

Synthesis, Physicochemical and Antimicrobial Studies of Schiff base derived from 2, 4-dinitrophenyl hydrazine with Salicylaldehyde and its Co (II) and Ni (II) Complexes

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ABSTRACT

A Schiff base ligand derived from salicylaldehyde and 2, 4-dinitrophenylhydrazine was synthesized, along with its Co(II) and Ni(II) complexes (CoL₂ and NiL₂). These compounds were characterized by melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility, infrared analysis, and UV-visible spectrophotometry. The metal-ligand ratio in the complexes is 1:2. All complexes exhibited low molar conductance values (5.2-11.0), indicating their non-electrolytic nature. The synthesized ligand and its metal (II) complexes were evaluated for antibacterial activity against five bacterial isolates (*Escherichia coli*, *Proteus mirabilis*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*) and three fungal isolates (*Fusarium solani*, *Aspergillus fumigatus*, and *Candida albicans*) using the well diffusion method. The results demonstrated that the metal complexes exhibited greater antimicrobial activity compared to the Schiff base ligand.

Keywords: Isolates, Conductance value, Synthesis, Non-electrolytic, *Fusarium solani*

INTRODUCTION

Schiff bases metal complexes have occupied a central place of importance in the development of coordination Chemistry. The literature on these complexes ranges from the purely synthetic to modern Physico-chemical as well as biochemically relevant studies. Many Schiff base complexes are found to have antibacterial, antifungal, anti-inflammatory and antileukaemic [1]. Since then, a large number of Schiff base complexes have been prepared and even now they comprise the major portion of the current literature on coordination chemistry. The chemistry of Schiff bases and their complexes has been repeatedly reviewed by several workers [2]. A Schiff base (or azomethine), is named after its inventor, Hugo Schiff and it is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen. Schiff bases have the general formula of R₁R₂C=NR₃, where R₃ is an aryl or alkyl group that makes the Schiff base a stable

imine [3]. Generally Schiff bases are prepared under acid or base catalysis or with heat (Sheikh and Muhammad 2010). Schiff bases can be synthesized from a reaction of an aromatic amine and a carbonyl compound by a nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine. Schiff base form an important group of compounds in chemistry due to their useful physical and chemical properties and large number of reactions they undergo. They have wide use in industry due to their interesting pharmacological activity. Schiff bases exhibit excellent characteristics and structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural scaffolds [3]. The synthesis of the coordination compounds of the Schiff's base ligands having N, S-donor binding sites has attracted a considerable attention because of their potential biological activities [4]. The main features

of these compounds are their preparative accessibility, diversity, structural variability and versatile coordinating properties [5]. Schiff bases derived from aromatic aldehydes are more stable than those derived from lower aliphatic aldehydes and primary aromatic amines. Schiff bases can be used in the degradation of organic compounds and in radiopharmaceuticals [6]. Transition metals have an

outstanding ability to form complexes by accepting a number of lone pair electrons from the ligands [7]. Schiff base may be bidentate, tridentate, tetradentate, pentadentate (polydentate) if the number of donor atoms present in one molecule of the ligand attached to the central metallic atom is 2,3,4 and 5 respectively [8].

MATERIALS AND METHODS

All the reagents used were analytic grade and salicylaldehyde and 2, 4 – nitrophenyl hydrazine were obtained from Sigma-Aldrich. All the solvents were used without further purification. The glassware used were washed with detergent, rinsed with distilled water and dried in an oven at 110°C before used. Electric balance model H30AR was used for weighing. Melting/decomposition temperature were determined using Gallen Kamp melting point apparatus. Molar conductance measurements were

carried out in DMSO using Denver instrument model 20. Jenway 6305 uv-visible spectrophotometer was used for uv-visible analysis. IR spectra of the Schiff base and metal (II) complexes were recorded using Scimadzu FT-IR Fourier transform spectrophotometer in the range 4000 – 400cm⁻¹. Microbial and fungal identification as well as studies were carried out at the department of Microbiology, Bayero University Kano Nigeria.

