SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITIES OF SCHIFF BASE DERIVED FROM THIOUREA AND ANISALDEHYDE AND ITS FIRST ROW TRANSITION METAL (II) COMPLEXES

BY

BASHIR UMAR SAMBO
SPS/12/MCH/00041

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NOVEMBER, 2016

DECLARATION

I hereby declare that this work is the product of my own research efforts; undertaken under the supervision of Dr. IBRAHIM TAJO SIRAJ and has not been presented and will not be presented elsewhere for the award of a degree or certificate. All sources have been duly acknowledged.

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BASHIR UMAR SAMBO Date
SPS/12/MCH/00041

CERTIFICATION

This is to certify that the research work in this dissertation and its subsequent preparations by BASHIR UMAR SAMBO SPS/12/MCH/00041 were carried out under my supervision.

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Dr. I. T. Siraj
Supervisor

Date

APROVAL PAGE

This is to certify that this dissertation has been examined and approved for the award of Master of Science Degree in INORGANIC CHEMISTRY

_____	_____
External Examiner	Date
_____	_____
Internal Examiner	Date
_____	_____
Dr. I. T. Siraj Supervisor	Date
_____	_____
Dr. H. Musa Head of Dept/Chief Examiner	Date
_____	_____
Dr. Nafiu Hussaini Faculty of Science SPS Representative	Date

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DEDICATION

I would like to dedicate this work to my mother Haj. Rabiat Umar Sambo and my Late Father Alh.Umaru Sambo. May Almighty Allah (S.W.T) reward them with Jannatul Firdaus, Ameen.

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ABSTRACT

Schiff base derived from thiourea and o–anisaldehyde was synthesized. The Schiff base was reacted with metal (II) chlorides to synthesize the corresponding metal (II) complexes. The synthesized Schiff base and its metal (II) complexes were characterized based on their melting point/decomposition temperature, molar conductance, percentage yield, solubility, infrared and magnetic analysis. Job's method of continuous variation revealed that all the metal (II) complexes are in 1:1 Metal-Ligand ratio. The complexes were found to decomposed at a temperature range of (215-275)$^{\circ}$C. All the metal (II) complexes have low molar conductance values (1.1 – 4.0) $\Omega^{-1}cm^{2}mol^{-1}$, indicating that they are non-electrolytes. The magnetic moment values (2.2 -5.7) B.M showed that all the metal (II) complexes are paramagnetic in nature. All the compounds were found to be soluble in dimethylsulfoxide(DMSO) but insoluble in n-hexane, petroleum ether, chloroform and carbon tetrachloride(CCl_4). Physical and analytical data suggest that the Schiff base acted as tetradentate ligand towards the metal ions via azomethine-N and methoxy-O. The synthesized Schiff base and its respective metal (II) complexes were screened for their antibacterial and antifungal activity against *Staphylococcus aureus*, *Escherichia coli* and *Aspergillus flavus, Mucor indicus specie* respectively. The Schiff base showed minimal activity against all the tested organisms at all concentrations, while the complexes showed higher activity.

CHAPTER ONE

1.0 INTRODUCTION

The concept of the coordinate bond (also known as dative bond) lies at the core of coordination chemistry. Molecular structure is interpreted in terms of covalent bond formed through shared pairs of electrons. The coordinate bond arises from the donation of a pair of electrons (a lone pair) from an orbital on one atom to occupy an empty orbital on what will become its partner atom. The ligand providing the lone pair is coordinated to the transition metal atom receiving that lone pair of electrons, the coordinating entity, and the ligand can be small as an atomic ion or as large as polymer. The key characteristic is the presence of one or more lone pairs of electrons on an electronegative donor atom e.g. N, O, S. etc. Moreover, the vast majority of existing organic molecules can act as ligands (Geoffrey, 2010). Schiff bases which are condensation products of primary amines and carbonyl compounds (aldehyde or ketone) are perfect example of ligands.

Schiff bases are compounds containing azomethine group (–C=N–) formed by condensation of primary amines and carbonyl compounds. Generally, Schiff bases are prepared under acid/base catalysis or with heat. The common Schiff bases are crystalline, these are feebly basic but at least some form insoluble salts with strong acids. They are readily hydrolyzed by aqueous acids to give back the amines and carbonyl compounds. Schiff bases have been widely used in many fields such as biological, inorganic, analytical and drugs synthesis, as ligands in the field of coordination chemistry. Schiff bases complexes have been used in catalytic reactions and as models for biological

system and also as fine chemicals and medical substrates (Awadallah and El-halabi, 2010).

1.1 Thiourea

Thiourea(CH_4N_2S) (IUPAC name, 2–thiourea) also known as thiocarbamide, sulfourea; is a white crystalline solid. Broadly, thiourea refers to a class of compounds with the general formular (R^1R^2N) (R^3R^4N) C=S.

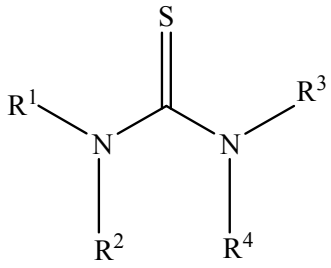
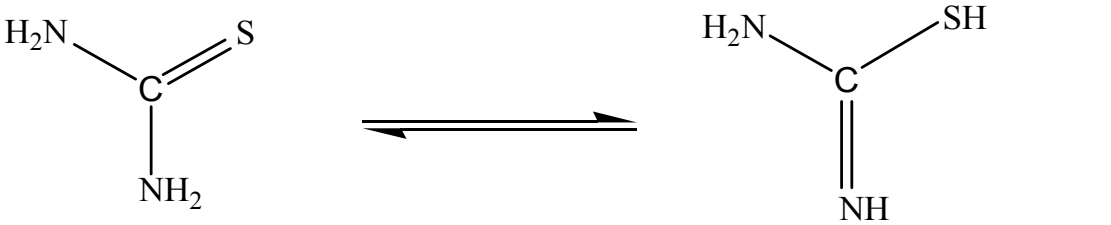


Fig 1.1.1: General structure of a thiourea

It occurs in two tautomeric forms and has three functional groups amino, imino and thiol (BUA, 1995).



Thiourea (thioene form) Iso Thiourea (thiol form)

Scheme 1.1.1: Tautomeric forms of thiourea

Thiourea is soluble in polar protic and aprotic organic solvents, and insoluble in non-polar solvents (BUA, 1995). When heated to decomposition, thiourea emits toxic fumes

of nitrogen oxide and sulfur oxides. It is structurally similar to urea, except that oxygen atom is replaced by a sulfur atom, but the properties of urea and thiourea differ significantly (BUA, 1995).

Thiourea is found to occur naturally in laburnum Shrubs, and as metabolite of *Verticillium alboatrum* and *Bortrylio cinerea*. Thiourea as an emerging class of compounds was first synthesized by Neuki 1873(BUA, 1995). However, thiourea can be produced from ammonium thiocyanate (Mertschenk *et al.,* 2002), but more commonly it is produced by the reaction of hydrogen sulfide with calcium cyanamide in the presence of carbon dioxide Mertschenk *et al.,* 2002).

$$CaCN_2 + 3H_2S \longrightarrow Ca(SH)_2 + CS(NH_2)_2$$

Scheme 1.1.2: Preparation of thiourea from calcium cyanamide.

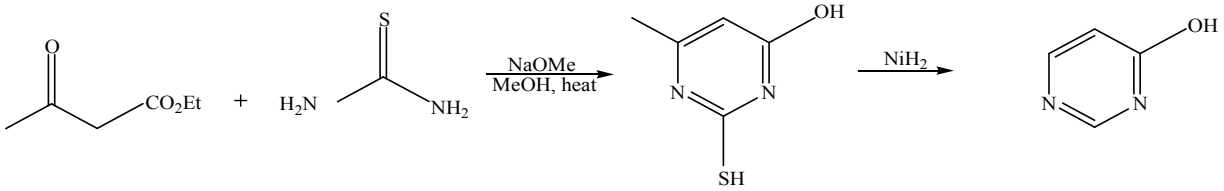
Thiourea can also be prepared by calcium hydrosulphide method which involves addition of cyanamide to a solution of calcium hydrosulphide such that the temperature is controlled around 70 – 80°C (Srinivasa *et al.,* 2003).

$$2CaCN_2 + Ca(SH)_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2CS(NH_2)_2$$

Scheme 1.1.3: Preparation of thiourea from calcium hydrosulphide method.

Thiourea is commonly employed as a source of sulfide, e.g. for converting alkyl halides to thiols. Such reaction proceeds via the intermediary of isothiouronium salts. The reaction capitalizes on the high nucleophilicity of the sulfur center and easy hydrolysis of the intermediate isothiouronium salt (Speziale, 1963). It is used as a building block to pyrimidine derivatives. Thus, thiourea condenses with β–dicarbonyl compounds (Foster

and Snyder, 1963). The amino group on the thiourea initially condenses with a carbonyl, followed by cyclization and tautomerization. Desulfurization delivers the pyrimidine.



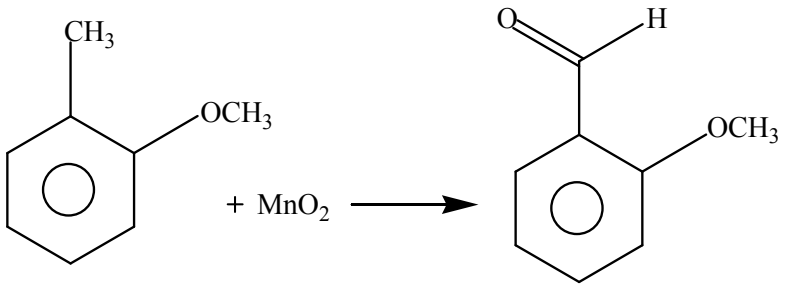
Scheme 1.1.4: Preparation of pyrimidine using thiourea as a building block.

Thiourea finds its application in the manufacture of amino resins, herbicides, fungicides, insecticide, plant growth regulators, photographic paper. It also finds use in electrochemical process, pharmaceutical industries, textile processing, hydrometallurgy, rubber industry and petroleum industry (Srinivasa *et al.,* 2003).

1.2 Anisaldehyde

Anisaldehyde is an organic compound that is commonly encountered in the fragrances, both synthetic and natural. The compound consists of a benzene ring with an aldehyde and a methoxy group. It has a strong aroma (Hammershmidt *et al.,* 2003).

Anisaldehyde is prepared commercially by oxidation of methoxytoluene (p-cresyl methyl ether) using manganese dioxide. It can also be produced by oxidation of anethole, a related fragrance that is found in some alcoholic beverages (Hammershmidt *et al.,* 2003).



Scheme 1.2.1: Preparation of anisaldehyde by oxidation of methoxytoluene

Being structurally related to vanillin, anisaldehyde is widely used in the fragrance and flavour industry. Anisaldehyde is used as an intermediate in the synthesis of other compounds important in pharmaceuticals and perfumery, ortho-anisaldehyde has a scent of licorice (Hammershmidt *et al.,* 2003).

1.3 Transition Metals

Three series of elements are formed by filling the 3d, 4d and 5d shells of electrons; together this comprises the d-block elements. They are often called 'transition elements' because their position in the period table is between the s-block and p-block elements, and their properties are transitional between the highly reactive metallic elements of the s-block, which typically forms ionic compounds and the element of the p-block which are largely covalent. Typically the transition elements have an incomplete filled d-orbital. One of the most striking features of the transition elements is that the elements usually exist in several different oxidation states due to their unfilled d-orbital which make them available for redox reactions and are good Lewis acids forming wide range of complexes with donor ligands. These properties make them suitable for complex formation.

