ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES DEPARTMENT OF CHEMISTRY

Template Synthesis and characterization of Cd (II) and Cr (III) Schiff base Metal complexes Derived from Ethylenediamine, Acetyl acetone and Dithiocarbamates

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August 2024

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TEMPLATE SYNTHESIS AND CHARACTERIZATION OF Cd (II) and Cr (III) SCHIFF BASE METAL COMPLEXES DERIVED FROM ETHYLENEDIAMINE, ACETYLACETONE AND DITHIOCARBAMATES

A Thesis Submitted to School of Graduate Studies of Addis Ababa University in Partial Fulfilment of the Requirements for the Degree of Master of Science in Chemistry

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DECLARATION

I the undersigned confirm that the results reported in this work were obtained by research carried out by under supervision of advisor in the Faculty of science, Department of Chemistry, Addis Ababa University in the academic year 2023. No paper in any scientific journals or presentation in any international conference was made with the results in this paper. All materials used in this investigation have been properly recognized.

By:

Haile Zerihun Signature _____ Date _____

ABSTRACT

Cd (II) and Cr (III) Schiff base complexes were synthesized by template synthesis method. Cd (II) hydrated salts was reacted with Acetylene acetone and ethylenediami-ne in 1:2:1 molar ratios and Cr (III) anhydrous salt was reacted with Acetylene acetone, carbon disulfide and ethylenediamine in 1:1:2:2: molar ratios and N,N bis(acac)en Schiff base was synthesized by mixed en and acac in 1:2 molar ratios. Schiff base Cr (III) complex were coloured but Cd (II) complex was colourless. The product obtained Schiff base, Cr (III) and Cd (II) complexes were structurally investigated on the basis of conductance, magnetic susceptibility, IR, NMR etc. studies. The conductivity measurement of synthesized Cr (III) complex showed electrolyte, but Cd (II) complex was non-electrolyte and magnetic susceptibility showed Cr (III) complex was paramagnetic and Cd (II) was diamagnetic. At the last it is proposed that both the Cd (II) and Cr (III) complexes were showed octahedral geometry.

Key words: Schiff base, Acetylacetone, Ethylenediamine, Cr (III) and Cd (II) complexes, Carbon disulfide and template method

ACKNOWLEDGEMENT

First of all, I would like to give praise, glory and thanks for my God for giving me the strength throughout my study to carry out this work.

I would like to express my deepest gratitude and respect to my advisor Prof. Yonas Chebude for his guidance, continuous encouragement, facilitating suitable condition in the laboratory and comments throughout this thesis.

I am very thankful to my family and Ms. Dinknesh who help me to use the wifi service during my research work.

I would like also thank Addis Ababa University, chemistry department for providing materials and chemicals necessary to accomplish my study.

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LIST OF ABBREVIATIONS AND SYMBOLS

