



Synthesis, Spectroscopic and Anti-Microbial Assessment of Metal (II) Complexes of Schiff Base Ligand Derived from 4-(Tert Butyl)-O-Phenylenediamine, 5-Nitro Salicylaldehyde and 5-Chloro-2-Hydroxy Acetophenone.

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KEYWORDS

Schiff base;
Metal (II) complexes;
antimicrobial studies.

ABSTRACT

In this study, the metal complexes of Schiff base ligand were synthesized using Nickel (II) acetate tetrahydrate, Zinc (II) acetate dihydrate, and Cadmium (II) acetate dihydrate, in reacting with 4-tertbutyl-o-phenylenediamine, 5-nitro salicylaldehyde, and 5-chloro-2-hydroxyacetophenone, respectively. The UV-Vis, Fourier transform infrared and ESI-Mass spectrometric characterizations enabled the analysis of the synthesized metal complexes. Molar conductivity investigations indicate all complexes are diamagnetic and non-electrolyte in nature. In pursuance of evaluating the chelation effects of metal ions, the Schiff bases and their Nickel, Zinc, and Cadmium complexes have been tested for their antibacterial activities on a variety of pathogens such as *E. coli*, *Klebsiella pneumonia*, *Bacillus subtilis*, and *Staphylococcus aureus*. Additionally, the zone of inhibition method was utilized to test the antifungal activity of the Schiff bases using two different pathogens such as *Candida albicans* and *Aspergillus Niger*.

INTRODUCTION:

In Schiff bases, a single functional group C=N is in its structure, which has wide range of applications with primary amines and carbonyl compounds in various industries including polymers, vitamin market industries, coordination chemistry, analytical chemistry, pigments, dyes, enzymes, and model biomolecules for vitamins and enzymes (1-8). A Schiff base containing aromatic aldehydes is more stable due to its conjugation system. It is unstable and simply polymerizes when Schiff bases contain aliphatic aldehydes. Metal ions can be formed by azomethine nitrogen using Schiff bases that contain amino acids as their ligands. For biological processes to occur, a C=N relationship between azomethine derivatives and heterocyclic compounds containing N, O, and S. Schiff bases are widely known for their antimicrobial properties. The azomethine, in particular, has a very

important chemical and biological role because of the lone electron pair in the nitrogen atoms sp^2 hybridized orbital. Tetra dentate ligand generally tend to form stable complexes with transition metals more effectively than Schiff bases [9-13] due to their chelating properties. The goal of this study was to prepare Schiff base ligand from 5-nitro salicylaldehyde, 5-chloro-2-hydroxyacetophenone and 4-(tert-butyl)-o-phenylenediamine in reacting with metal complexes such as Ni (II), Zn (II), and Cd (II). These studies confirm the formation of complexes between the ligand and metal (II) based on results obtained from the UV-Vis, FTIR, 1H -NMR, ESI-MASS spectra, and P-XRD analysis.



Materials and Procedures:

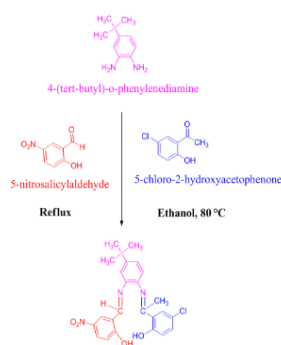
The AR grade chemicals 4-tert-butyl-o-phenylenediamine, 5-nitro-salicylaldehyde and 5-chloro-2-hydroxyacetophenone are used in this work were purchased from Alfa Aesar chemicals. Nickel (II) acetate tetrahydrate, Zinc (II) acetate dehydrate and Cadmium (II) acetate dihydrate, were supplied by Sigma Aldrich. For the synthesis, the chemicals used directly without any further purification.

Characterization:

The Perkin-Elmer spectrophotometer with the range of 4000-400 cm^{-1} was used to record the infrared spectra of the ligand and its compounds. The Bruker Avance-II 400 NMR spectrometer was used to examine the Schiff base ligand with metal complexes, ^1H NMR spectra in DMSO using TMS as an internal standard was recorded by operating at 500 MHz. The ESI-Mass spectrum verified the molecular weight of metal complexes. The produced ligand and metal complexes were examined by UV-visible absorption spectra between 200 and 800 nm.