Preparation of Schiff base

The Schiff base ligand was obtained by the condensation of equimolar mixture of salicylaldehyde (10mmol=1.08cm³) with 2, 4-dinitrophenylhydrazine (10mmol=1.198g) in ethanol and then refluxed on a hot plate with stirring for

3hrs. The orange crystalline solid obtained was filtered, washed with ethanol and then recrystallized from methanol and dried in a desiccator over calcium chloride (CaCl₂) for three days [9, 10,11].

Preparation of Complexes

A solution of Schiff base was prepared in a round bottom flask by dissolving 10mmols (2.66g) of the Schiff base in 30cm³ of methanol. A hot methanolic solution of 5mmols of the respective metal (II) and (III) chloride was mixed with the Schiff base solution

and refluxed for 4hrs with continuous magnetic stirring. On cooling, a coloured complex was separated, filtered, washed with methanol and diethyl ether and then dried in desiccator for three days [12, 13, 14].

Determination of Number of Coordinated Ligand

3mmolar dimethyl sulphoxide (DMSO) solution of the ligand and the metal chlorides were prepared. The following ligand to Metal salt ratio (ml); 1:15, 3:13, 5:11, 7:9, 9:7, 11:5, 13:3, 15:1 were taken from the ligand solution and each of the metal chloride solution respectively. A total volume of 16ml was maintained (in that order) throughout the process and the mole fraction of the ligand was calculated in each mixture. The solution of the metal chlorides

were scanned (as blank) to find the wavelength of maximum absorption (λ_{max}) for that particular metal ion. The machine was fixed at λ_{max} (in each case) before taking the absorbance values. The absorbance values were extrapolated against mole fraction of the ligand and the number of coordinated ligand (coordination number) was determined [15, 16].

Molar Conductivity Measurement of the Complex

Solution of each metal (II) complex (0.001mol/dm³) was prepared in DMSO and molar conductance was measured.

2000 and 1000 µg/well of the Schiff base and the metal complexes. Wells (6mm in diameter) were dug in the agar media with the help of a sterile metallic borer. Ciprofloxacin 5µg/disc was used as controls. The wells were incubated immediately at 37°C for 24hrs. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard [4].

Antibacterial Activity

The antibacterial activity of Schiff base (C₁₃H₁₀O₅N₄) and its metal (II) complexes were assayed against five bacterial isolates (*Escheria coli*, *Proteus mirabilis*, *Klebsiella pneumoniae*, *Pseudomonas aureginosa* and *Staphylococcus aureus*) by the reported method. The suspension of each microorganism was rubbed onto the surface of solidified nutrient agar (N.A.) already poured into Petri dishes with swap stick. The stock solution was suitably diluted to get dilution of 4000,

Antifungal Activity

The antifungal activity of Schiff base (C₁₃H₁₀O₅N₄) and its metal (II) complexes was assayed against three fungal species (*Fusarium solani* *Aspergillus fumigate* and *Candida albicans*) by the reported

method. The suspension of each microorganism was rubbed onto the surface of solidified potato dextrose agar (PDA) already poured into Petri dishes with swap stick. The stock solution was suitably diluted to get dilution of 4000, 2000 and 1000 µg/well of the Schiff base and the metal complexes. Wells (6mm in diameter) were dug in the agar media with

the help of a sterile metallic borer. Manozef µg/well was used as the control. The wells were incubated immediately at 37°C for 48hrs. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard [4].