The transition metals under investigation are;

1.3.1 Manganese

Manganese is the twelfth most abundant element by weight in the earth's crust and is mined as the ore pyrolusite (MnO_2). This is a secondary material which has been formed by alkaline waters leaching from igneous rock and depositing it as MnO_2. Manganese form many complexes, but the equilibrium constants for their formation in aqueous solution are not compared to those for divalent cations of succeeding elements (Fe–Cu) because the Mn(II) ion is the largest of these and it has no ligand field stabilization energy in its complexes (Cotton and Wilkinson, 1972).

1.3.2 Iron

Iron is the fourth most abundant element in the earth's crust and is the second most abundant metal. The most common ores are hematite (Fe_2O_3), magnetite (Fe_3O_4), limonite FeO(OH) and siderite ($FeCO_3$). Iron is extracted from its oxides in a blast furnace. Fe^{2+} ions form many complexes; the most important one is hemoglobin (the red pigment in blood). Most of the complexes are octahedral, though a few tetrahedral halide complexes $[FeX_4]^{2-}$are formed (Lee, 1990).

1.3.3 Cobalt

There are many ores which contain Co such as cobaltite ($CoAs_2S$), Smaltite ($CoAs_2$) which are commercially important; these are found together with Ni ores, often with a Cu ores and sometimes with Pb ores. Co resembles iron and is very tough. It is harder and has a higher tensile strength than steel. Co (II) forms a number of complexes, but these are less stable than those of Co (III). Co (II) complexes may be tetrahedral or octahedral. Since there is only a small difference in stability between them, the two forms sometime exist in equilibrium. Co (II) ions are very stable and difficult to oxidize (Lee, 1990).

1.3.4 Nickel

Nickel is the twenty-second most abundant element by weight in the earth's crust. Commercially important Ni ore include sulphides, which are usually mixed with Fe or Cu sulphides and alluvial deposits of silicates and oxide/hydroxides. Pentlandite $(Fe,Ni)_9S_8$ is the most important ore. The chemistry of Ni is simplified by the dominance of the (+2) oxidation state. Octahedral and square planar complexes are commonly formed and a few tetrahedral, trigonal bipyramidal and square-based pyramid structures are also formed (Lee, 1990).

1.3.5 Copper

Copper is moderately abundant and is the twenty–fifth most abundant element in the earth's crust. Its common ores include chalcopyrite ($CuFeS_2$) which has metallic luster and similar in appearance to pyrites (FeS_2). Cu (II) oxidation state is the most important and stable form of Cu, it has the electronic configuration of d^9. Its compounds are typically colored due to d–d spectra and the compounds are paramagnetic. Most of Cu (II) complexes and compounds have a distorted octahedral structure and are blue or green (Lee, 1990).

1.4 Aim of the Study

The aim of this research work is to synthesize Schiff base derived from thiourea and o-anisaldehyde and subsequently complexe the synthesized Schiff base with the first row divalent transition metals, (Mn(II), Fe(II), Co(II), Ni(II) and Cu(II).

1.5 Objectives of the Study

The objectives of this research work are to:

i. Synthesize Schiff base derived from thiourea and o-anisaldehyde and its corresponding complexes with divalent transition metals (Mn(II) Fe(II), Co(II), Ni(II) and Cu(II),
ii. Characterize the synthesized Schiff base and its complexes based on their melting point/decomposition temperature, molar conductance, percentage yield, solubility, UV-Visible, infrared and magnetic analysis and
iii. Carry out Antimicrobial evaluation of both the Schiff base and its complexes.

CHAPTER TWO

2.0 LITERATURE REVIEW

Compounds with the structure of –C=N– (azomethine group) are known as Schiff bases, which are usually synthesized by the condensation of primary amines and carbonyl compounds (Ali *et al.,* 2012). They were first reported by Hugo Schiff in 1864 (Cimerman *et al.,* 2000).

Schiff base ligands are broadly studied in coordination chemistry, due to their facile synthesis, electronic properties and good solubility in common organic solvents. Transition metal complexes, particularly with oxygen and nitrogen donor Schiff bases are of specific interest because of their ability to involve in unusual configurations, structural ability and their sensitivity to molecular environments (Golcu *et al.,* 2005) Schiff base ligands are very effective in constructing supra molecular architectures such as coordination polymers, double helixes and triple helicates (Ziessel, 2001). Schiff bases can accommodate different metal centers involving various coordination modes in which the homo and hetero metallic complexes with varied stereochemistry have been synthesized successfully. They have numerous applications in many fields like antibacterial, antiviral, antifungal agents, homogenous or heterogeneous catalysis and magnetism. The anticancer activities of these complexes are enhanced in comparison to the free ligand (Hodnett *et al.,* 1970).

Abdlseed and El-ajaily (2012) reported the synthesis of a Schiff base derived from the reaction of salicylaldehyde and thiourea and its complexes with Cr(III), Pb(II) and TiO(IV) ions. The synthesized complexes were investigated by CHNS elemental

analysis, molar conductance and magnetic moment measurements, infrared and electronic spectroscopy. The thermo gravimetric analysis (TGA) was carried out for $[TiO.H_2O].10H_2O$ complex to establish the hydrated and coordinated water molecules present in the complex. The CHNS elemental analysis shows the formation of 1:1 [M: L] complexes. The obtained molar conductance values revealed non-electrolytic nature. The magnetic moment value, 4.10BM of Cr(III) complex exhibited the existence of paramagnetic phenomena, while, values for Pb(II) and TiO (IV) complexes were zero, which indicated the presence of diamagnetic phenomena.

Manich base, [1-(piperidin-1-yl (thiopen-2-yl) methyl] thiourea was prepared by treating thiophene-2-carbaldehyde piperidine and thiourea. Metal complexes of Mn(II), Co(II) Mo(II), Cu(II) and Zn(II) were prepared by reacting the respective metal (II) salts with the above mentioned Manich base. Both the Schiff base and the complexes were characterized by physical methods such as elemental analysis, melting point and thin layer chromatography (TLC) and spectral methods such as IR, UV-visible, ^{1}H NMR, ^{13}C NMR and mass spectral studies. The complexes were further characterized using molar conductivity, magnetic susceptibility and thermal studies. The obtained molar conductance values (112.4-128.6) $\Omega^{-1}cm^2mol^{-1}$ indicated electrolytic nature of all the complexes. The magnetic moment values obtained (1.75–5.86) B.M shows the existence of paramagnetic phenomena. Based on the analytical and spectral data octahedral geometry has been proposed for all the complexes. *In vitro* antimicrobial study was carried out for both compounds and the results indicated that the complexes were more active than the free ligand (Rathakrishnan *et al.,* 2014).

Rizwan and Santha (2012) listed a Schiff base ligand by condensation of o-vanillin with allylthiourea in 1:1 molar ratio. The Schiff base metal complexes of Zn(II), Ni(II) and Cu(II) were prepared using the corresponding metal salts and the synthesized Schiff base also in 1:1 molar ratio. The metal complexes were characterized using molar conductivity, UV-Visible and IR spectroscopy. The molar conductance values of the complexes were in the range (1.0-9.0) $ohm^{-1}cm^2mol^{-1}$ indicating non-electrolytic nature of the complexes. The metal complexes shows $\pi \rightarrow \pi^*$ transition at 250nm, $n \rightarrow \pi^*$ at 350nm and d-d transition at 460nm. Based on the data square planar geometry was suggested for all the complexes. The ligand and the metal complexes were screened for antibacterial activity against *Klebsiella pneumonia, Basillus cerus* and *Pseudomonas aeruginosa* and fungicidal activity against *Aspergillus niger, Candida albicans and Candida kefyr.* The results revealed that the synthesized compounds were potent against all the microbes under investigation.

Al-Obaidi (2012) reported the synthesis of four mixed ligands and the complexes of Cu(II) and Zn(II) containing benzylidenethiourea (obtained by the condensation of benzaldehyde and thiourea) as the primary ligand and (acetamide or thioacetamide) as an additional ligand. The compounds were characterized using magnetic susceptibility and molar conductance measurements, as well as by UV-Visible and IR spectroscopy. The interaction of the complexes with Calf Themus (CT) DNA was studied using absorption spectra, while the concentration of deoxyribo nucleic acid (DNA) in gel electrophoresis remained constant at 10μL. They exhibited absorption hypochromicity increase during the binding of the complexes to calf thymus DNA. The complexes showed enhanced antimicrobial activities than the free ligand. A theoretical treatment of the formation of

complexes in the gas phase was studied. This was done by using the HYPERCHEM-6 program for the molecular mechanics and semi-empirical calculation. The higher molar conductance values (105-119) $ohm^{-1}cm^2mol^{-1}$ of the complexes in DMSO show their electrolytic nature. The complexes exhibited intense bands at (215-265) nm region which attributed to charge transfer transition. The Cu complexes showed magnetic moment values in the range (1.85 – 1.88) μB which indicated the monomeric nature of the complexes and the characteristics for a distorted octahedral structure. A comparison of the antimicrobial results of the ligands and their complexes indicated that the metal complexes exhibited higher activity than the ligands. Moreover, the Cu (II) complexes were more active than the Zn(II) complexes against all the tested microorganisms.

Thiourea derived Schiff base ligand and its Ni(II) and Cu(II)complexes have been synthesized. The ligand and its complexes were characterized by FTIR, UV and CHN. The electrical properties of the compounds were studied. The maximum value of the conductivity was $1.23\times10^{-4}ohm^{-1}cm^{-1}$. The Schiff base chelate complexes were identified by FT-IR spectrophotometer. New bands which were not present in the spectrum of the free Schiff base appeared at (460-450) cm^{-1} and (635-630) cm^{-1}which are attributed to M-O and M-S vibrations, respectively. Electronic absorption of the free ligand showed a band at 320nm which may be attributed to($\pi \quad \pi$)transitions, which shifted in the Ni(II) and Cu(II) chelates. The intensity of these bands in both Schiff base chelates is consistent with square planar (dsp^2) structure (Al-Assadi, 2011).

Synthesis of bis-imines by the condensation of urea and thiourea with various substituted aromatic aldehydes in ethanol and acetic acid has been reported by (Sonnekar *et al.,* 2013).

All the bis-imines were confirmed from melting point and spectral data analysis. The infrared spectra of the free ligands were obtained over a spectral range of 400-4000 cm ^{1}.The absence of absorption bands associated with the –CHO aldehyde group and $–NH_2$ amino groups stretching were noted in the Schiff base, indicating the loss of the aldehydic group (1740-1720) cm ^{1} and amine (3500-3100) cm ^{1} stretching frequencies respectively in the synthesized ligands. The bands observed at (1640-1690) cm ^{1} were assigned to the stretching vibration of the imine group of the ligands. The compounds were screened for antimicrobial activity against bacterial species, *Escherichia coli, Staphylococcus aureus* and *S. typhi* using agar cup method and antifungal activity against *Aspergillus niger, P. chrysogenus, F. Moneliforme* and *A. flavus* using poison plate method. The metal complexes exhibits moderate to excellent antibacterial and antifungal activities.