Synthesis of Schiff base ligand: (L_5)

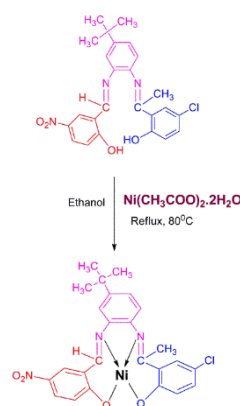
To prepare the solution of 4-tert-butyl-o-phenylenediamine (1.53g, 10mmol), absolute ethanol (20 ml) was stirred and the solution was mixed with a solution of 5-nitrosalicylaldehyde (1.67g, 10mmol) dissolved in absolute ethanol (20 ml) and added to the solution of 5-chloro-2-hydroxyacetophenone (1.70g, 10mmol). A stirring solution is given a magnetic stimulation for 30 minutes to begin the magnetic stimulation. Also, the solution mixture is refluxed for six hours at 80°C and the end product was obtained. After several washes with hot ethanol, the product was dried and stored for the characterization.



Scheme 1: Synthesis of Ligand (L_5)

Synthesis of Nickel (II) complexes: (L_5C_1)

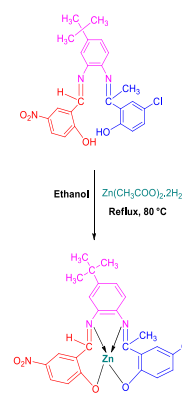
Nickel (II) acetate tetrahydrate (0.5017g, 2mmol) and prepared ligand (0.9078g, 2mmol) are taken 1:1 ratio uniformly and dissolved in ethanol. This mixture was stirred for 30 minutes and refluxed for 80°C for 6 hours. The resulting product was obtained and washed well with hot ethanol and dried. The dried product was used in further characterization.



Scheme 2: Synthesis of Nickel (II) complexes (L_5C_1)

Synthesis of Zinc (II) complexes: (L_5C_2)

The Zinc (II) acetate dihydrate (0.4390g, 2mmol) is uniformly dissolved in ethanol at a 1:1 ratio with the prepared ligand (0.9078g, 2mmol). A 30-minute stirring period was followed by 6 hours of refluxing at 80°C . A good wash with hot ethanol was done, and the resulting product was dried. Further characterization was carried out using the dried product.

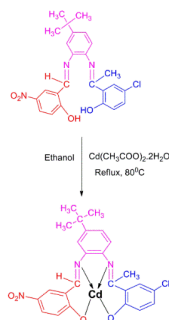


Scheme 3: Synthesis of Zinc (II) complexes (L_5C_2)



Synthesis of Cadmium (II) complexes:(L₅C₃)

A 1:1 mixture is prepared with Cadmium (II) acetate dihydrate (0.5330g, 2mmol) and prepared ligand (0.9078g, 2mmol) in ethanol. After stirring the mixture for 30 minutes, it was subjected to a 6-hour reflux at 80°C. In order to characterize the product, it was rinsed with hot ethanol and dried.



Scheme 4: Synthesis of Cadmium (II) complexes (L₅C₃).

Physical data and Molar conductance:

An instrument for measuring conductance at room temperature was used to prepare ligand and metal complexes at 10⁻³ mol concentrations in the DMF solvent. All complexes behave like non-electrodes based on the observed low molar conductance values of 8.6 -16.4 (Mho cm² mol⁻¹) [14]. The physical data given in table 1.

Table (1) :Physical properties of the of the Ligand and its metal(II) complexes

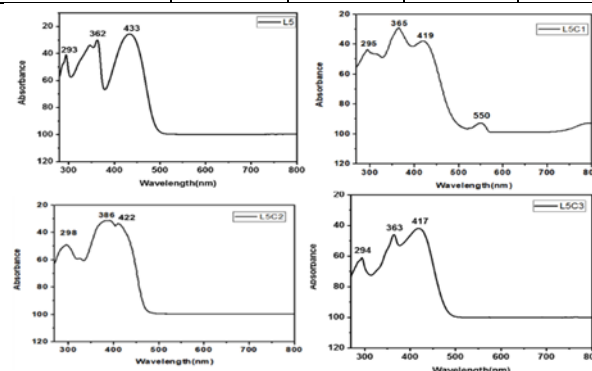
S.No	Compound	Molecular Formula	Molecular weight	Melting Point	Molar Conductance (Mho cm ² Mmol ⁻¹)
1	Ligand	C ₂₄ H ₂₆ ClN ₃ O ₄	453.92	184	-
2	Complex-I	C ₂₅ H ₂₂ ClN ₃ NiO ₄	522.61	190	13.2
3	Complex-II	C ₂₅ H ₂₂ ClN ₃ O ₄ Zn	529.29	188	8.6
4	Complex-III	C ₂₅ H ₂₂ CdClN ₃ O ₄	576.32	186	16.4