RESULTS AND DISCUSSION

The condensation of ethanolic solution of salicylaldehyde (10mmol=1.08cm³) with 2,4-dinitrophenylhydrazine (10mmol=1.198g) in a ratio 1:1 produced an orange crystalline solid Schiff base ligand with a percentage yield of 67.22, it is soluble in common organic solvents but insoluble in water. The Schiff base further reacted with 3d metal ion in a ratio 1:2 and produced the respective coloured Metal (II) complexes with a percentage yields of 89.67 and 81.68 respectively (Table 2). The result showed that the Schiff base and the complexes are all coloured. This is due to charge transfer spectra of the d-d transition whose spacing or splitting correspond to the wavelength available in the visible region [15, 16, 17] the magnitude of the splitting depends on the geometry of the metal complex, oxidation state of the central metal and the nature of the ligand, whether it is weak field ligand, that causes small separation or strong field ligand that causes large energy separation. The charge transfer occur when an electron jumps from a predominantly ligand orbital to predominantly metal orbital, giving rise to a ligand-to-metal charge-transfer (LMCT) transition. The melting point of the synthesized Schiff base is 220 were found to be sharp (melting point range ±0.5°C) indicating high purity. The decomposition temperatures of it corresponding metal (II) complexes of Co(II) and Ni(II) are in the range 250°C and 246°C respectively (Table 1). All the metal (II) complexes have high decomposition temperature suggesting that they thermally stable and cannot be easily decompose. The stability of the complexes is attributed to chelate effect of the ligand which can be explained in thermodynamic terms by large value of stability constant, positive enthalpy (H) and negative entropy (S) [16,17]. The solubility tests carried out on the ligand and its Nickel (II) complex revealed that they are soluble in most common organic solvents but slightly soluble in methanol and acetone and insoluble in water (Table 2). The molar conductance measurements of the complexes in 10⁻³ M dimethylsulphoxide are in the range 5.2 – 11.0 ohm⁻¹CM⁻² Mol⁻¹, which are relatively low, indicating their non-electrolytic nature (Table 3). The FT-IR spectra data of the relevant functional groups of the Schiff base and the change in absorption frequencies in their

corresponding transition metal (II) complexes on chelation are presented in table 4. This enable metal - ligand chelation mode, hence the geometry of the complexes to be determined. In the spectra of the free schiff base, a broad band at 3268cm⁻¹ assigned to ν(O-H) stretching vibration which disappeared in the spectra of all the complexes as shown in table 4. The strong peak at 1616cm⁻¹ is attributed to azomethine ν(C=N) group [18]. On chelation these absorption band shifted to lower frequencies (bathochromic shift) at a range 1615-1618cm⁻¹ are all observed for Co (II) and Ni (II) metal complexes prepared, which indicate the participation of the azomethine nitrogen in coordination to the metal ions [19, 20]. This is due to the increase in electron density and force constant of the metal with azomethine nitrogen lone pair. At low frequency, peak of strong and medium intensity with absorption bands at 608-620 and 405-412cm⁻¹ in the metal(II) chelates, respectively are assigned to ν(M-N) and ν(M-O) stretching vibration respectively which confirms the coordination of metal ions through azomethine nitrogen and phenol oxygen resulting from the deprotonation of phenol, as shown in Table 4. The magnetic susceptibility measurements provide information regarding the structure of the metal complexes. The magnetic moment value of Co (II) complex is 1.50 BM. The magnetic moment value Ni (II) complexes are zero. These indicates the diamagnetic character of Ni (II) complexes. The metal (II) complexes have tetrahedral geometry. The synthesized ligands and its metal (II) complexes were screened for their antibacterial activity against five bacterial isolates viz; *E. coli*, *S. aureus*, *P. aureginosa* and *K. Pneumoniae* *S. aureus* and antifungal activity against three fungal species (*C. albicaus*, *F. solani* and *A. fumigates*). The results of these studies revealed that all the compounds and the ligand showed significant antibacterial and antifungal potency. The ligand showed lower activity against the isolates compared to the complexes. The result is shown in Table 5 and 6 below. From the analyses of the complexes the general molecular structure has been proposed below:

