrimidine schiff base and its Cu(II), Ni(II), Co(II), Pt(II), and Pd(II) complexes. Turk J. Chem, 36, 189-200.

Sunjuk, M., Najjar, Al., Shtaiwi, M., Eswed, B., Noaimi, M., Essa, L., & Sweidan, K. (2022). Transition metal complexes of schiff base ligands prepared from reaction of aminobenzothiazole with benzaldehydes. Inorganics, 10(43), 1-13.

Silversteins, R. M., Webster, F. X., & Kiemle, D. J. (1991). Spectrometric identification of organic compounds, John Wiley and Sons, 72-108.

Sharma, Y. R. (2016). Elementary organic spectroscopy principles and chemical applications, 69-137.

Nakamoto, K. (2009). Infrared and Raman spectra of inorganic and coordination compounds: Part A, John Wiley and Sons, 1-416.

Lever, A. B. P. (1984). Inorganic electronic spectroscopy, 2nd ed.; Elsevier New York, 1-888.

Bellamy, L. J. (1975). The infrared spectra of complex molecule, John Wiley and Sons, 1-407.

Dyer, J. (1965). Application of absorption spectroscopy of organic compounds, 1-168.

Shriner, R. L., Hermann C. K. F., Morrill, T. C., Curtin, D. Y., & Fuson,

R. C. (2004). The systematic identification of organic compounds, 8th ed.; John Wiley and Sons, Inc, 1-736.

Kadhim, S. H., Alla, I. Q. A., & Hashim, T. J. (2017). Synthesis and characteristic study of Co(II), Ni(II), and Cu(II) complexes of new schiff base derived from 4- amino antipyrine. International Journal of Chemical Sciences, 15(1).

Lever, A.B.P. (1984). Inorganic electronic spectroscopy, 2nd ed.; Elsevier New York, 101-670.

Choudhary, G. L., & Kumar, A. (2020). Synthesis and spectral characterization of Co(II), Ni(II), and Cu(II) complexes of quinoline based schiff bases (QBSB). International Journal in Physical and Applied Science, 07, 70-75•

Silversteins, R. M., Webster, F. X., & Kiemle, D. J. (1976). Spectrometric identification of organic compounds, John Wiley and Sons..

Reddy, S., Shankara, B. S., Murli Krishan, P., Basavaraj, C., & Mahesh Hindawi B. (2013). Synthesis, characterization, and antibacterial activity of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes of schiff`s base type ligands containing benzofuran moiety. International Journal of Inorganic Chemistry, 1-10.

Hermle, J., & Meyer, G. (2011). Tetra--acetato-bis[(1, 3-benzothiazole)copper(II)](Cu-Cu). Acta Cryst, 67, 1089.

Ahmed, A., Sherif. El, Taha., & Eldebrs, M. A. (2011). Synthesis, thermal and spectral characterization of nano sized NiX, MgXAl2O4 powder as new ceramic pigment via combustion route using 3 – Methyl pyrazole -5-one as fuel. Spetrochimica Acta, Part A, 79, 1803-1814.

Carcelli, M., Mazza, P., Pelizzi, C., & Zani, F. (1995). Antimicrobial and genotoxic activity of 2,6 - diacetylpyridine bis (acylhydrazones) and their complexes with some first

transition series metal ions. X-ray crystal structure. J. Inog. Biochem, 57, 43-62.

El-Sherif, A. A., & Eldebss, T. M. A. (2011). Synthesis, spectral characterization, solution equilibria, In vitro antibacterial and cytotoxic activities of Cu(II), Ni(II), Mn(II), Co(II) and Zn(II) complexes with schiff base derived from 5-bromosalicylaldehye and 2- aminomethylthiophene. Spectrochimica Acta Part A, 79, 1803-1814.

A.L. Koch. (2003). Bacterial Wall as Target for Attack: Past, Present, and Future Research. clin. Microbial. Rev, 16, 673.

Tweedy, B. G. (1964). Synthesis, characterization and antibacterial activity of mixed ligand (HL) complexes Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) with azide(N3-). Phytology, 55, 910.

Chohan, Z. H., Arif, M., Akkhtar M., & Supuran C. T. (2006). Metal-based antibacterial and antifungal agents: Synthesis, characterization, and In vitro biological evaluation of Co(II), Cu(II), Ni(II) and Zn(II) complexes with amino acid-derived compound. Bioinorganic Chemistry and Applications, 1-13.

Nagesh, G. Y., & Swamy, B. H. M. M. (2015). Synthesis, characterization and biological relevance of some metal (II) complexes with oxygen, nitrogen and oxygen (ONO) donor schiff base ligand derived from thiazole and 2-hydroxy-1-napthaldehyde. J. Mol. St, 1085, 198.

Saghatforoush, L. A., Chalabian, F., Aminkhani, A., Nezhad, G. K., & E, Ershad. (2009). Synthesis, spectroscopic, characterization

and antibacterial activity of new Co(II) complexes of unsymmetrical tetradentate (OSN) schiff base ligand. European Journal of Medicinal Chemistry, 44, 4490- 4495.

Chew, K. B., Tarafder, M. T., Crouse, K. A., Ali, A. M., Yamin B. M., & Fun, H. K. (2004). Synthesis, characterization and bioactivity of metal complexes of bidentate N-S-isomeric schiff base derived from S- methyl dithio corhazate [SMDTC] and the X-ray structure of the bis[S(2-furyl-methyl-β-N-2-uryl methyl ketone)]dithiocarbazate cadmium(II) complex. Polyhedron, 23, 1385-1392.

Kumar, A., & Kumar, A. (2022). In vitro microbial study of metal complexes Cu(II) with reference to schiff base ligand and antibiotics. International Journal of Research in Pharmacy and Pharmaceutical Sciences, 07, 14-19.

Wahab, Z. H. A., Mashaly, M. M., Salman, A. P., Shetray, B. A.

E. L., & Faheine, A. A. (2004). Co(II), Ce(II) UO2 (VI) bis-salicylathothiosemi carbazide complex, thermal studies and antimicrobial activity. Spectro Chem Acta, Part A, 60, 2861.

Sigel, A., & Sigel, H. (1995). Metal ions in biological systems, 1st ed., 1-824.

Kumar, A., & Kumar, A. (2022). In vitro microbial study of metal complexes Cu(II) with reference to schiff base ligand and antibiotics. International Journal of Research in Pharmacy and Pharmaceutical Sciences, 07, 17-18.