UV-Visible Studies:

A UV-visible spectrum was recorded for all the complexes and for the Schiff base ligand in the presence of ethanol. Table 2 lists the UV-visible band corresponding to the given spectral data, as shown in the figure 1. The benzene ring in the ligand π - π^* transition caused the absorption band to appear at 293 nm. In the ligand, there appears to be a transition between azomethine and hydroxyl groups at 362 nm, which can be attributed to this transition. The band at 433nm was due to the ligand n - π^* transition. The benzene ring π - π^* transition band complexes are experimental in the 294-298 nm range. The UV-visible spectrum of the complexes azomethine group's (-HC=N) π - π^* transition band at 363-386nm was confirmed[15]. At 417-422 nm, the complex band can be seen because of a transition between n - π^* . It has been suggested that this complex d-dchange is due to the appearance of a new distinctive band in the range of 550 nm.

Table (2): The UV-Visible spectral data of the Ligand and its metal(II) complexes

Compound	π - π^* (nm)(benzene)	π - π^* (nm) (-HC=N)	n- π^* (nm)	d-d(nm)
L ₃	293	362	433	-
L ₃ C ₁	295	365	419	550
L ₃ C ₂	298	386	422	-
L ₃ C ₃	294	363	417	-





Analysis using an FT-IR spectroscope:

The spectra of the FT-IR measurements provided evidence that the values of the ligand and (Ni(II), Zn(II), and Cd(II)) complexes were appropriate and this information is presented in Table 3. It is presented in figures 2, 2a, 2b and 2c. Illustrating the stretching frequency of the azomethine group (-HC=N) in the peak ligand at 1602 cm^{-1} . It was discovered that the stretching vibration of the C-O ligand was the cause of the peak that was observed at 1324 cm^{-1} . This was realized to determine the cause of the peak. Due to the stretching vibration of the -OH ligand which is responsible for the peak at 3377 cm^{-1} , there was a peak at 3377 cm^{-1} . Among the metal (II) complexes, the azomethine group (-HC=N) was observed to peak at $1549\text{--}1599\text{ cm}^{-1}$ in the metal (II) complexes. A peak appears at 1602 cm^{-1} , which is attributed to vibrations caused by stretching the C-O bond in the ligand, which resulted in the azomethine group shifting from a higher frequency to a lower frequency. C-O bonds were stretched due to vibrations caused by stretching of the C-O bond, thus resulting in a peak appearance at $1288\text{--}1312\text{ cm}^{-1}$. There is a theory that -OH stretching vibrations at $2959\text{--}3301\text{ cm}^{-1}$ are caused by complexes interacting with water molecules through coordination (15-17). A peak was seen at a $434\text{--}479\text{ cm}^{-1}$ frequency within M-O stretching vibrations. In the final phase, Fourier transform infrared spectroscopy was used to verify the presence of the metal and ligand complex. This was accomplished by confirming that the peak at $491\text{--}521\text{ cm}^{-1}$ results from the stretching vibrations of the M-N molecule.

^1H NMR Spectroscopic analysis of Ligand:

For the purpose of this Schiff base ligand ^1H NMR spectra investigation, DMSO d_6 was utilized as the solvent for recording the spectra, and Tetramethyl silane (TMS) as the internal standard. ^1H nuclear magnetic resonance spectrum of the metal complexed Schiff base ligand is shown in figure 3. Because the azomethine group (-HC=N) on the azomethine molecule was present, a multiplet signal was detected at

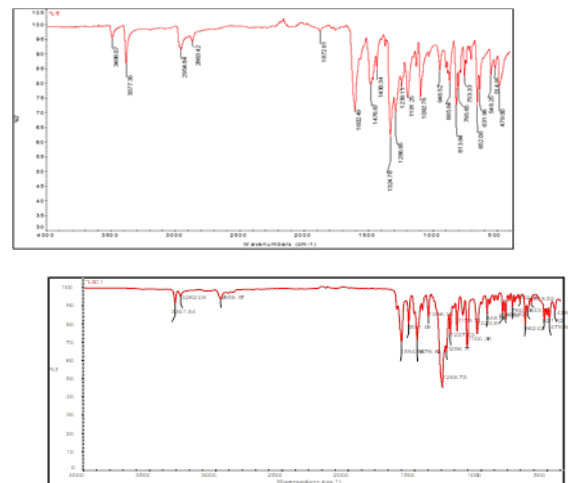


Figure 2(a). FT-IR spectrum of complexes Ni (II)- (L₅C₂)