A series of novel metal complex derivatives of thiourea Schiff base has been synthesized. The transition metal (II) complexes were formed by the reaction of Co(II), Ni(II), Zn(II), Fe(II) and Cu(II) nitrates with the Schiff base. The compounds were characterized using infrared (FT-IR); electronic spectral (UV), elemental analysis, melting points and x-ray diffraction (XRD) analysis etc. The IR spectral bands in the complexes at (410-497) cm^{-1} were characteristics of metal–nitrogen bond which indicated that the nitrogen atom of the ligand was coordinated. The strong bands at (3200-3640) cm^{-1} was assigned to *ν*O-H group and (1648-1679) cm^{-1} band was also assigned to *ν*C=N group. Powder XRD patterns were recorded in the 2θ range RIGAKU Miniflex-II with Cu-Kα1 radiation (λ=1.5406) between 100 and 800 with a step size of 0.02. The powder X-ray diffractogram of cobalt (II) complex indicated its crystalline nature. The complexes are

probably polymers with octahedral structure. The compounds were screened for antibacterial and antifungal activities. The metal complexes exhibits moderate to excellent antibacterial and antifungal activities (Sonnekar *et al.,* 2014).

New Schiff bases 1, 3-bis-(2-hydroxy-benzylidene)-thiourea(L1) and 1,3-bis-(2-hydroxy-benzylidene)-urea(L2) have been synthesized and reported by Al-obaidi(2012). These ligands were complexed with transition metal ions (Mn(II) , Co(II), Ni(II)). The prepared complexes were characterized by elemental analysis, IR, UV-Visible and atomic absorption methods. The IR spectra showed bands at 1610 $cm^{-1}$and 1620 cm^{-1} in the spectrum of L1 and L2 respectively due to υ(C=N) stretching which shifted to the lower frequencies in the spectra of the complexes. The negative shift generally in υ(C=N) further suggested the coordination to metal ions through nitrogen atom (-C=N) of the Schiff's base, in addition a weakened and lowered 1250 cm^{-1} peak due to υ(C=S) stretching vibrations was also observed, which suggested additional coordination through the Sulphur in L1. The carbonyl stretching frequency in L2 decreases to (1605-1620) cm^{-1} compared to the free ligand at 1685 cm^{-1}, due to coordinaton of the ligand to the metal. The complexes gives different color to that of the transition metal salts and the ligands, this was an important indication to coordinate occurrence, therefore these colorful complexes show different characteristic absorption bands in position, intensity when compared with the bands of the ligand and this was another indication for the coordination. The UV-Visible spectra of the two prepared ligands (L1, L2) in ethanol showed three absorption bands. The first band (370) nm represented (n - π*) while the second band (300-310) nm represented (π - π*) and the third band (270-275) nm is called (B-band) for phenyl group. Octahedral structure was proposed for all the complexes. The

free ligands and its complexes were tested for their antibacterial activities against two types of human pathogenic bacteria *Staphylococcus aureus* and *Escherichia coli,* the compounds show different activity of inhibition on growth of the bacteria.

A series of bisthiourea ligands, 1,2-bis (N′-2-methoxybenzylthiourea)-4-chlorobenzene (TI), 1,2-bis (N′-3-methoxybenzylthiourea)-4-chlorobenzene, (TII) and 1,2- bis (N′ -4-methoxybenzylthiourea)-4-chlorobenzene, (TIII) and their Cu(II) complexes have been successfully synthesized. The products have been characterized by elemental analysis (CHNS), IR spectroscopy, ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR), melting point and magnetic susceptibility determination method. The effective magnetic moments of the Cu(II) complexes Cu(TI), Cu(TII) and Cu(TIII) were found to be in the range of (1.23-2.21) B.M. These values correspond to the one unpaired electron. The paramagnetism of the complexes agrees with the square planar geometry around the copper (II) ion. The antibacterial activity of the ligands and their Cu(II) complexes were tested by disc diffusion method against four strain of bacteria (*Basillus subtillis, Pseudomonas aeruginosa, Escherichia coli* and *Staphylococcus aureus.* The results indicated that the efficacy of the compounds against Gram positive bacteria is higher than Gram negative bacteria. The antibacterial activity of the metal complexes is higher than the ligands (Nur *et al.,* 2012).

Synthesis of N-acylurea and N-acylthiourea Schiff bases and their Co(II) and Ni(II) complexes of the general formular $ML_2X_2.nH_2O$ [M=Ni(II) or Co(II), L=N-acylurea or N-acylthiourea, X=Cl and n=6] have been synthesized and characterized by melting point, magnetic susceptibility, elemental analysis, infrared and electronic spectral studies. The melting point of the Schiff bases was observed at (165-215)$^{\circ}$C and that of the

complexes at (179-240)°C. The magnetic moment values for the complexes ranges from (2.81-3.87) B.M. Based on the magnetic and spectral data, a tetrahedral structure has been suggested for the metal complexes. The antimicrobial activity of the synthesized compounds was determined against five different species each, for bacteria and fungi which includes *Bacillus subtilis*, *Escherichia coli, Klebsiella pneumonia, Pseudomonas aeruginosa, staphylococcus aureus and Aspergillus flavus, Aspergillus niger, Candida albicans, Penicillium Sp. Tritophora Sp*. respectively. The metal complexes recorded greater inhibitory activity on the organisms compared to their corresponding free ligands (Joshua *et al.,* 1995).

CHAPTER THREE

3.0 MATERIALS AND METHODS

All reagents and solvents used were of analytical grade and were used without further purification.

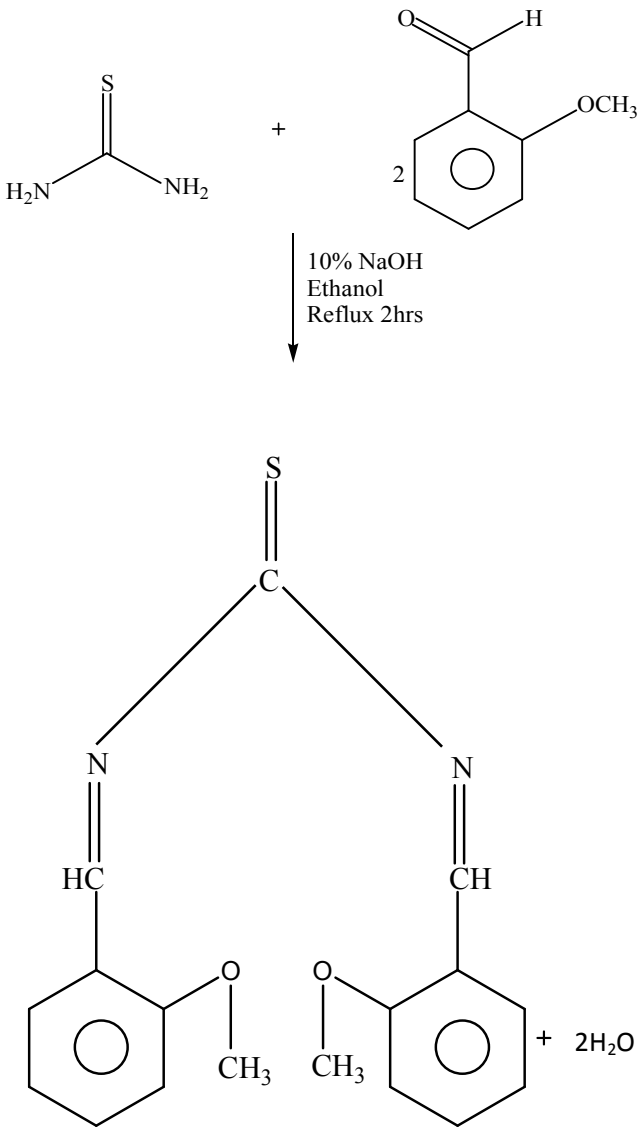
3.1 Apparatus

Glass wares used were washed with detergent, rinsed with distilled water and dried in an oven at 110°C before use. All weighing were carried out on an electric Mettle balance model H3OAR, melting/decomposition temperature were determined using Galenkamp melting apparatus. Molar conductance measurements were carried out in DMSO using Jenway conductivity meter 4010 model. Jenway 6305 UV-Visible Spectrophotometer was used for UV- absorbance measurements. Magnetic susceptibility measurement was conducted using magnetic susceptibility balance MK1 model, infrared spectral analysis were recorded using Cary 630 Fourier transform infrared (FTIR) Agilent technologies in the range of (650–4000) cm^{-1}. Bacterial and fungal isolates (Bacteria: *E coli* and *S. aureus,* Fungi: *A. flavus* and *M. species*) were obtained and identified at the Department of Microbiology, Bayero University Kano. Nutrient Agar (NA) and Potatoes Dextrose Agar (PDA) were used as bacterial and fungal media respectively.

3.2 Preparation of the Ligand

Anisaldehyde (2.723g, 0.02mol) in 25cm^3 ethanol was added to a solution of thiourea (0.07612g, 0.01 mol) also in ethanol (25cm^3) and few drops of 10% sodium hydroxide (NaOH) were added to adjust the pH, the mixture was then refluxed with stirring for two hours. The obtained solution was concentrated using water bath and the concentrate was

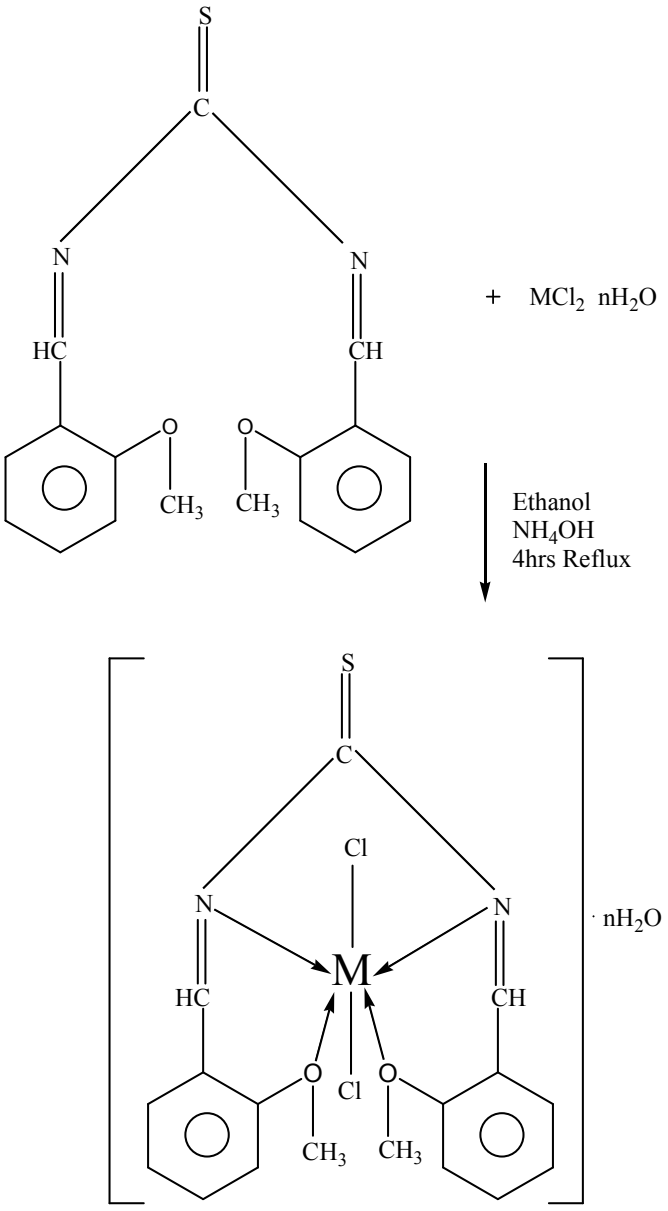
cooled using ice cubes. The resulting precipitate was collected by filtration and then washed with anhydrous diethyl ether and dried in a desiccator over calcium chioride (Abdlseed and El-ajaily, 2012).