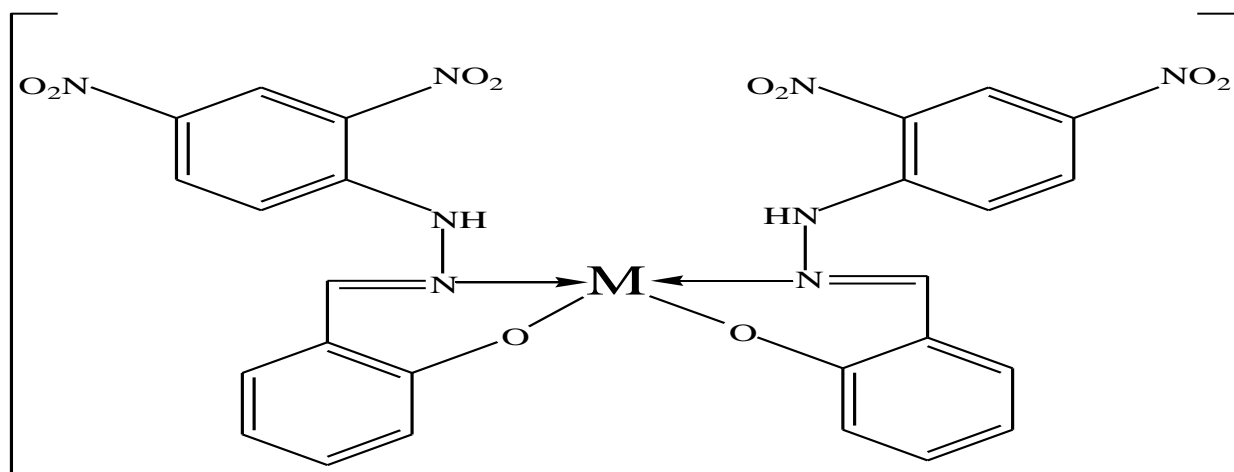


Figure 1a: Co and Ni

Key; M=Co, Ni.

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

Compound	% Yield	Colour	Melting/ Decomposition Temperature (°C)
L	67.22	Pale Orange	220
[CoL ₂]	89.67	deep Orange	250
[NiL ₂]	81.68	Orange	246

Table 2: Magnetic moment values of the Metal (II) Complexes

Complexes	Xg(g ⁻¹)	Xm(mol ⁻¹)	μ _{eff} (BM)	Property
[CoL ₂]	1.44x10 ⁻⁶	944x10 ⁻⁶	1.50	Paramagnetic
[NiL ₂]	-	-	Dia	Diamagnetic

Table 3: Solubility of Schiff base and its Metal (II) Complexes

Compound	H ₂ O	MeOH	EtOH	Acetone	DMF	DMSO
L	IS	SS	S	SS	S	S
CoL ₂	IS	SS	S	SS	S	S
NiL ₂	IS	SS	S	SS	S	S

IS= Insoluble, SS= Slightly soluble and S= Soluble

Table 4: Infrared Spectral Data

Compound	- OH (cm ⁻¹)	- C = N (cm ⁻¹)	M - N (cm ⁻¹)	M - O (cm ⁻¹)
L	3268	1616		
CoL ₂		1618	608	405
NiL ₂		1615	620	412

Table 5: Determination of Ligand to Metal ratio for Nickel (II)

Vol of 0.003M Zn ²⁺ (cm ³)	Vol of 0.003M Schiff base (cm ³)	Mole Fraction Schiff Base	Absorbance
7.5	0.5	0.0275	0.180
6.5	1.5	0.1125	0.776
5.5	2.5	0.3875	0.980
4.5	3.5	0.4625	1.282
3.5	4.5	0.575	1.881
2.5	5.5	0.6125	1.988
1.5	6.5	0.6875	1.106
0.5	7.5	0.7625	0.834

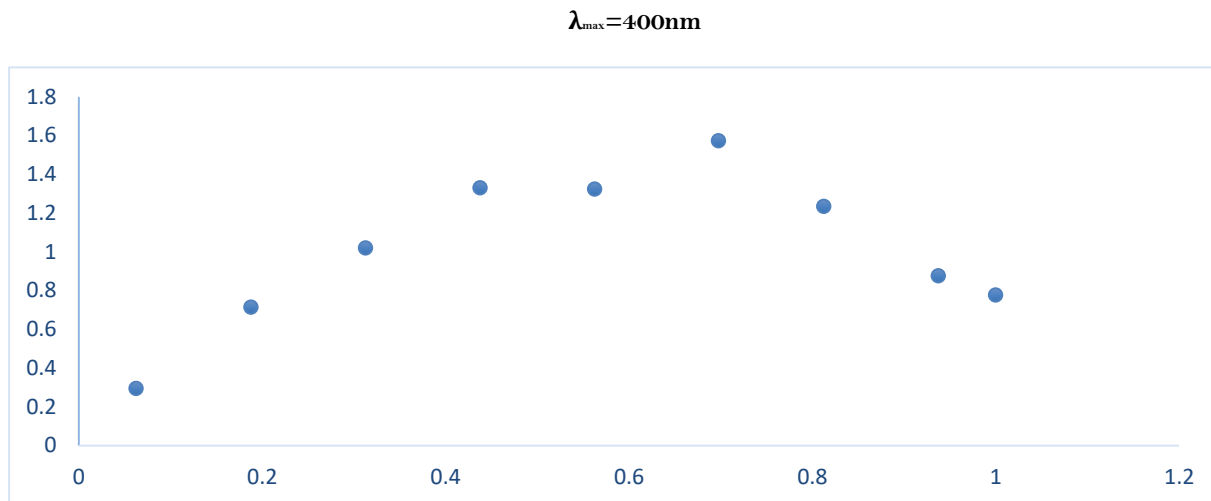


Fig. 1. Plot of Absorbance of Ni²⁺ - Schiff base against Mole fraction

Table 6: Determination of Ligand to Metal ratio for Cadmium (III)