Figure 1: UV-Visible spectrum of ligand and metal(II) complexes

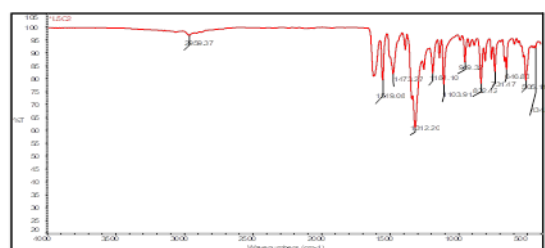


Figure 2(b). FT-IR spectrum of complexes Zn (II)- (L₅C₂)

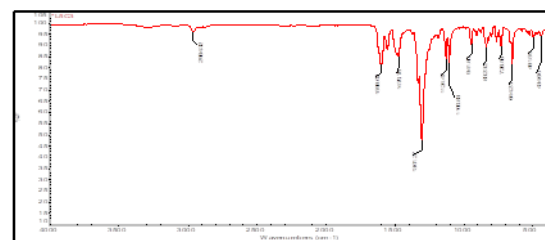


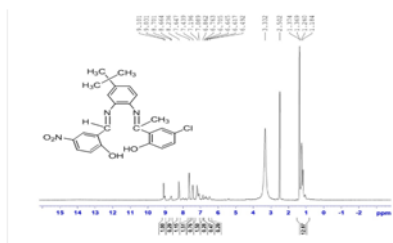
Figure 2(c). FT-IR spectrum of complexes Cd (II)- (L₅C₂)

Figure 2. FT-IR spectrum of ligand (L₅)

a concentration of 9.10 ppm. The CH proton signal was observed to have a frequency of 3.3 ppm in this investigation. The presence of protons resulted in detecting a proton signal at a concentration of 6.49 ppm for aromatic alcohols. The protons that come from the phenolic group are the ones responsible for the 7.6ppm signal, as can be seen in the graph.

**Table (3): The FT-IR spectral data of the Ligand and its metal(II) complexes**

Compound	$\nu(-\text{C}=\text{N})$	$\nu(-\text{C}-\text{O})$	$\nu(-\text{OH})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
L ₅	1602	1324 ⁺	3377	-	-
L ₅ C ₁	1594	1288	3301	479	521
L ₅ C ₂	1549	1312	2959	434	505
L ₅ C ₃	1599	1301	2964	434	491

Figure 3. ¹H NMR Spectrum of Ligand**The ESI Mass spectra of complex Ni (II)**

According to the ESI mass spectrum of complex (I) (L₅C₁), the peak of the (M+2) ion peaks is located at M/Z 524.8146 is shown in figure 4. Data obtained in this study are in good agreement with the molecular formula proposed. This (M+2) peak mass spectra confirm the complex formation.

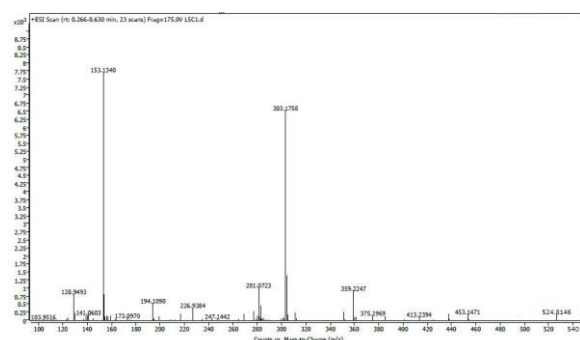


Figure 4. Mass spectrum of Ni (II) complex

A spectrum of Ni (II) complex based on P-XRD:

A powder XRD pattern of Ni (II) complexes recorded in the range of (2 θ = 0–70) is shown in figure 5. XRD patterns indicate the crystalline nature of the metal complexes and indicate that they are amorphous. A

crystallite peak is averaged at 2 degrees in Ni (II) complexes.