IR.....Infrared

FT…… IR- Fourier Transform Infrared

UV……Vis -Ultraviolet-visible

Nm…… Nanometre

PPm ……..Parts per million

Mp ……. Melting point

Λ_M …….. Molar conductance

DMF…….. Dimethylformamide

NMR …… Nuclear magnetic resonance

X_g ..... Gram susceptibility

X_M ……Molar susceptibility

μ_{eff} ……Effective magnetic moment

Mw ……..Molecular weight

Q ……..Quaternary

n…….. Number of unpaired electrons

M…….Molarity

M …… Metal

BM ……. Bohr Magnetons

DMSO …… Dimethylsulfoxide

cm…… Centimeter

L……Lligand

$CDCl_3$……...Deutrated chloroform

δ ……... Chemical shift

K……Specific conductance

DEPT……Distortion less enhancement polarization transfer

C=N……..Azomethine or imine group

Acac……. Acetyl acetone

En…….Ethylenediamine

Cr…….Chromium metal

Cd…….. Cadmium metal

DTCs……Dithiocarbamates

$CrCl_3$…….Chromium chloride

$Cd(NO_3)_2.4H_2O$……. Hydrated Cadmium nitrate

CS_2……Carbon-disulfide

CHAPTER-ONE

1. INTRODUCTION

A lone pair of electrons from a ligand are transferred to an empty orbital in a metal ion, forming transition metal complexes, also known as coordination complexes, which are molecules with a metal centre (ion) attached to ligands (atoms, ions, or molecules)(1). The evolution of coordination chemistry has been greatly aided by metal complexes of Schiff bases, an important class of ligands (2). Schiff bases are frequently employed as chelating agents in coordination chemistry; in general, bi-, tri-, or tetra-dentate ligands are better able to form extremely stable complexes with transition metal ions (3). Additionally, the kind of Schiff base and metal ion determines the synthesis, characteristics, and structure of Schiff base complexes (4). Schiff bases are adaptable ligands that are produced under various circumstances by employing common solvents to condense carbonyl groups (ketone or aldehyde) with primary amines while releasing water molecules. Schiff bases can alternatively be referred to as imines or azomethines (5, 6, and 7). Since Schiff discovered these kinds of compounds in 1864, a vast number of Schiff bases and their metal complexes have been produced and characterised for a variety of purposes (8). The chemistry of the metal complexes of Schiff bases, including nitrogen, oxygen, and other donors, has received a lot of interest lately due to its significance (9). Schiff base metal complexes, for example, that contain donors of nitrogen, oxygen, and sulphur have demonstrated a variety of biological actions, including antiviral, antimicrobial, anti-inflammatory, and anticancer properties (7).

I describe here the template synthesis and characterisation of Schiff bases and certain transition metal ions (Cd^{+2} and Cr^{+3}) of Schiff bases that are obtained from the current work of dithiocarbamtaes, acetyl acetone, and Ethylenediamine. In coordination chemistry, the term "template synthesis" describes these kinds of complicated formation reactions involving Schiff base components, such as amines, aldehydes, and ketone compounds combined with metal salts (8).

1.1 Statement of the problem

Due to their growing significance, Schiff bases and related complexes have drawn more attention as bio-inorganic chemistry has advanced. For instance, chemotherapy and surgery are two treatments for a class of human disorders called cancer that are used in the biomedical areas, but they have a lot of contrary effects. These days, a lot of Schiff bases and their metal complexes are synthesised and found in many medications, which are widely used to treat illnesses in humans like cancer and other conditions. In order to study Cd (II) and Cr (III) Schiff base complexes for various applications, the Schiff base ligand, which is produced from ethylenediamine, acetyl acetone, and Dithiocarbamates, was synthesised and characterised in this thesis.

1.2. Significance of the study

The study's outcome will be utilised as abases by investigators seeking to produce recently generated ligands and by investigators interested in synthesising Schiff base complexes. This is because of their extensive use in a variety of industries, including biological, agrochemical, fungicidal, analytical chemistry, and industry. This is the result of my investigation. Create the Cd (II) and Cr (III) metal complexes of Schiff bases using acetyl acetone, dithiocarbamate, and ethylenediamine. These compounds can be studied for their beneficial structural properties and a range of uses.

1.3. OBJECTIVES

1.3.1. General objectives

- The main aim of this work is the template synthesis and characterization new metal complexes of Cd (II) and Cr (III) from a Schiff base, derived from the condensation Ethylenediamine, acetyl acetone and dithiocarbamtaes with solvent conditions

1.3.2. Specific objectives

- To synthesis the Schiff base ligand from ethylenediamine and acetyl acetone using condensation.
- To synthesis Cd (II) metal complex, derived from Cd (II) metal salt, acetyl acetone and ethylenediamine using template method.
- To synthesis Cr (III) metal complex, derived from Cr (III) metal salt, acetyl acetone, carbon disulfide and ethylenediamine using template method.
- Cr (III) transition metal of Schiff base, which is obtained by carbon disulfide, and acetyl acetone condensation with ethylenediamine.
- To characterize the synthesized Schiff base ligand and complexes using the data those were obtained from different instruments.

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CHAPTER-TWO

2. LITERATURE-REVIEW

2.1. Coordination complexes (compounds)

Although coordination chemistry is a well-established and extensively researched field of inorganic chemistry, there are always several novel advancements being made in this field. New perspectives in coordination chemistry of transition metals were made possible by the preparatory work done at the turn of the century by Jorgenson, Werner, and numerous others (4). In actuality, Alfred Werner (1866–1919), whose work on coordination compounds earned him the 1913 Chemistry Nobel Prize, is primarily responsible for the development of the contemporary theory of coordination chemistry (4, 10, and 11).