Vol of 0.003M Zn ²⁺ (cm ³)	Vol of 0.003M Schiff base (cm ³)	Mole Fraction Schiff Base	Absorbance
7.5	0.5	0.04321	0.1128
6.5	1.5	0.1125	0.776
5.5	2.5	0.3875	1.180
4.5	3.5	0.4250	1.282
3.5	4.5	0.5375	1.391
2.5	5.5	0.7125	1.498
1.5	6.5	0.8875	1.189
0.5	7.5	0.9625	0.183

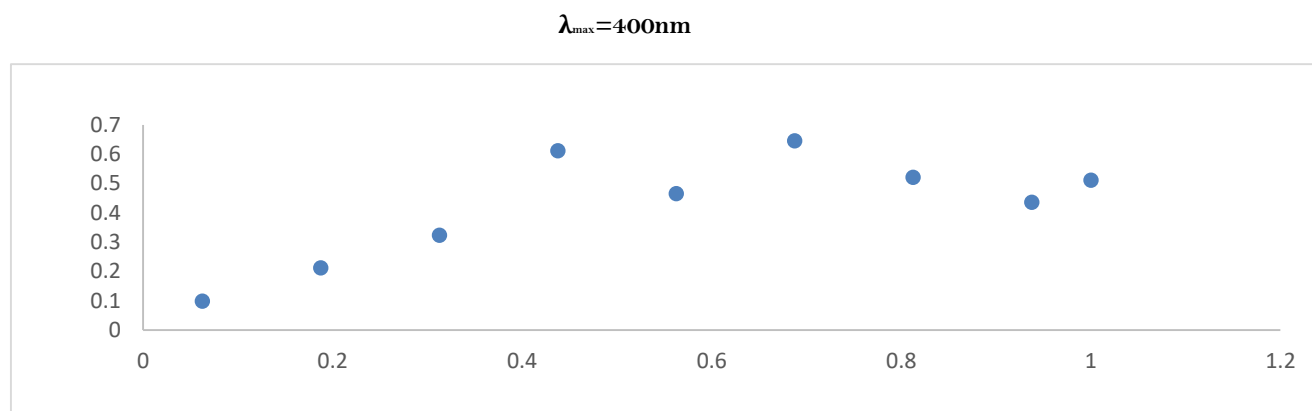


Fig. 2. Plot of Absorbance of Cd³⁺ - Schiff base against Mole fraction

Table 7: Antibacterial Activity Profile of the Compounds

Isolates / Conc. (ug/ml)	L			[CoL ₂]			[NiL ₂]			Control
	1000	2000	4000	1000	2000	4000	1000	2000	4000	
<i>Proteus mira.</i>	11	14	14	08	09	10	12	14	14	25
<i>E. Coli</i>	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI	25
<i>P. aureginosa</i>	NZI	NZI	12	NZI	14	14	12	12	14	29
<i>kleb. Pneumonie</i>	09	10	11	NZI	NZI	NZI	9	10	10	06
<i>Stap. Aureus</i>	12	14	14	10	11	15	NZI	10	10	25

NZI=No Zone of Inhibition

Table 8: Antifungal Activity Profile of the Compounds

Isolates / Conc. (ug/ml)	L			[CoL ₂]			[NiL ₂]		
	1000	2000	4000	1000	2000	4000	1000	2000	4000
<i>C. albicans</i>	NZI	NZI	NZI	NZI	NZI	NZI	09	10	17
<i>F. solani</i>	NZI	NZI	NZI	NZI	NZI	09	NZI	NZI	NZI
<i>A. fumigate</i>	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI

L= C₁₃H₁₀O₅N₄

NZI=No Zone of Inhibition

CONCLUSION

A Schiff base ligand derived from salicylaldehyde and 2, 4-dinitrophenylhydrazine were synthesized on the basis physical, spectral and analytical data. The synthesized Schiff base were neutral and adopted same chelating modes with the respective Co²⁺ and Ni²⁺ through N-O donor sides. The synthesized Schiff base their Ni (II) and Co (II) complexes were synthesized successfully and characterized on the basis of melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility infrared analysis and UV visible spectrophotometry. Characterization showed the complexes to be non-electrolytes, with variable degree of solubility in water and common organic solvents. The Schiff base behaves as bidentate ligand and is coordinated to the central metal ion through the azomethine and O from the hydroxyl

group. The metal (II) complexes have tetrahedral geometry. The synthesized ligands and its metal(II) complexes were screened for their antibacterial activity against five bacterial isolates viz; *E. coli*, *S. aureus*, *P. aureginosa* and *K. Pneumoniae* *S. aureus* and antifungal activity against three fungal species (*C. albicans*, *F. solani* and *A. fumigates*). The results of these studies revealed that all the compounds and the ligand showed significant antibacterial and antifungal potency. The ligand showed lower activity against the isolates compared to the complexes. The ability of these compounds to show antimicrobial activity indicates that they can be further evaluated for medicinal and/or environmental application.