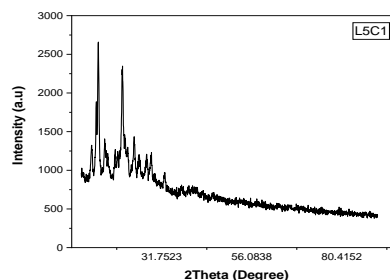


Figure 5. PXRD spectrum of Ni(II) Complex

Antimicrobial Assay:

An antibacterial activity test was conducted on a nutrient agar medium using the disc diffusion method to test the ligand and complexes against *E. coli*, *Klebsiella pneumoniae*, *Bacillus subtilis*, and *Staphylococcus aureus*. The compounds were tested for their biological activity at concentrations of 30, 60, 90, and 120 (l) in DMSO compared to a control (Clotrimazole) at specific concentrations ranging between 30 and 120 (l). The incubation process was carried out on seeded plates at 35°C for 24 hours. A potato dextrose agar medium containing 20 grams of starch was tested for its antifungal efficacy. The extent of the inhibitory zone around each disc was determined by measuring its diameter (mm). In 1000 mL of distilled water, 20g of dextrose and 15g of agar powder were dissolved to make a solution. The compounds were compared to a standard (Chloramphenicol) at the same concentrations and the same position in the body of the test. As part of our investigation, we evaluated the fungicidal activity of the compounds.

In a study evaluating the effectiveness of Schiff base and its metal complexes against Gram-positive bacteria and fungi, we determined that Schiff base and its metal complexes were antimicrobials. The results of antimicrobial screening of ligand and metal complexes are presented in Table 4-5, while the results of antimicrobial screening of ligand and metal complexes are presented in Figure 6-9. The above observations indicate that most of the complexes exhibit quite high activity compared to their free ligand counterparts (18-20).

**ANTIBACTERIAL ACTIVITIES:**

Organisms: *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, *Klebsiella pneumoniae*.

Concentration (μl): 30, 60, 90, 120 Control: Chloramphenicol

Organisms	Sample Code	Control	Concentration (μl)			
			30	60	90	120
<i>Escherichia coli</i>	L5	19	17	20	22	25
	L5C1	20	19	21	23	26
	L5C2	19	14	17	19	22
	L5C3	20	16	19	21	24
<i>Bacillus subtilis</i>	L5	21	12	15	17	19
	L5C1	22	14	16	19	21
	L5C2	22	9	12	14	16
	L5C3	22	12	14	16	18
<i>Staphylococcus aureus</i>	L5	22	16	18	20	22
	L5C1	21	18	20	22	24
	L5C2	22	12	14	16	19
	L5C3	21	14	16	18	20
<i>Klebsiella pneumoniae</i>	L5	19	14	16	19	21
	L5C1	19	16	18	20	22
	L5C2	19	10	12	15	17
	L5C3	20	12	15	17	19

Table 4: Antibacterial Activities of zone of inhibition of ligand and metal(II) complexes at various concentration

According to chelation theory, metal chelates can be made to have increased activity under certain conditions and this may be explained by the chelation theory [21]. In general, chelation is a process where the ligand acts as an enhanced bactericidal agent, killing more bacteria than the ligand alone does without chelation. In the complex, the positive charge of the metal is partially exchanged with the donor atoms in



the ligand, and there is a possibility that the electrons in the donor atoms could be delocalized during the chelating process. A lipophilic metal chelate is more likely to penetrate the lipid layer of the bacterial membrane because of this. In general, chelated complexes are thought to deactivate a variety of cellular enzymes essential to these organisms metabolism. The presence of metal ions may also affect solubility, conductivity, and dipole moment, which may contribute to increased biological activity of metal (II)

complexes compared to the corresponding ligand. The ligand and complexes had a lower biological activity than the standard used. In addition to having a good zone of inhibition against all four microorganisms, the complex L_5C_1 also exhibits a good zone of inhibition against Nickel(II), Zinc (II) and Cadmium (II) complexes.

Thus, the complexes show a significant inhibition against the selected microorganisms, demonstrating their antibacterial properties.

Antibacterial Activity of Graphical Representation of Ligand and its Metal (II) Complexes