The nature of metal-ligand connections, the structure, chemistry, stabilities, and other aspects of metal complexes have all been greatly expanded upon by these concepts (4). According to Werner's research, metal ions can have two distinct valences: a secondary valence, or coordination number, which is the total number of ligand-metal bonds that are bonded to the metal ion, and a primary valence, or oxidation state, which is equivalent to the positive charge on the metal ion (10).

Any of a class of compounds with chemical structures where ligands (neutral molecules, anions, or groups of atoms) surround a core metal atom (or ion) by coordinate covalent bonds is called a coordination compound (complex) (12).Metallic elements with entire d or f shells in either the neutral or cationic state are known as transition metals. Because of these imperfect valence shell orbitals, it can take in electrons from Lewis bases to create coordination complexes far more quickly than other elemental groups. Lewis bases known as ligands are required to have at least one pair of non-bonding electrons in order to contribute to a metal atom or ion (13). Because transition metals have distinct oxidation states, transition metal complexes are cationic, neutral, or anionic entities in which a transition metal is coordinated by ligands (14).

2.2-Schiff bases and its preparation

When any primary amine interacts under particular circumstances with a carbonyl component (an aldehyde or ketone), substances known as Schiff bases are created. To put it another way, it is a nitrogen analogue of acetone or aldehyde in which an azomethine or imine (-HC=N-) functional group has taken the place of the carbonyl group (CO). Schiff base compounds are hence referred to as imines structurally. Schiff bases are prepared using organic solvents such as methanol, ethanol (common), tetrahydrofuran, and 1, 2-dichloroethane. The German chemist Hugo Schiff's name, which was first used in 1864 to characterise the results of the reaction between primary amines (of the RNH_2 or $ArNH_2$ type) and carbonyl compounds, is the source of the term imine, sometimes known as Schiff's base. Chemical compounds with the general structure $R_2C=NR'$ (where R' differs from H) are regarded as a subclass of imines, which defies Schiff bases.

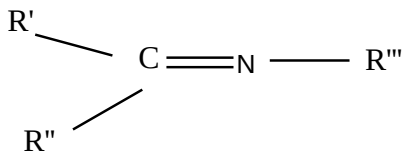
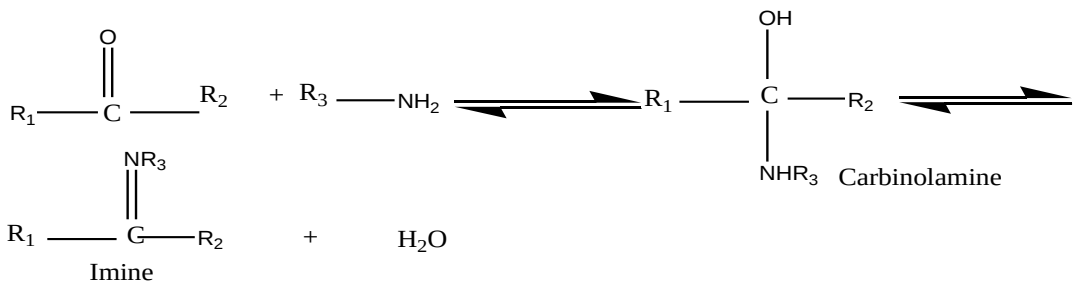