(Scheme 3.1.1: Schiff base formation)

3.3 Preparation of the Complexes

The synthesized Schiff base (3.12g, 0.01mol) solution in ethanol ($25cm^3$) was added to $25cm^3$ ethanolic solution of the appropriate metal (II) chloride (0.01mol). Few drops of ammonium hydroxide solution were added slowly to adjust the pH and then the mixture was refluxed for 4hrs. The obtained solution was concentrated using water bath and the concentrate was cooled using ice cubes. The resulting precipitate was collected by filtration and then washed with anhydrous diethyl ether and dried in a desiccator over $CaCl_2$ (Abdlseed and El-ajaily, 2012).



(Scheme 3.1.2: Schiff base Metal Complex formation)

3.4 Solubility test for the Schiff base Ligand and its Complexes

Solubility test of the ligands and their respective complexes were carried out in distilled water, methanol, ethanol, DMSO, dimethyl formamide (DMF), acetone, chloroform, carbon tetrachloride, n-hexane and petroleum ether. About 2mg of each of the Schiff

bases and the complexes was added to 2ml of the corresponding solvent in a test tube and the solubility observed.

3.5 Molar Conductance Measurement of the Complexes

Molar conductance of the complexes were carried out in DMSO by dissolving 0.5gm of each sample in 5ml of the solvent in a test-tube, the electrode was inserted and the reading taken.

3.6 Magnetic Susceptibility Measurement

The prepared metal complex was inserted into a given capillary tube up to a given mark and then inserted into the magnetic susceptibility balance and the reading recorded. The magnetic moment was calculated using the following relation:

$$Xv = \frac{C(R - R_{\circ})}{10^9 \times M}$$

Where;

Xv = Volume Susceptibility

C = 1 (Constant of Proportionality)

R = Reading obtained of sample placed in the tube.

$R_{\circ}$ = Reading obtained of the pre-weighted empty sample tube.

M = Mass of the sample

The mass susceptibility (X_g) is calculated using:-

$$X_g = \frac{Xv}{Density}$$

Where,

$$Density = \frac{Mass of the Sample}{Length \times Area}$$

The magnetic moment is calculated as

$X_m = X_g \times$ molar mass

$\mu_{eff} = 2.828 (X_m T)^{½}$

T = Absolute temperature.

3.7 Melting Point/Decomposition Temperature Determination

Melting point of the Schiff bases and the decomposition temperature of the metal complexes were determined by inserting a small amount of each sample into a capillary tube and then inserted into Gallenkamp melting point apparatus. The temperatures at which the ligand melts and the complexes decomposed were recorded.

3.8 Determination of Metal to Ligand Ratio in the Complex Compounds

The numbers of coordinated ligands in the complex compounds were determined using Job's method of continuous variation (Angelici, 1971). 0.003 mmol solution of the ligand and the metal chloride were prepared. The following ligand to metal salts ratio (ml); 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9 were taken from the ligands solution and each of the metal chloride solutions respectively. A total volume of 10ml was maintained (in that

order) throughout the process and the mole fraction of the ligands was calculated in each mixture. The solutions of the metal chlorides were scanned (as blank) to find the wave length of maximum absorption (λ_{max}) for the particular metal ion (Angelici, 1971). The machine was fixed at λ_{max} (in each case) before taking the absorbance values. A plot of absorbance against mole fractions was made by extrapolation; mole fraction (x_i) at maximum absorbance was recorded, which was the point where the metal ion and the ligand are in stoichiometric ratio. The number of coordinated Schiff base ligand to metal ion was calculated using the relation;

$$\bar{n} = \frac{x_i}{1-x_i}$$

Where $\bar{n}$ = number of coordinated ligand, and
x_i= mole fraction at maximum absorbance

3.9 Determination of Water of Hydration

A small amount of the sample was taken and measured and then heated in an oven at a temperature of about 110°C until a constant weight is obtained, then the weight of the anhydrous sample was determined. The difference in the mass of the hydrated compound and the subsequent mass of the anhydrous compound will be the mass of water removed.

3.10 Infrared analysis of the ligands and its complexes

Infrared spectral analyses of the Schiff base and its metal (II) complexes were carried out using Cary 630 FTIR Agilent technologies. The solid samples were placed onto the crystal and a little force was applied to ensure good contact between the sample and the surface of the crystal and then scanned to acquire data using a minimum of 4 scans with a scan range of 4000-650 cm^{-1}.

3.11 Determination of Chloride ions in the Complex Compounds

Chloride ions were determined qualitatively by initial treatment of the solution of the complexes in ethanol/methanol with silver nitrate solution and then by digestion of the complexes in 2M nitric acid. The substances were then dissolved in distilled water and filtered, the filtrates were treated with silver nitrate solution.

3.12 Antibacterial Activity Test

The ligand and its complexes were dissolved separately in DMSO to have three different concentrations (15µg, 30µg and 60µg) per disc. They were placed on the surface of the culture media (nutrient agar) and incubated at 37°C for 24hrs. Then *in vitro* antibacterial activity against *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) of the ligand and its complexes were carried out by disc diffusion method. The diameter of the zone of inhibition produced by the ligands and the complexes were compared with the standard. (Yusha'u and Salisu, 2011).

3.13 Antifungal Activity Test

The ligand and its complexes were dissolved separately in DMSO to have three different concentrations (15µg, 30µg and 60µg) per disc. They were placed on the surface of the culture media (potatoes dextrose agar) and incubated at room temperature for 48hrs. The *in vitro* antifungal activity against *Aspergillus flavus* and *Mucor inducus specie* of the ligand and its complexes were carried out by disc diffusion method. The diameter of zone of inhibition produced by the ligand and the complexes were compared with the standard. (Hassan *et al*., 2006).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

Results of the characterization, antibacterial and antifungal activity of the synthesized Schiff base and its metal (II) complexes are presented in the following Tables:

Table 4.1: Physical Properties of the Schiff Base and its Metal (II) Complexes.

S/N	Compound	% Yield	Colour	Decomposition Temp (°C)	Melting Point Temp (°C)
1	Ligand L	53.5	Cream	-	160
2	$[CuLCl_2].2H_2O$	82.3	Green	260	-
3	$[NiLCl_2].3H_2O$	80.5	Light green	220	-
4	$[MnLCl_2].4HO$	70.7	Milk	275	-
5	$[CoLCl_2].4H_2O$	58.8	Deep blue	215	-
6	$[FeLCl_2].4H_2O$	79.0	Reddish brown	230	-

L = o-anisaldehyde-thiourea Schiff base

Table 4.2: Molar Conductivity Values of the Metal (II) Complexes

S/N	Compound	Specific Conductivity (ohm^{-1} cm^{-1})	Molar Conductivity (ohm^{-1} cm^2mol^{-1})
1	$[CuLCl_2].2H_2O$	769×10^{-6}	3.3
2	$[NiLCl_2].3H_2O$	803×10^{-6}	4.0
3	$[MnLCl_2].4H_2O$	221×10^{-6}	1.1
4	$[CoLCl_2].4H_2O$	486×10^{-6}	2.5
5	$[FeLCl_2].4H_2O$	691×10^{-6}	3.5

L = o-anisaldehyde-thiourea Schiff base

Table 4.3: Solubility Test of the Schiff Base and its Metal (II) Complexes

S/N	Compounds	Water	Methanol	Ethanol	DMSO	DMF	Acetone	Chloroform	n-hexane	Pet-ether	Carbon tetrachloride
1	Ligand L	SS	S	S	S	SS	S	IS	IS	IS	IS
2	$[CuLCl_2].2H_2O$	SS	SS	S	S	SS	SS	IS	IS	IS	IS
3	$[NiLCl_2].3H_2O$	S	SS	S	S	SS	SS	IS	IS	IS	IS
4	$[MnLCl_2].4H_2O$	SS	S	IS	S	SS	SS	IS	IS	IS	IS
5	$[CoLCl_2].4H_2O$	IS	S	SS	S	SS	SS	IS	IS	IS	IS
6	$[FeLCl_2].4H_2O$	IS	S	SS	S	SS	SS	IS	IS	IS	IS

L= o-anisaldehyde-thiourea Schiff base

S = Soluble

SS= Slightly Soluble

IS= Insoluble

Table 4.4: Magnetic Susceptibility values of the metal (II) complexes

S/N	Compound	$\Psi_g(g^{-1})$	$\Psi_m(mol^{-1})$	μeff(BM)
1	$[CuLCl_2].2H_2O$	4.24409×10^{-6}	1.747×10^{-3}	2.21
2	$[NiLCl_2].3H_2O$	1.0067×10^{-5}	4.087×10^{-3}	3.45
3	$[MnLCl_2].4H_2O$	2.6804×10^{-5}	1.0802×10^{-2}	5.71
4	$[CoLCl_2].4H_2O$	1.7465×10^{-5}	7.108×10^{-3}	4.63
5	$[FeLCl_2].4H_2O$	1.953×10^{-5}	7.889×10^{-3}	4.88

L = o-anisaldehyde-thiourea Schiff base

Table 4.5: IR Spectral Data of the Schiff Base and its Metal (II) Complexes

S/N	Compound	υ(C = N)	υ(M – N)	υ(C – O)	υ(C = S)	υ(OH)
1	Ligand L	1601	–	1289	1689	
2	$[CuLCl_2].2H_2O$	1620	758	1246	1687	3274
3	$[NiLCl_2].3H_2O$	1603	752	1240	1687	3267
4	$[MnLCl_2].4H_2O$	1601	752	1240	1687	3267
5	$[CoLCl_2].4H_2O$	1657	758	1246	1687	3347
6	$[FeLCl_2].4H_2O$	1657	758	1246	1687	3136

L = o-anisaldehyde-thiourea Schiff base

Table 4.6: UV-Visible values of the metal (II) complexes

Compound	Maximum Absorbance (A)	Mole fraction at maximum absorbance (Xi)	Number of coordinated ligand ($\bar{n}$)
$[CuLCl_2].2H_2O$	0.5204	0.5	1
$[NiLCl_2].3H_2O$	0.1474	0.5	1
$[MnLCl_2].4H_2O$	0.11801	0.5	1
$[CoLCl_2].4H_2O$	0.1506	0.5	1
$[FeLCl_2].4H_2O$	0.0925	0.5	1

Table 4.7: Antibacterial activity of the Schiff base and its Metal (II) Complexes