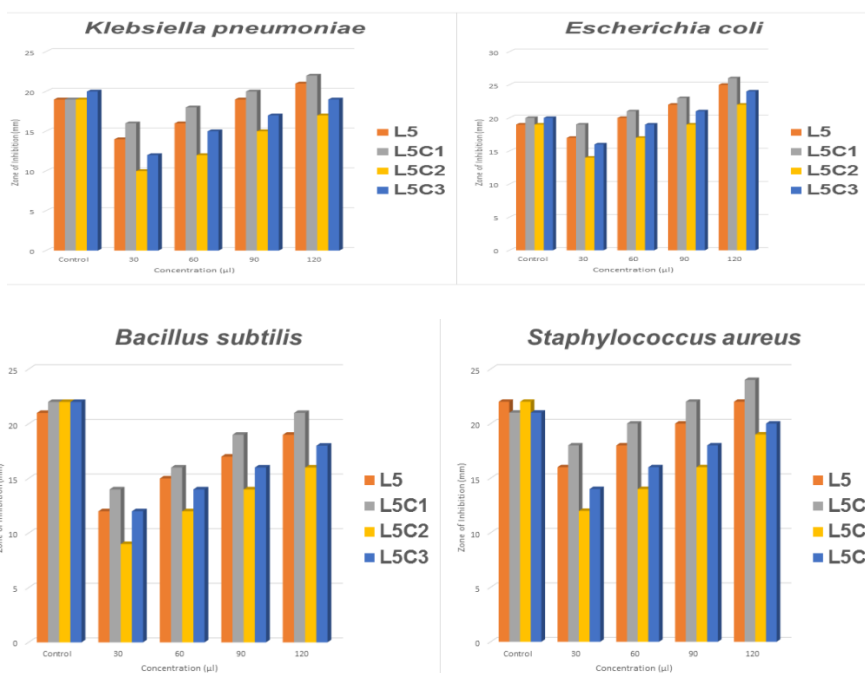
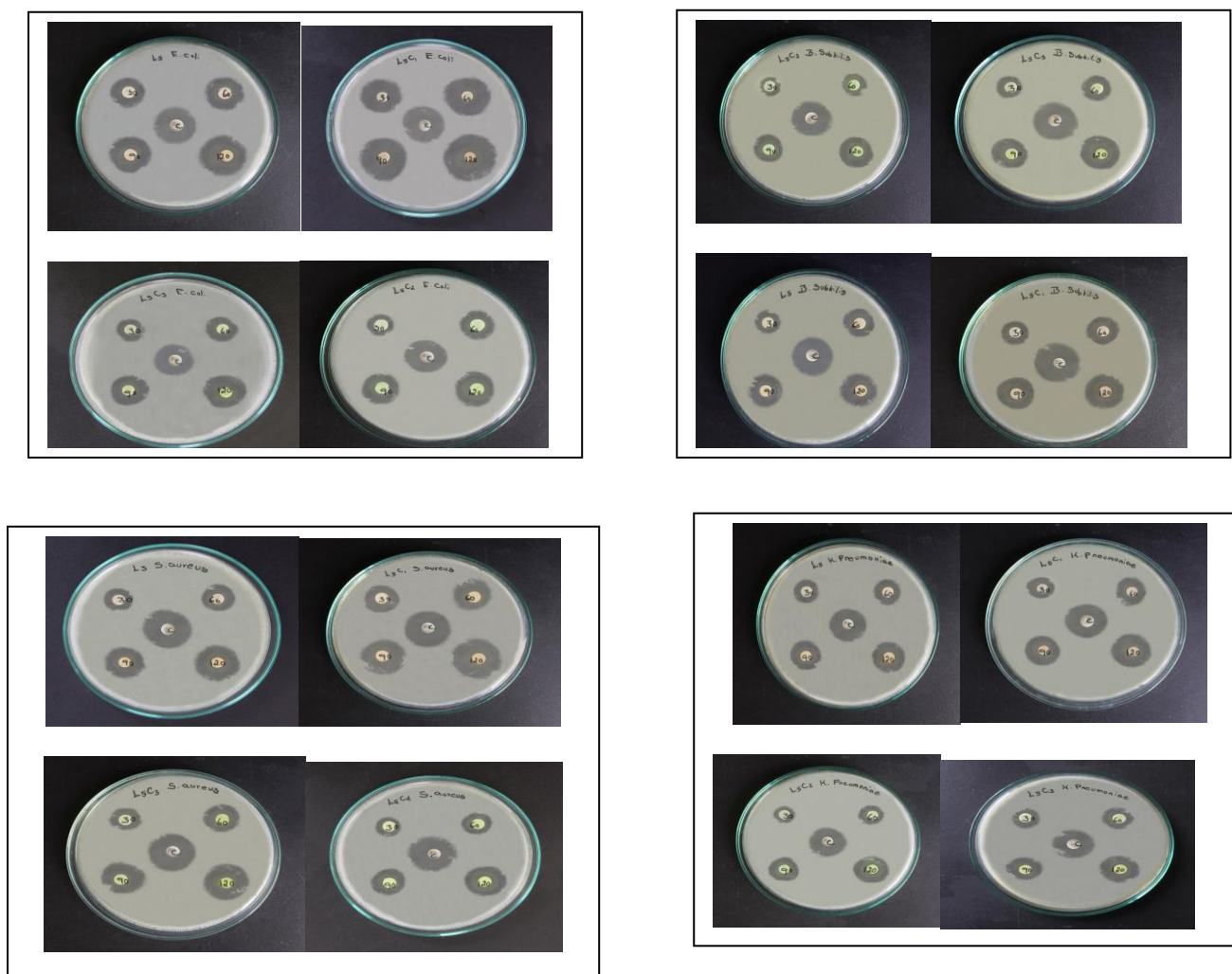