PLATE 1: SHOWING THE ZONE OF INHITION OF SHIFFBASE



PLATE 2: SHOWING THE ZONE OF INHIBITION OF Ni (II) COMPLEX

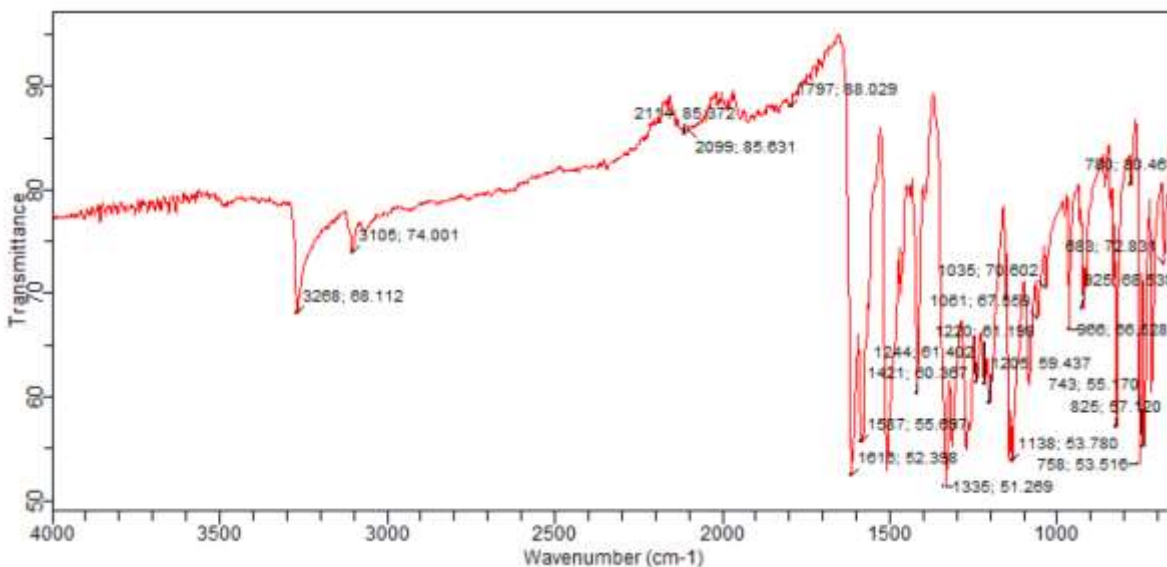


PLATE 3: SHOWING THE ZONE OF INHITION OF Co (II) COMPLEX

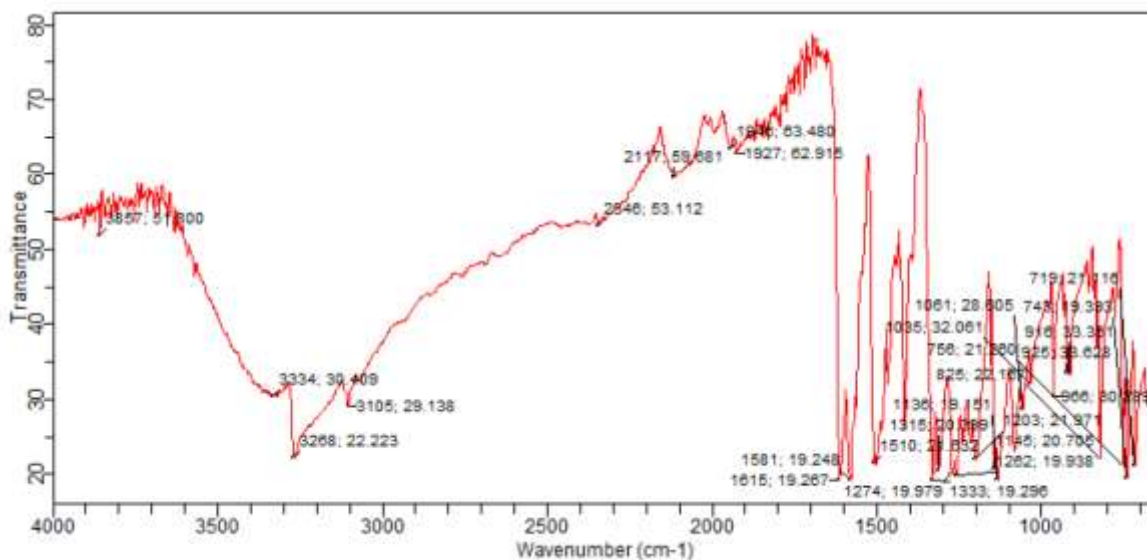


PLATE 4: ANTIFUNGAL RESULT AGAINST *Canadida Albicans* WITH (COL)

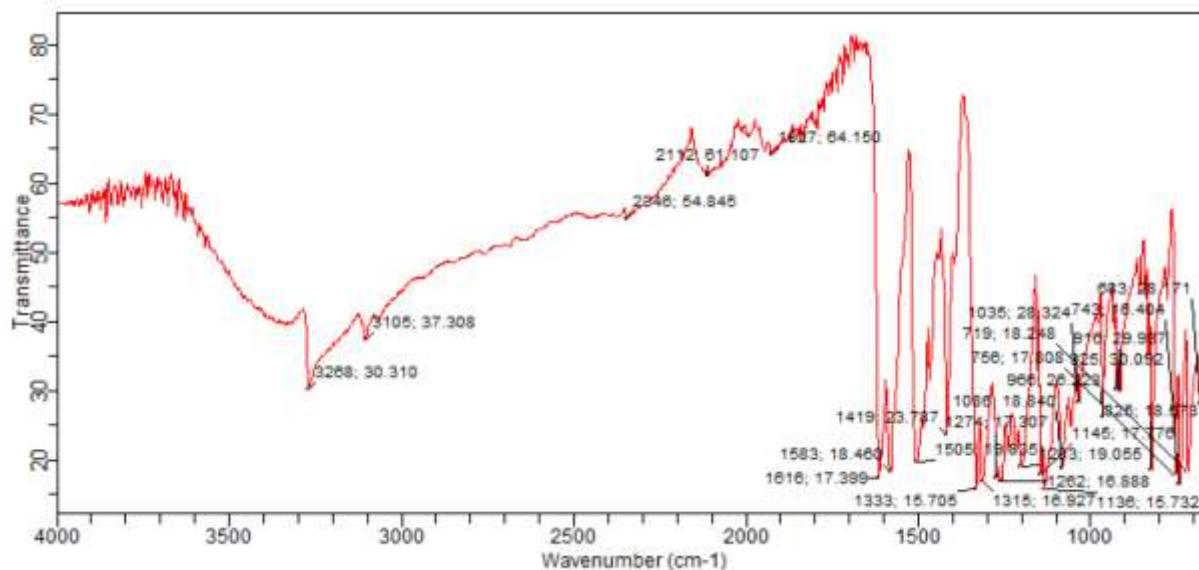
Appendix 1a: Infrared spectral of L



Appendix 1b: Infrared spectral of Ni (II) complex



Appendix 1c: Infrared spectral of Co (II) complex



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