Test organism	Compound	Zone of Inhibition (mm)/Concentration) (µg/disc)			Control (mm) (60µg/disc)
		60	**30**	**15**	
Staphylococcus aureus	Ligand, L	11	10	09	Ampiclox 22
	$[CuLCl_2].2H_2O$	13	10	08	
	$[NiLCl_2].3H_2O$	15	14	12	
	$[MnLCl_2].4H_2O$	16	14	12	
	$[CoLCl_2].4H_2O$	18	16	14	
	$[FeLCl_2].4H_2O$	11	08	06	
Escherichia coli	Ligand, L	13	10	08	Ampiclox 22
	$[CuLCl_2].2H_2O$	14	12	09	
	$[NiLCl_2].3H_2O$	11	09	08	
	$[MnLCl_2].4H_2O$	06	06	06	
	$[CoLCl_2].4H_2O$	25	24	17	
	$[FeLCl_2].4H_2O$	13	10	09	

L = o-anisaldehyde-thiourea Schiff base

Table 4.8: Antifungal activity of the Schiff base and its Metal (II) Complexes

Test organism	Compound	Zone of Inhibition (mm)/Concentration (µg/disc)			Control (mm) (60µg/disc)
		60	**30**	**15**	
Aspergillus flavus	Ligand, L	06	06	06	Grisofulvin 32
	$[CuLCl_2].2H_2O$	15	13	12	
	$[NiLCl_2].3H_2O$	15	13	11	
	$[MnLCl_2].4H_2O$	06	06	06	
	$[CoLCl_2].4H_2O$	13	11	10	
	$[FeLCl_2].4H_2O$	06	06	06	
Mucor indicus spp.	Ligand, L	11	09	06	Grisofulvin 31
	$[CuLCl_2].2H_2O$	12	08	06	
	$[NiLCl_2].3H_2O$	14	12	10	
	$[MnLCl_2].4H_2O$	06	06	06	
	$[CoLCl_2].4H_2O$	20	17	14	
	$[FeLCl_2].4H_2O$	06	06	06	

L = o-anisaldehyde-thiourea Schiff base

4.2 Discussion

Schiff base was prepared using a procedure reported by Abdlseed and El-ajaily (2012). Thiourea was condensed with ortho anisaldehyde, for 2 hours.

The Schiff base prepared was converted to metal complexes according to the procedure reported by (Abdlseed and El-ajaily, 2012). The Schiff base was treated with metal(II) ions namely; Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) separately under reflux for 4hrs to give the respective metal (II) complexes.

The Schiff base was found to be coloured (Table 4.1) and the new colour formed was different from the colours of the thiourea and the anisaldehyde used, this may be the first indication for the formation of the Schiff base. Upon complexation the colour of the Schiff base was also observed to change in most of the complexes (Table 4.1) different from that of the corresponding metal salts used, the changes in colour may be due to electrons transfer, also suggesting complexation may have been achieved. Though, other characterization techniques are necessary to confirm the formation of the compounds.

The percentage yield obtained for the Schiff base was found to be significant. The complexes were also prepared in high yield as shown in (Table 4.1); which may be due to the purity of the reactants and the optimization of the reaction. This might indicate their easy synthetic procedures which may easily be reproduced.

Decomposition temperature can be used to determine the stability of a complex compound with respect to heat. Results obtained for the complexes prepared (Table 4.1) showed high decomposition temperature values, indicating that these complexes are

thermally stable, but can decompose at a temperature range of (200-275) $^{\circ}$C. The stability of the complexes may be due to chelation.

The ability of a complex to form ions in solutions is determined by it electrolytic nature. Complexes that produces ions in solutions are said to be electrically conducting while those that do not are electrically neutral i.e. none conducting. The molar conductance measurement of the complexes prepared was carried out in DMSO solution at room temperature using the procedure reported by (Geary, 1971). The conductance values observed in this work were low within the range (1.1–4.0) $\Omega^{-1}cm^2mol^{-1}$ (Table 4.2), which shows that these complexes are non-electrolytes and therefore neutral.

The solubility test of the ligands and their respective complexes were carried out in different solvents and the compounds were found to be soluble in DMSO, methanol and ethanol, slightly soluble in DMF, acetone and distilled water and insoluble in petroleum ether, n-hexane, chloroform and CCl_4 as shown (Table 4.3). These shows that the compounds are polar, as like dissolve like.

The presence or absence of an unpaired electron(s) in an orbital of a metal in a complex compound determines whether a complex is paramagnetic or diamagnetic. Values of the magnetic susceptibility measurement of the synthesized complexes (table 4.4) indicated that they are all paramagnetic in nature. The complexes showed the following magnetic moment values; Cu(II) complex 2.21 B.M, Ni(II) complex 3.45 B.M, Mn(II) complex 5.71 B.M, Co(II) complex 4.63 B.M and Fe(II) complex 4.88 B.M which are all within the normal range of values observed for octahedral metal(II) complexes as reported in the

literature (Gehad *et al.,* 2006). These results showed that all the complexes mentioned above are six–coordinated and probably octahedral in shape (See Table 4.4).

The IR spectrum of the Schiff base formed was observed to differ with the spectra of the aldehyde and the thiourea. The spectrum of the aldehyde with band at 1685 cm^{-1} assigned to *ν*(C=O) was found to disappear in the spectrum of the Schiff base, also, weak peak at 3255cm^{-1} corresponding to primary amine (NH_2) in the spectrum of thiourea was observed to be absent in the spectrum of the Schiff base. Instead, new peak at 1601cm^{-1} corresponding to *ν*(C=N) was observed in the spectrum of the Schiff base which was absent in the thiourea and anisaldehyde spectra. This new peak that was observed is an indication that condensation has occurred and consequently a thiourea-anisaldehyde Schiff base has been formed.

The IR spectrum of the Schiff base with that of the complexes were compared to study the bonding mode of the ligand to the metal in the complexes (Table 4.5). The IR spectrum of the ligand showed a band at 1601cm^{-1} which is assigned to *ν*(C=N) stretching vibration, a feature found in most of the reported Schiff bases (Jezowska *et al.,* 1988). This band was also observed in the spectra of the complexes but has shifted (1601–1657) cm^{-1}, suggesting that the ligand has coordinated to the respective metal ions, resulting in the formation of the complexes. Furthermore new bands in the regions (668 – 767) cm^{-1} attributed to *ν*(M–N) stretching vibration may be considered as an additional indication for the coordination of the Schiff base to the respective metal(II) ions. The band at 1289 cm^{-1} assigned to *ν*(C–O) vibration in the spectrum of the Schiff base has shifted to lower frequency (1240–1246) cm^{-1} in the spectra of the complexes indicating its involvement in coordination through the oxygen atom. These data suggest that the

azomethine–N and methoxy–O are involved in the coordination with the metal (II) ion in the complexes. The broad bands in the range (3136 –3347) cm^{-1} assigned to ν(O–H) in the spectra of all the complexes is a feature indicating the presence of water of hydration. Similar results were reported by a similar work of Abdlseed and El-ajaily, (2012).

Estimation of the metal to ligand ratio was achieved by using Job's method of continuous variation (Angelici, 1971). The results showing mole fraction of the ligand (o-anisaldehyde-thiourea) and absorbance for the respective metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}) are presented in (Table 4.6). Plot of absorbance against mole fraction in each case gives a curve with maximum absorbance corresponding to the ligand's mole fraction used in calculating the number of coordinated ligand, which suggested 1:1 metal–ligand ratio in all the complexes indicating one Schiff base ligand is coordinated to one metal atom. However, literature and some analytical results suggested the complexes to be octahedral, in addition to the Schiff base which is tetradentate two chlorine atoms were further coordinated to the metal(II) ion. This was further confirmed qualitatively. Initial treatment of the solution of the metal complexes with silver nitrate did not give any precipitate indicating the absence of chlorine or other halides atoms outside the coordination sphere. But when the complexes were digested with nitric acid (to break the bonds) and treated with silver nitrate a precipitate was observed which indicated the presence of coordinate chlorine atom.

The antibacterial activity test of the Schiff base and its metal (II) complexes have been determined. The diameter of the inhibition zones were measured and recorded for each treatment as shown in (Table 4.7). It has been observed that the Schiff base showed

minimal activity against the tested organisms at all concentrations but the complexes behave differently. *Staphylococcus aureus* was found to be susceptible to Mn(II), Co(II) and Ni(II) complexes as high activity was recorded. Co (II) complexes also showed a very high activity against *Escherichia coli* but Cu(II) and Fe(II) complexes showed moderate activity against all the tested organisms. *Escherichia coli* was found to be resistant to Mn(II) complex.

Sensitivity of the fungal isolates to the ligand and its respective metal (II) complexes indicated that Co(II) and Ni(II) complexes showed high activity against all the two isolates while that of Cu(II) showed moderate activity but Mn(II) and Fe(II) complexes showed no activity. The ligand recorded no activity against *Aspergillus aureus* and low activity against *Mucor indicus spp.* The results are shown in (Table 4.8).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Schiff base derived from the reaction of o-anisaldehyde and thiourea and its metal complexes with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) ions have been prepared and investigated. The synthesized Schiff base acted as tetradentate ligand. IR, conductivity, magnetic and other studies indicated that the metal (II) ions coordinated to the azomethine –N and methoxy oxygen–O. All the respective metal (II) complexes were evaluated *in vitro* against two bacterial (Gram positive and Gram Negative) and two fungal strains. The antimicrobial data revealed that the activity of the ligand and its respective metal (II) complexes against the tested microorganisms increases with the increase in concentrations. Though the ligand and its complexes showed low activity compared to the standard antimicrobial (Ampiclox and Grisofulvin) used for bacteria and fungi respectively, they may still be a potent antimicrobial agents looking at their activity at higher concentration. Interestingly, Co(II) complex showed higher activity than the standard antimicrobial used with respect to *Escherichia coli* with 25mm zone of inhibition as against the Ampiclox at 22mm as shown in Table 4.7. The results suggested that if further work is done on the Co (II) complex, it might be a better antimicrobial against *Escherichia coli* compared to Ampiclox.

Based on the analytical and spectroscopic results the structure of the Schiff base and its complexes can be proposed as in Figures 4.2.1and 4.2.2

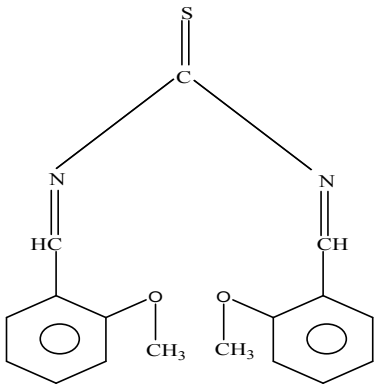


Fig. 4.1: Proposed structure of the Schiff base

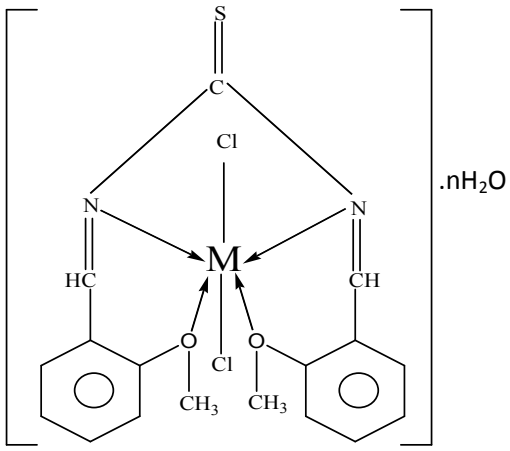


Fig.4.2: Proposed structure of the Complexes (M=Mn^{2+}, Fe^{2+}, Co^{2+}, $Ni^{2+}$and Cu^{2+}).