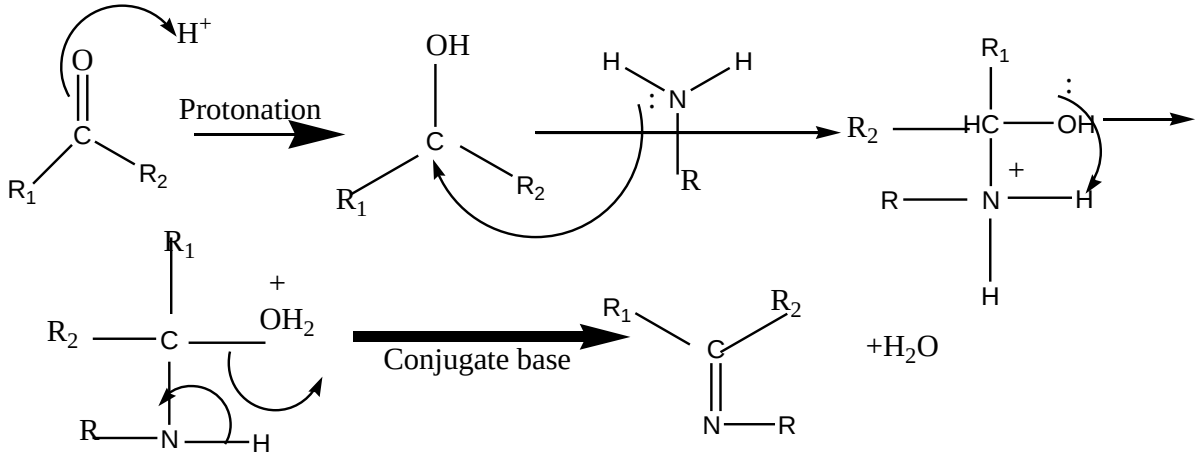
Figure-1: structure of Schiff bases (azomethine group)

The distinct structural pieces that defined Schiff bases, where R_1, R_2, and R_3 are either alkyl or aryl groups or more frequently other types of groups. H atoms could also be represented by R_1 or R_2. These are a broad class of substances that are distinguished by having a double bond connecting the carbon and nitrogen atoms. Their adaptability stems from the numerous ways in which they can be combined with different aryl or alkyl substituents (15, 16, and 17).The reversible process of forming a Schiff base from aldehydes or ketones is illustrated in the following scheme, which details the precise mechanism involved.



Scheme 1: Reversible reaction of a Schiff base formed from an aldehyde or ketones.

The amine combines with the aldehydes or ketones in the first stage of the mechanism to form carbinolamine, an unstable addition product. When heated or subjected to acidic or basic catalysis, the carbinolamine loses water. Actually, the Schiff base formation is a series of addition-based and elimination-based reactions. Because carbinolamine is an alcohol, dehydration reactions are catalysed by acids and bases. The following illustrates how Schiff base ligand is made from acid catalyzed dehydration processes.



Scheme-2: Reaction mechanism of Schiff base ligand in acid medium

Yet, as amines are basic substances, the acid concentration cannot be allowed to get too high. Schiff base ligands are extremely varied and play a major role in chemistry, particularly in the creation of Schiff base complexes, which have the ability to form stable complexes with nearly all metal ions. Because Schiff bases contain sulphur, oxygen, or nitrogen, they function as excellent chelating agents. In coordination chemistry, these substances often function as bi-, tri-, tetra-, or multi-dentate ligands. For instance, Schiff bases typically contain NO (bi-dentate

ligands) or N_2O_2 (tetra-dentate ligands) -donor atoms (groups), however atoms of sulphur, nitrogen, or selenium can take the place of the oxygen atoms. Additionally, Schiff bases are essential to contemporary coordination chemistry and have a wide range of uses, including in the food, dye, and analytical industries as well as in catalysis, fungicidal, agrochemical, and biological activities. Furthermore, the biological activity of azomethine derivatives, including their antimicrobial (antibacterial and antifungal), anticancer, and diuretic properties, depends on the C=N bond (15, 17).

2.3 The chemistry of Schiff base metal complexes

Schiff bases, which are ligands that coordinate to metal ions via azomethine nitrogen and are formed from amino and carbonyl compounds, are a significant class of ligands that have been thoroughly explored (18). Stated differently, Schiff bases have been crucial in the advancement of coordination or inorganic chemistry (19).For example, researchers have continued to be interested in the chemistry of metal complexes with Schiff base ligands that contain nitrogen and oxygen as donor atoms (20).

Due to their versatile production, strong solubility in common solvents, exceptional coordination ability, and capacity to form complexes with a wide range of transition metals and stabilise a variety of oxidation states, this type of Schiff base ligand has found widespread application (21). Schiff bases are thought to be excellent chelating agents due to their relative ease of preparation, synthetic flexibility, and the unique property of the C=N group. This is especially true when a functional group, such as -OH or -SH, is present close to the azomethine group, forming a five or six membered chelate ring with the metal ion.