Figure:6 Graphical Representation of Ligand and its Metal (II) Complexes



Figure 7:Antibacterial Activity of zone of Inhibition of Ligand and its Metal (II) Complexes



ANTIFUNGAL ACIVITIES:

Organisms: *Candida albicans* and *Aspergillus niger*

Concentration (μ l): 30, 60, 90, 120 Control: Clotrimazole

Organisms	Sample Code	Control	Concentration (μ l)			
			30	60	90	120
<i>Candida albicans</i>	L5	24	15	17	19	22
	L5C1	24	17	19	21	24
	L5C2	24	13	15	17	19



	L5C3	23	11	13	15	17
<i>Aspergillus niger</i>	L5	21	17	19	21	23
	L5C1	22	19	21	23	25
	L5C2	22	13	15	17	20
	L5C3	22	15	17	19	22

Table 5: Antifungal Activities of zone of inhibition of ligand and metal(II) complexes at various concentration

Aspergillus niger is more effectively controlled by Nickel (II), Zinc (II) and Cadmium (II) complexes in fungicidal screening. Antifungal activity of Nickel (II), Zinc (II) and Cadmium (II) complexes has been demonstrated. The L_5C_1 complex demonstrates good antifungal activity against two microorganisms.

Antifungal Activity of Graphical Representation of Ligand and its Metal (II) Complexes