5.2 Recommendations

Further analysis such as; mass spectroscopy, x-ray crystallography and micro analysis need to be carried out to fully establish the structures of the compounds. The ability of the Schiff base and its respective metal (II) complexes to show antimicrobial potency suggest that they can be further evaluated for cytotoxicity, medicinal and environmental applications.

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APPENDICES

Appendix IA: Calculation of the Percentage Yield of the Schiff base

Percentage yield of the ligand were obtained using the following equation;

$$\%\,\text{Yield of the ligand} = \frac{\text{Expeimental yield}}{\text{Theoeretical yield}} \times 100\%$$

1.0mmole of thiourea and 2.0mmole of anisaldehyde produced 1.0mmole of thiourea-anisaldehyde Schiff base.

$$CH_4N_2S + 2\ C_8H_8O_2 \rightarrow C_{17}H_{16}O_2N_2S + 2H_2O$$

Example

Theoretical yield of thiourea-anisaldehyde Schiff base = 15.6g

Experimental yield of thiourea-anisaldehyde Schiff base = 8.35g

$$\%\,\text{Yield} = \frac{8.35\text{g}}{15.6\text{g}} \times 100\%$$

% Yield of the ligand = 53.53%

Therefore, percentage yield of thiourea-anisaldehyde Schiff base is 53.53%.

Appendix IB: Calculation of the Percentage Yield of the Complexes

Percentage yield of the Metal(II) complexes were obtained using the above equation.

1.0mmole of thiourea-anisaldehydeSchiff base and 1.0mmole of metal (II) chloride produced 1.0mmole of thiourea-anisaldehydeSchiff base metal (II) complexes.

$C_{17}H_{16}O_2N_2S + CuCl_2 \rightarrow [MLCl_2].nH_2O$

Example

For thiourea-anisaldehyde copper (II) complex

1.0mmole of thiourea-anisaldehyde Schiff base and 1.0mmole of copper (II) chloride produced 1.0mmole of thiourea-anisaldehyde copper (II) complex

Theoretical yield of thiourea-anisaldehyde copper (II) complex = 8.230g

Experimental yield of thiourea-anisaldehyde copper (II) complex = 6.844g

$$\%\,\text{Yield of the Cu(II) Complex} = \frac{\text{Expeimental yield}}{\text{Theoeretical yield}} \times 100\%$$

$$\%\,\text{Yield} = \frac{6.844\text{g}}{9.652\text{g}} \times 100\%$$

% Yield of the complex = 70.91%

Hence, percentage yield of thiourea-anisaldehyde Copper (II) complex was found to be 70.91%.

The calculations were carried out in the same way to obtain the percentage yield of all the Metal (II) complexes of the respective thiourea-anisaldehyde Schiff base.

Appendix IC: Calculation of water of hydration

$[CuLCl_2].nH_2O$:

Weight of sample + filter paper = 0.665g

Weight of filter paper = 0.52g

Weight of sample =0.16g

Weight of sample and filter paper – weight of filter paper →0.6665g – 0.52g = 0.1465g

Initial weight of sample – final weight of sample →0.16g – 0.1465g = 0.0135g

$$\% \text{ of } H_2O = \frac{\text{Final weight of sample}}{\text{initial weight of sample}} \times 100\%$$

$$= \frac{0.0135\text{g}}{0.16\text{g}} \times 100\%$$

% of H_2O = 8.437%

Therefore, the percentage of water in $[CuLCl_2].nH_2O$ is 8.437%

Original weight of sample 0.16g = 100%

Mass of H_2O = 18g = 8.44%

$$= \frac{0.16\text{g}}{100} \times 8.44\% = 0.01304$$

$$= \frac{0.16\text{g}}{100} \times 91.56\% = 0.146496\text{g}$$

$$\frac{0.013504\text{g}}{18\text{gmol}^{-1}} = 0.00075022$$

$$\frac{0.146496\text{g}}{448\text{gmol}^{-1}} - 0.00032664$$

$$= \frac{0.00075022\text{mol}^{-1}}{0.00032664\text{mol}^{-1}} = 2.2967$$

n = 2.2967

Therefore, the number of water in $[CuLCl_2].nH_2O$ is 2.2967

The calculations were carried out in the same way to obtain the number of water of hydration in all the Metal (II) complexes of the respective thiourea-anisaldehyde Schiff base.

Appendix ID: Magnetic Susceptibility calculations

$[CuLCl_2].nH_2O$

$W_0 = 0.827g$

$W = 1.115g$

$R = -039$

$R_0 = -074$

$C = 1$

$L = 3.1cm$

Cross sectional area = 0.08245 cm^2

Calculations

Using;

$$\Psi_V = \frac{C^*(R - R_0)}{area}$$

Where,

$$C^* = \frac{C_{Bal}}{10^9}$$

$$\therefore \Psi_V = \frac{C_{Bal}(R - R_0)}{10^9 \times area}$$

$$= \frac{1 \times (-039 + 074)}{10^9 \times 0.08245}$$

$$\Rightarrow \frac{1 \times 10^{-9} \times 035}{0.08245}$$

$$\Psi_V = 4.2449 \times 10^{-7}$$

$$\Psi g = \frac{X_V}{density}$$

$$d = \frac{05g}{5ml} \Rightarrow 0.1g/ml$$

$d = 0.1g/cm^3$

$\therefore \Psi g = \frac{4.2449 \times 10^{-7}}{0.1}$

$\Psi g = 4.2449 \times 10^{-6}$

$\Psi m = Xg \times mm$

$= 4.2449 \times 10^{-6} \times 482.6$

$\Psi m = 2.0486 \times 10^{-3}$

$\mu_{eff} = 2.828\sqrt{\Psi mT}$

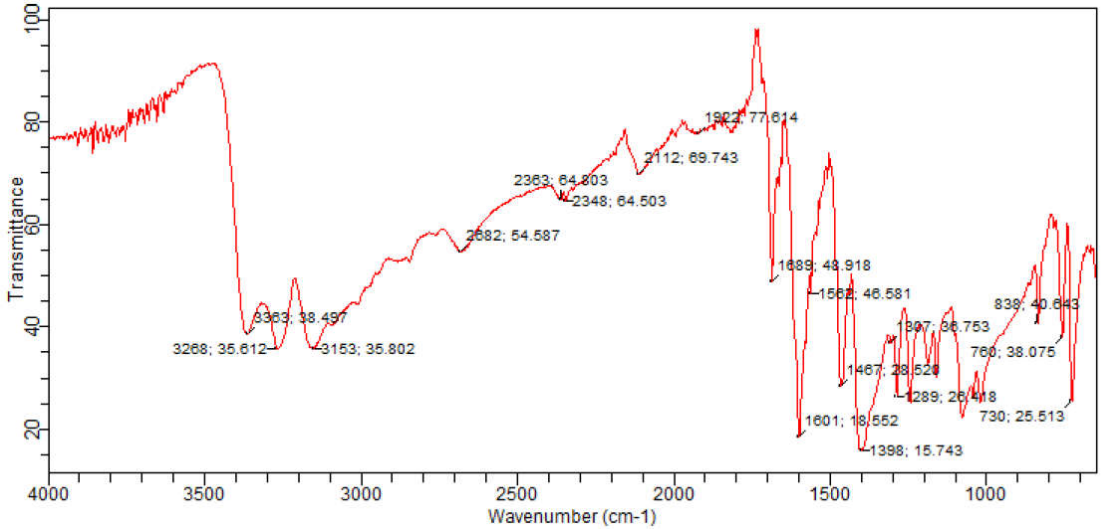
$= 2.2096$

$\mu_{eff} = 2.21$

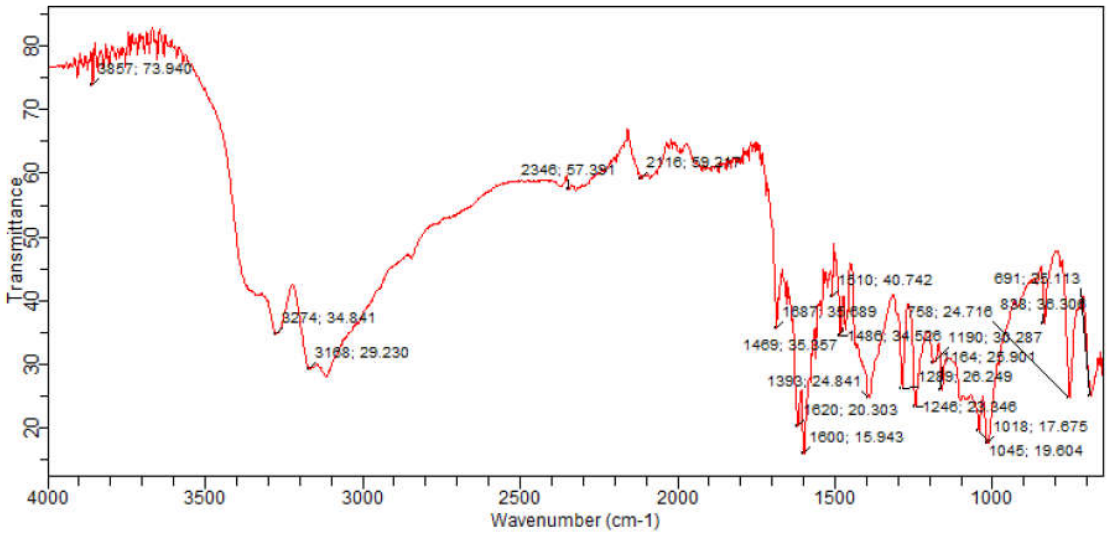
The calculations were carried out in the same way to obtain the magnetic susceptibility all the Metal (II) complexes of the respective thiourea-anisaldehyde Schiff base.