In other words, Schiff bases are typically ligands that are bi-, tri-, tetra-, or poly-dentate and have the ability to form extremely stable complexes with transition metals. Because of this, Schiff bases have frequently been employed as chelating ligands in the field of coordination chemistry, and transition metals are known to form Schiff base complexes (1). However, the type of ligand and metal ion determines the complex's properties (22). Because metal complexes of Schiff bases have many applications in various disciplines and are convenient to prepare, there is generally on going interest in synthesising Schiff base complexes of metal ions. The wide range application of Schiff base metal complexes came from the versatility of Schiff base reactions with many different transition metals (23).

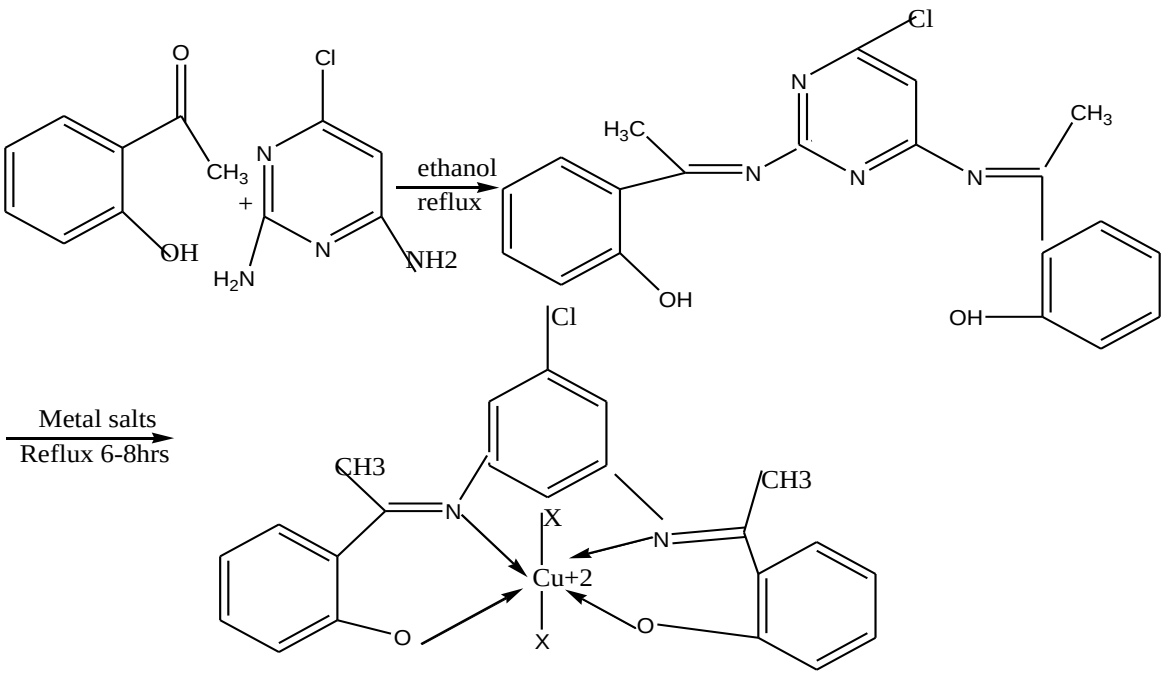
2.3.1 Methods of synthesis of Schiff base metal complexes

There are two important methods for the synthesis of Schiff base complexes; these are:

2.3.1.1: **Direct interaction of the Schiff base with the metal salts**

This process involves directly synthesising the Schiff base without the use of a metal ion or in the absence of one, and then adding the metal ion as a salt solution to synthesise the complex formation (24, 1). Nevertheless, "self-assembly" does not always indicate that a special agent that guides the reaction in a certain direction is present in the reaction system.