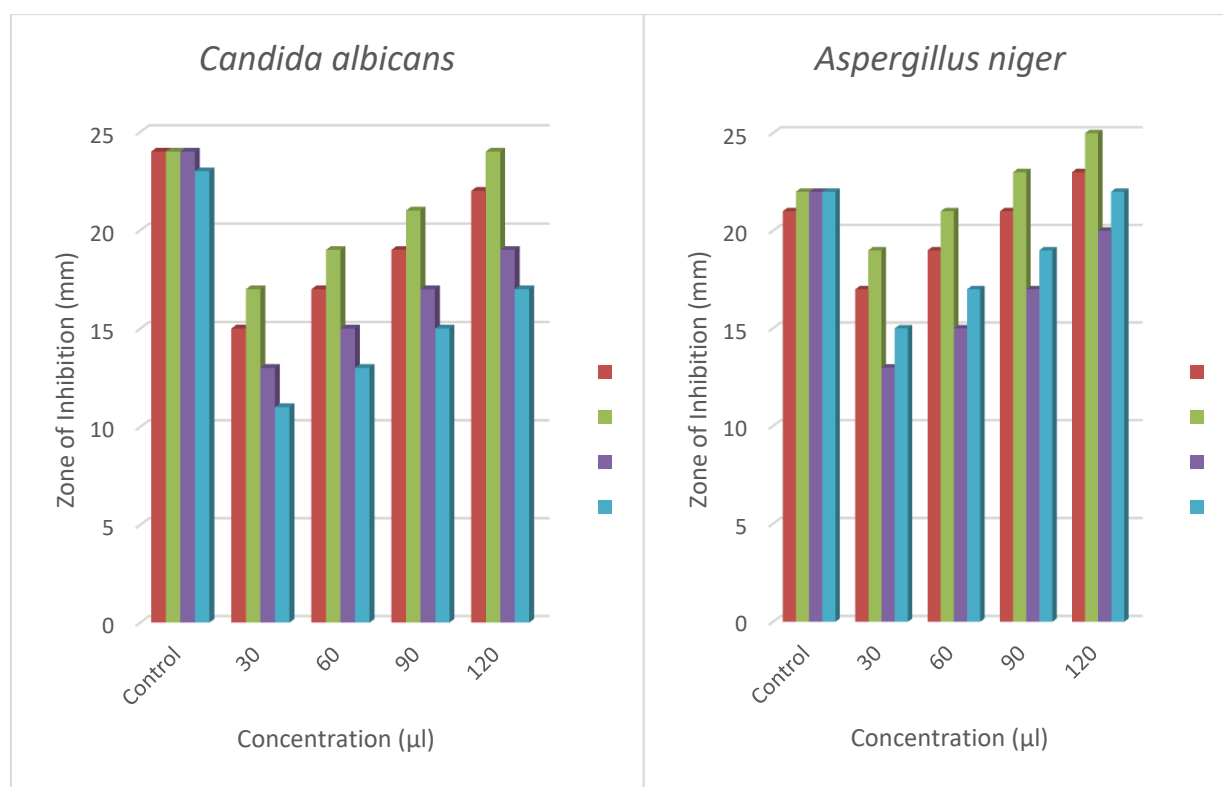
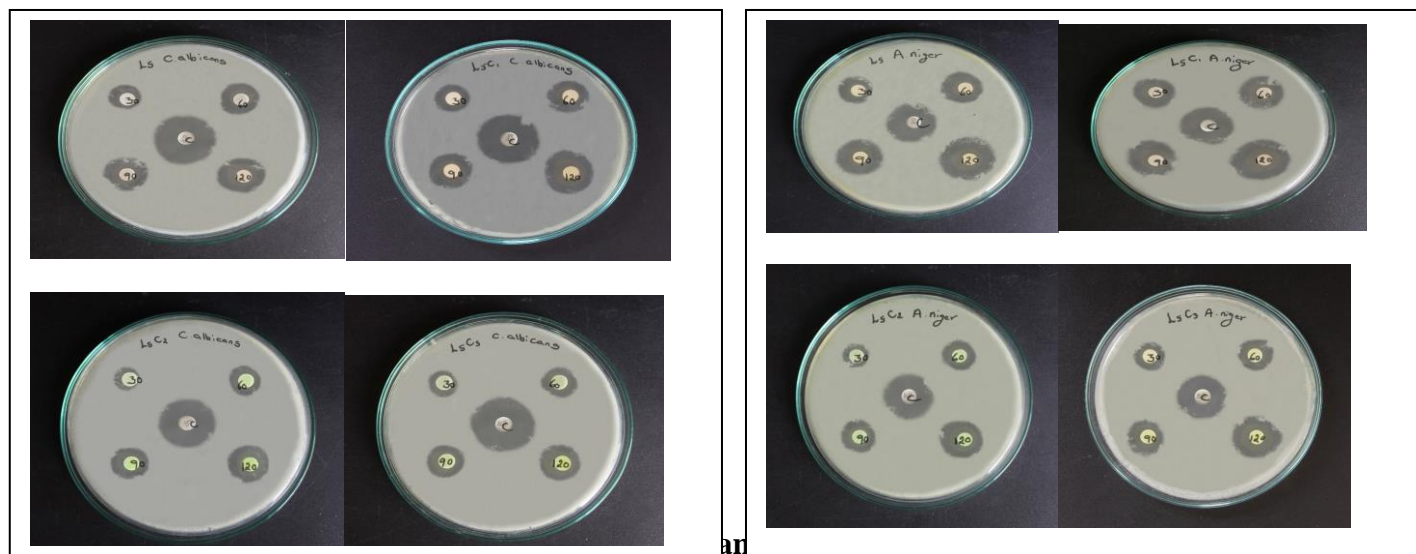


Figure:8 Graphical Representation of ligand and its Metal (II) Complexes



Antifungal Activity of Zone of Inhibition of Ligand and its Metal (II) Complexes



Conclusion:

The Schiff base ligand was synthesized by condensation of 4-tert butyl-o-phenylenediamine, 5-nitro salicylaldehyde, and 5-chloro-2-hydroxy acetophenone in combination with the three different appropriate nickel (II), zinc (II), and cadmium (II) complexes. UV-visible, FTIR, $^1\text{H-NMR}$ analysis were used to examine the ligand characteristics. Several techniques were used to analyze the structures of the produced compounds, including molar conductance, UV-Vis, FTIR, ESI-Mass spectrum analysis, and XRD studies. An in vitro investigation of transition metal (II) complexes with ligand was conducted to determine their antibacterial activity. The complexes of Nickel (II), Zinc (II), and Cadmium (II) show good antibacterial activity based on their zones of inhibition. L_5C_1 shows good antibacterial activity against each of the four tested bacteria tested. Furthermore, the complexes are antibacterial activity because they exhibit considerable inhibitory effects against the selected microorganisms. According to the results of the fungicide screen of Nickel (II), Zinc (II) and Cadmium (II) complexes were more effective at inhibiting *Aspergillus niger* than Nickel (II), Zinc (II), and Cadmium (II). A strong correlation exists between

the L_5C_1 complex and excellent inhibition compared to every other tested microbes.

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