Appendix II: FT-IR Spectra

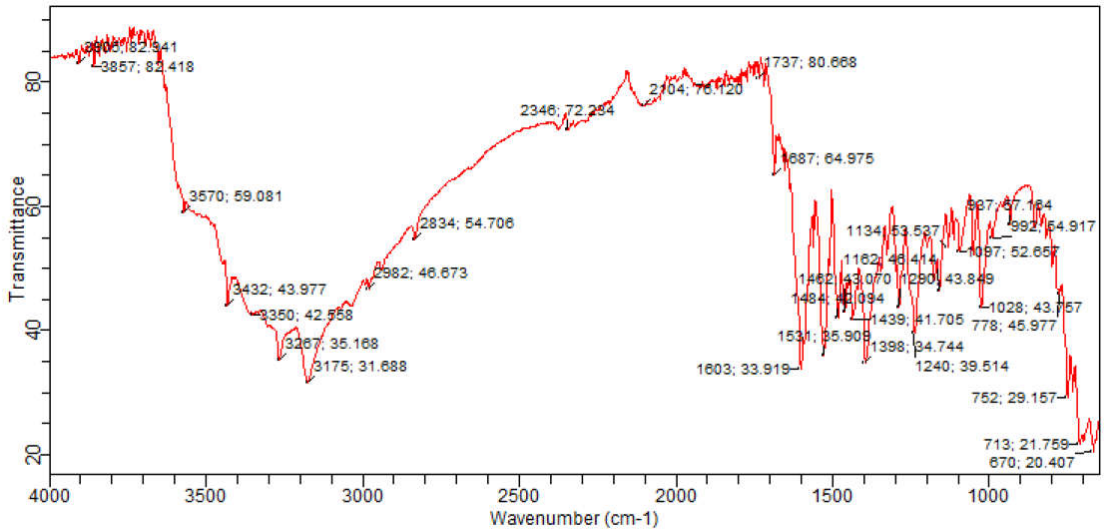
Appendix IIA: o-anisaldehyde-thiourea Schiff base



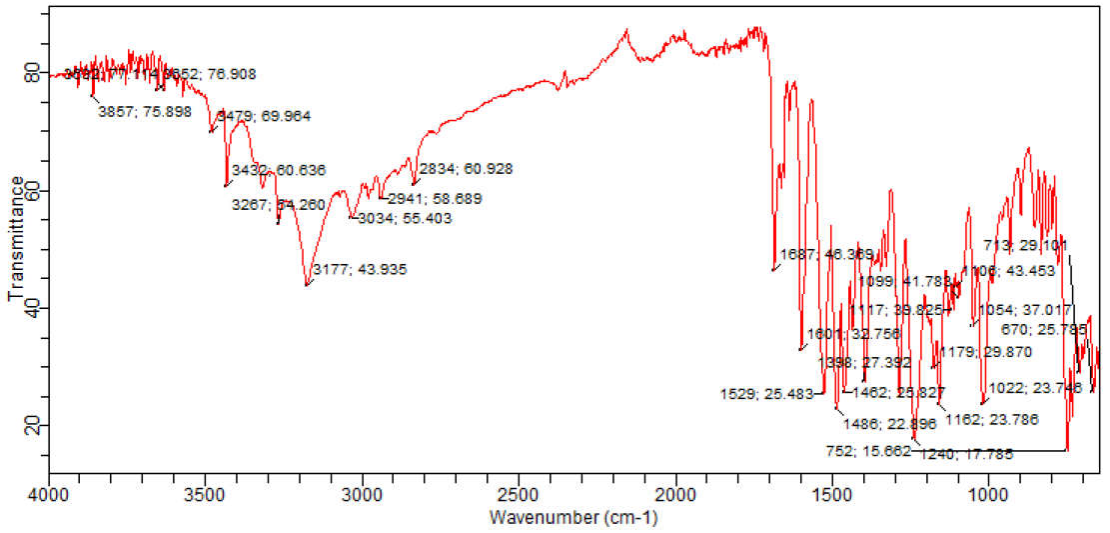
Appendix IIC: Cu(II) Complex



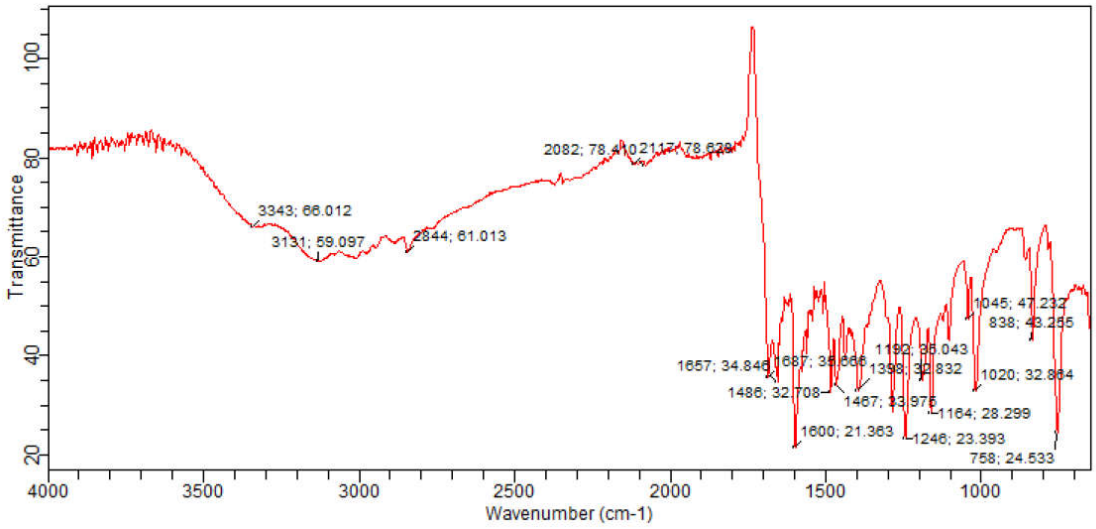
Appendix IID: Ni(II) Complex



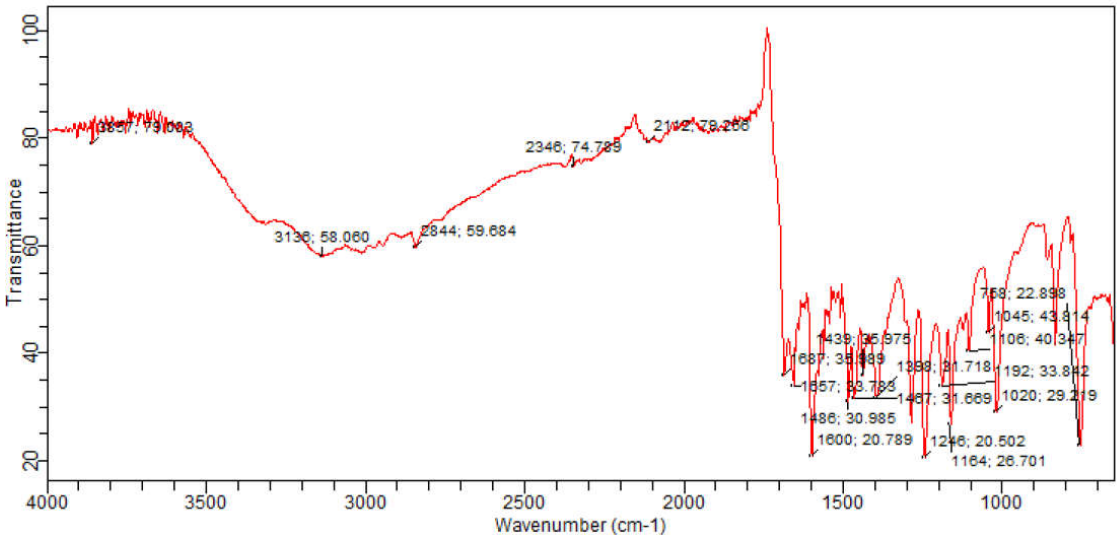
Appendix IIE: Mn(II) Complex



Appendix IIF: Co(II) Complex



Appendix IIG: Fe(II) Complex



Appendix III: UV-Visible values of the Schiff base and its metal (II) complexes

Appendix IIIA 1: Mole fraction of the ligand and absorbance values for (Cu) Cu^{2+} ion:

λ_{max}= 540nm

Cu : L	L mole fraction	Absorbance
09:01	0.10	0.0819
08:02	0.20	0.1189
07:03	0.30	0.2284
06:04	0.40	0.4503
05:05	0.50	0.5204
04:06	0.60	0.4036
03:07	0.70	0.2404
02:08	0.80	0.1860
01:09	0.90	0.0932

Appendix IIIA 2: Mole fraction of the ligand and absorbance values for (Co) Co^{2+} ion:

λ_{max}= 620nm

Co : L	L mole fraction	Absorbance
09:01	0.10	0.0736
08:02	0.20	0.0946
07:03	0.30	0.0964
06:04	0.40	0.1282
05:05	0.50	0.1506
04:06	0.60	0.1303
03:07	0.70	0.1083
02:08	0.80	0.0834
01:09	0.90	0.0822

Appendix IIIA 3: Mole fraction of the ligand and absorbance values for (Fe) Fe^{2+} ion:

λ_{max}= 580nm

Fe :L	L mole fraction	Absorbance
09:01	0.10	0.0902
08:02	0.20	0.0911
07:03	0.30	0.0913
06:04	0.40	0.0918
05:05	0.50	0.0925
04:06	0.60	0.0919
03:07	0.70	0.0918
02:08	0.80	0.0912

Appendix IIIA 4: Mole fraction of the ligand and absorbance values for (Mn) Mn^{2+} ion:

λ_{max}= 640nm

Mn : L	L mole fraction	Absorbance
09:01	0.10	0.0794
08:02	0.20	0.0842
07:03	0.30	0.0902
06:04	0.40	0.1053
05:05	0.50	0.1180
04:06	0.60	0.1031
03:07	0.70	0.1001
02:08	0.80	0.0929
01:09	0.90	0.0785

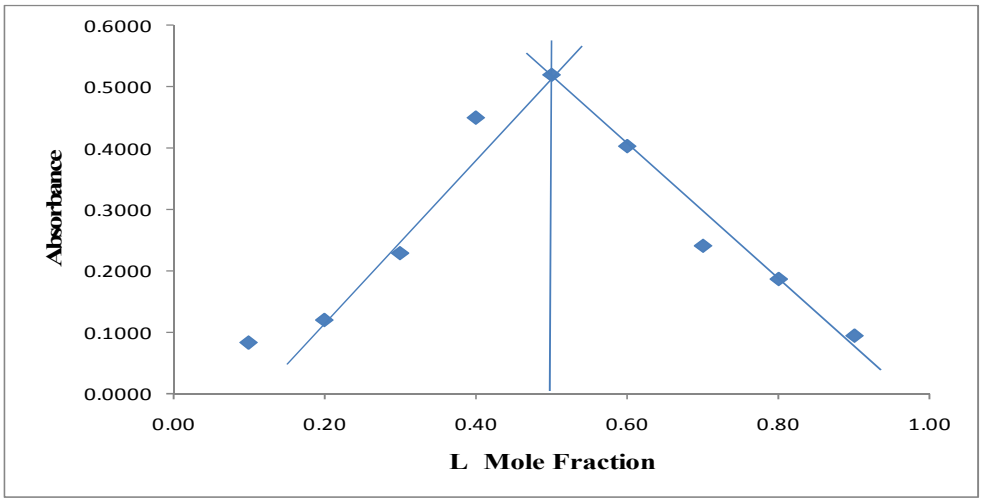
Table 4.6A 5: Mole fraction of the ligand and absorbance values for (Ni) Ni^{2+} ion:

λ_{max}= 700nm

Ni : L	L mole fraction	Absorbance
09:01	0.10	0.0845
08:02	0.20	0.0938
07:03	0.30	0.1092
06:04	0.40	0.1135
05:05	0.50	0.1474
04:06	0.60	0.1329
03:07	0.70	0.1081
02:08	0.80	0.0940
01:09	0.90	0.0893