Precursor-1 + precursor-2 →Schiff base + Metal salt solution→ Schiff base metal complexes, an example is shown below in scheme-2:



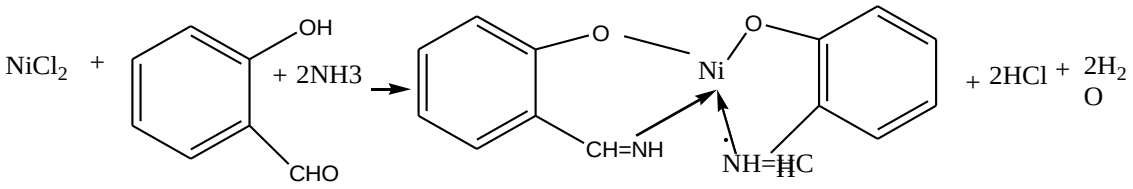
Scheme-3: Synthesis of the Schiff base complex by direct method

One of the advantages of this method is that it is possible to perform the spectral characterization of complexes by comparing with spectral data of the ligands.

2.3.1.2**: The template condensation of aldehyde (ketone), primary amine and metal salts**

Template synthesis in coordination chemistry refers to such complex formation reactions that occur between two or more molecules (ligand based reactions) coordinated to a metal ion (metal centre) (25). Precursor-1 + precursor-2 + metal salt solution→ Schiff base metal complex

Template synthesis can be considered a special case of so called ‘’self-assembly’’, which has long been used in organic chemistry for the synthesis of very complex organic compounds from rather simple substances. Methyl benzene C_6H_4 (OH)(CH=NH) in the presence of Ni(II) ion. The mixture undergoes condensation to give the Ni metal macro heterocyclic complex (In template synthesis the metal ion thus plays a useful role in directing the reaction to wards the desired ligand product, or aiding its isolation. A good example of synthesis that uses a template effect is the condensation reaction between nickel (II) chloride, 2 hydroxybenzaldehyde and ammonia m olecules with the formation of 1-hydroxy-2-imino scheme-3) (24).



Scheme-4: template methods of synthesis of Schiff base metal complexes

2.3.2: Types of template effects

Metal coordination imposes a specific geometrical orientation on ligand reactions, which can either greatly, boost or depend upon them. These reactions are known as metal template reactions. Kinetic template effects and thermodynamic template effects are the two primary categories of template effects.

I. The kinetic template effects

When the template effect arises from the stereochemistry imposed by metal ion coordination of some reactive functional groups (reactants), in a position promoting a series of controlled steps, a coordination or kinetic template effect occurs. Kinetic template influence the mechanistic path way.

II. The thermodynamic template effects

The term "thermodynamic templates" describes a process that has taken place and produced a more stable thermodynamic product that is present as a ligand and is stabilised by chelation to the metal ion (an equilibrium template effect). The observed reactivity variability can be explained by the modification of the ligands' electronic properties (such as acidity, flexibility, and conjugation) upon coordination. Metal complexes containing macro cyclic and acyclic poly dentate Schiff base ligands exhibit enhanced thermodynamic stability as a result of the chelating effect and coordinative sites. (25)

The template synthesis of metal macro heterocyclic compounds, a number of specific terms and expressions are used, the most important of which are the following:

A. Positive template

A template that brings together the reactive end groups of a molecule (molecules), facilitating intermolecular coupling.

B. Negative template

A template that prevents the reactive end groups of a molecule (molecules) coming together, suppressing intermolecular coupling and favouring intermolecular reactions (24).

2.3.3: Application of Schiff base metal complexes

Because they may be easily produced by condensation of primary amines and carbonyl compounds, such as aldehydes or ketones, also referred to as imines, Schiff base ligands are regarded as favoured ligands. The ability of Schiff bases to form complexes with transition metal ions makes them a valuable family of chemicals. Schiff base ligands can therefore be made with ease and combine to form complexes with nearly all metal ions. They have been thoroughly investigated and are coordinated to metal ions through azomethine nitrogen (26, 27, 28, 29).The active imine (C=N) connection present in the Schiff bases allows binding sites to be formed through nitrogen, including other hetero-elements like oxygen or/and sulphur. Transition metals can form complexes by binding with oxygen, nitrogen, or sulphur (29).