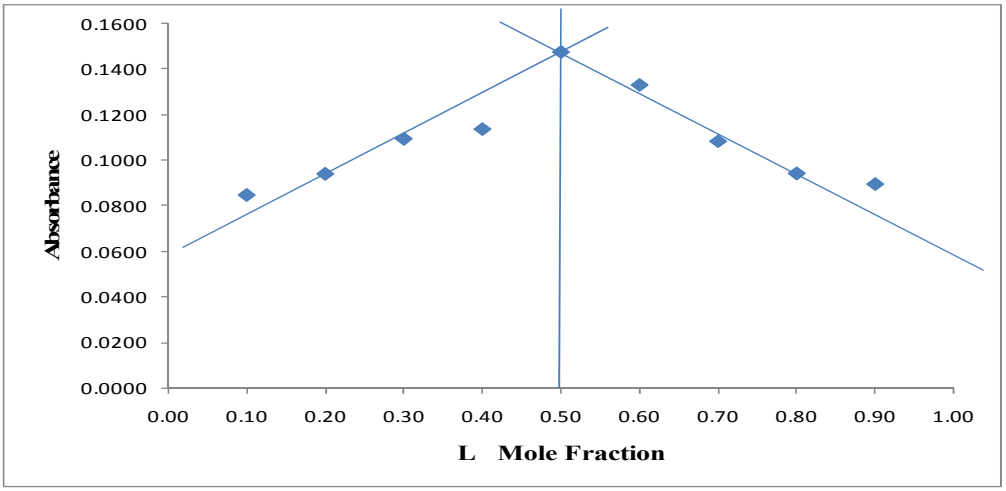
Appendix IIIB: UV-visible Results

λ_{max}= 540nm



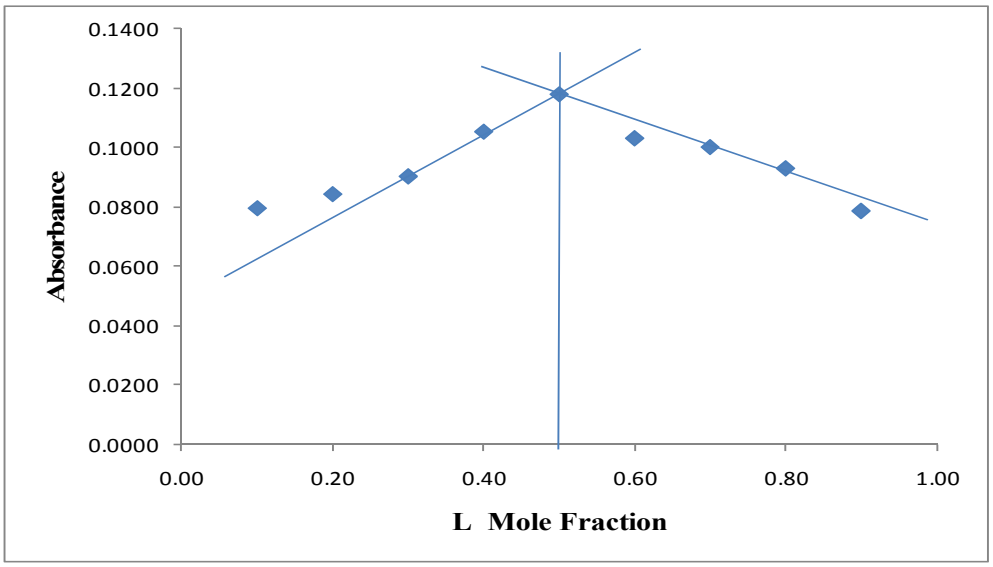
Plot of absorbance against mole fraction (Cu(II) Complex)

λ_{max}= 700nm



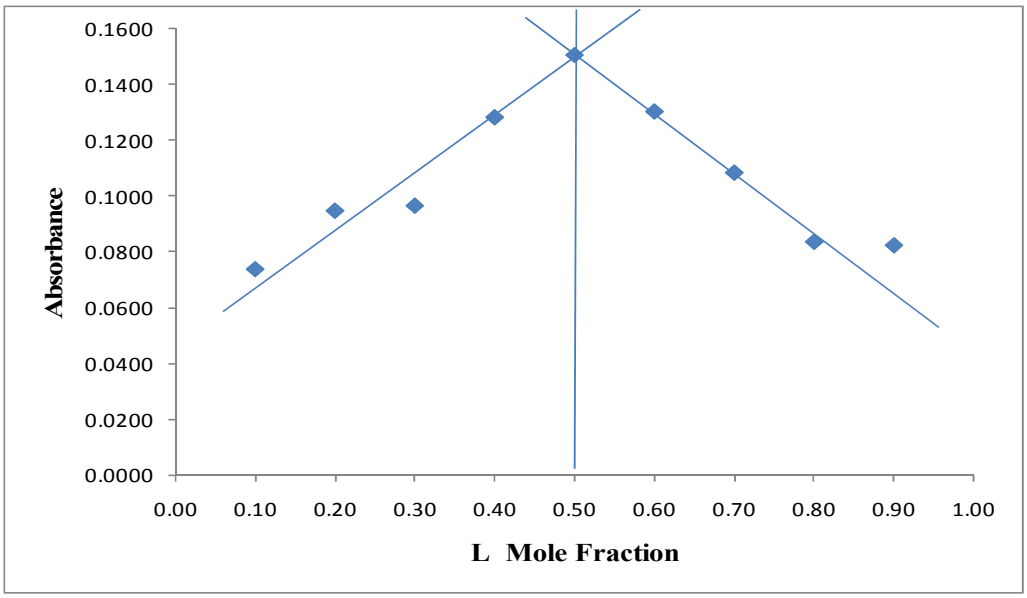
Plot of absorbance against mole fraction (Ni(II) Complex)

λ_{max}= 640nm



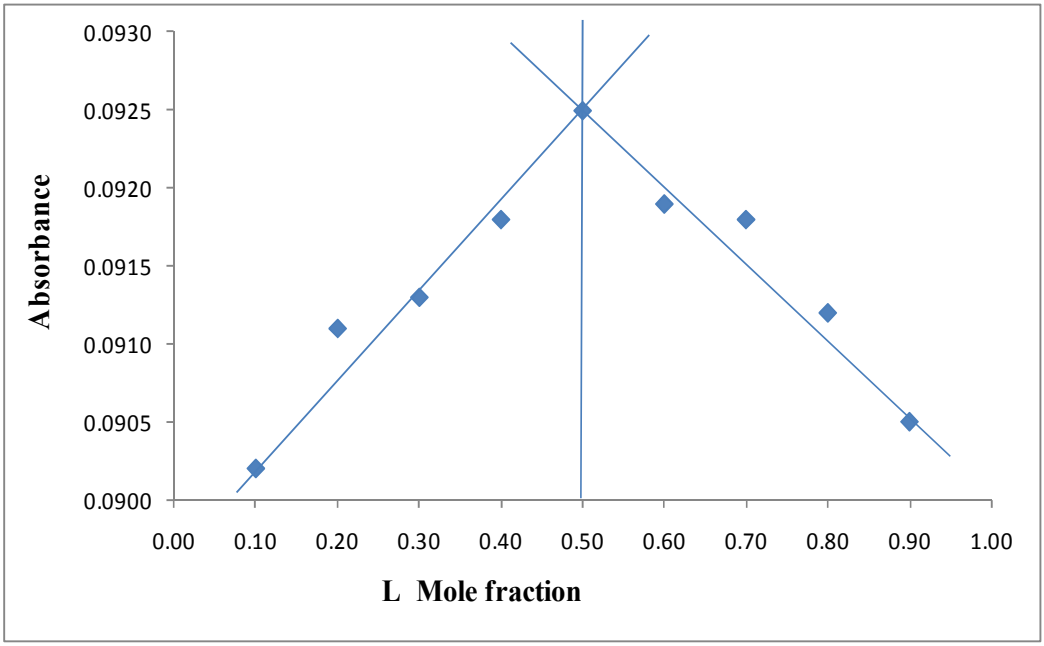
Plot of absorbance against mole fraction (Mn(II) Complex)

λ_{max}= 620nm



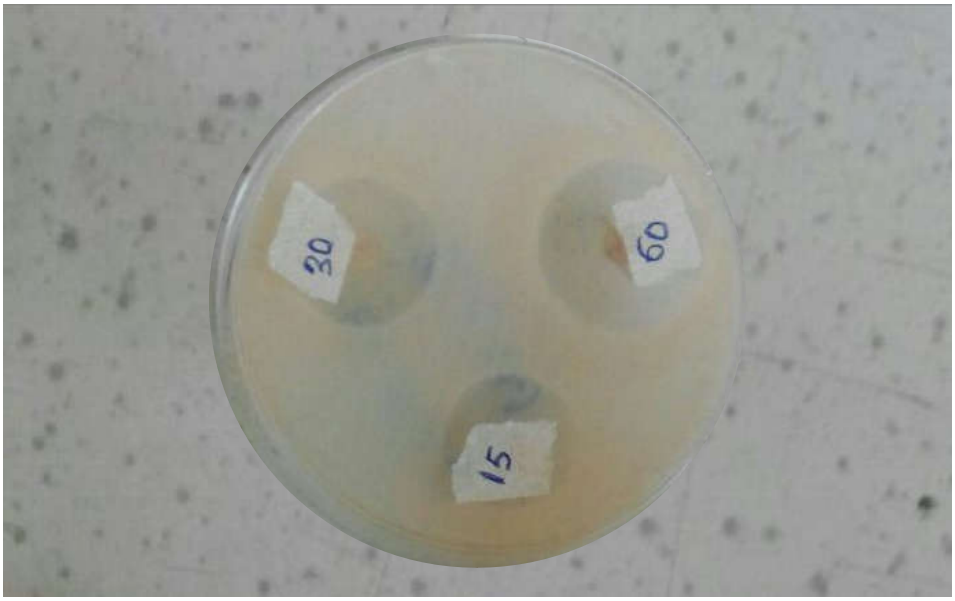
Plot of absorbance against mole fraction (Co(II) Complex)

λ_{max}= 580nm

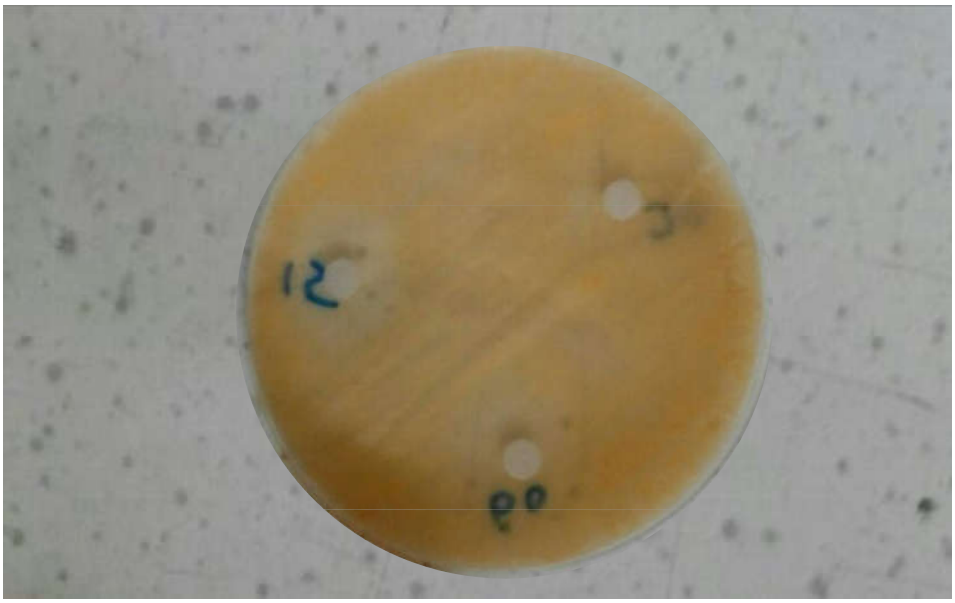


Plot of absorbance against mole fraction (Fe(II) Complex)

Appendix IV: Antimicrobial Activity



Antibacterial Result *E. coli* against $[CoLCl_2].4H_2O$



Anti fungal Result *Mocur indicus* against $[CoLCl_2].4H_2O$