For azomethine derivatives to have biological activity, the C=N bond is necessary. Thus, it has been observed that a number of azomethines have exceptional diuretic, anticancer, and antimicrobial (antibacterial and antifungal) properties (27, 29). However, compared to their

ligands, the metal complexes have increased biological activity (28). Due to the recognition that many of these Schiff bases and their complexes may serve as models for biologically significant species, interest in Schiff bases and their complexes has increased as the field of bio-inorganic chemistry has developed. Some of these activities include anti-bacterial, anti-fungal, anticancer, anti-oxidant, anti-inflammatory, anti-malarial, and antiviral properties (26–30).

Anticancer

Malignant neoplasms, sometimes known as cancer, are a class of disorders characterised by unchecked cell proliferation, invasion, and occasionally metastasis. Surgery and chemotherapy are part of its treatment; however the current chemotherapeutic medications have a lot of (many) negative effects. Recent research has revealed that Schiff base derivatives have strong anti-cancer capabilities, which is a major public health concern. To limit the proliferation of K562 tumour cells, for instance, ternary complexes of rare earth elements with salicyl aldehyde L-phenylalanine as Schiff base have demonstrated outstanding anticancer properties (26, 29).

Anti-malarial properties

When left untreated, malaria produced by four species of the plasmodium genus (P. falciparum, P. vivax, P. ovale, and P. malariae) causes major health issues. Finding a cure for this illness is top priority. Schiff base may have potential as a malaria preventive medication. N-[(1E)-methylene-5-nitro-1-naphthyl] of the 5-nitroisoquinoline Schiff bases, -1[2(trifluoromethyl) phenyl] methanamine was the most potent anti-malarial agent (29).

Anti-viral properties

Ag (I) Schiff base complexes containing glycine and salicylaldehyde shown up to 74% efficacy in ward suppression against the cucumber mosaic virus (27, 29). Good HIV-I inhibitors were thiazolines and azetidinones, which were produced by reacting Schiff bases with thioglycolic acid and chloral acetyl chloride, respectively. Treatment for SARS and HIV is more successful with i satin Schiff bases (29).

Anti-oxidant activity

The identification of molecules with antioxidant potential has sparked a lot of attention. Because synthetic antioxidants are more widely used and more cost-effective than natural antioxidants, researchers have chosen to employ the latter because they are known to be the most costly. In

order to effectively capture reactive oxygen species (ROS) and act as antioxidants, certain metal complexes have been studied. As an example, the antioxidant activity of the metal complexes with methyl and nitro substituents was shown to be higher than that of the complexes with 4-hydroxy groups. However, the complexes exhibited more activity in comparison to the ligand; this was caused by the metal ion's coordination interaction with the organic ligand (28).

Anti-inflammatory activities

Numerous Schiff bases have been discovered to have anti-inflammatory properties that may be useful. For instance, Schiff base derivatives of 4-aminophenazone (5-dimethyl-2-phenyl-1, 2-dihydro-3H-pyrazol-3-one) were prepared and tested in mice for their ability to reduce inflammation, reduce pain, and reduce fever. Furthermore, the most effective anti-inflammatory agent was Schiff bases, which were made from 4-amino-1, 5-dimethyl-2-phenylpyrazol-3-one, 2, 3-dihydroxybenzaldehyde, and N-(4-bromobenzylidene)-[2-2, 6-dichloroaniline) benzyl carbazide (29).

Antibacterial activity of Schiff base complexes

Antibiotic-resistant bacteria are the source of infectious illnesses with rising death rates. There is undoubtedly a pressing medical need for the creation of novel antibacterial medications. It has been determined that Schiff bases are prospective (perhaps effective) antibacterial agents (29). However, compared to their free ligands, the majority of the Schiff bases' metal complexes exhibit far stronger antibacterial activity. Examples of complexes exhibiting antibacterial activities against Escherichia coli, staphylococcus aureu, Klebsiella pneumonia, Mycobacterium smegmatics, P. aeruginosa, Enterobacter cloacae, and Micrococcus leteus are Co (II), Cu (II), Ni (II) and Mn (II), with Schiff bases derived from 2, 6-diacetylpyridine and 2-pyridinecarboxaldehyde with 4-amino-2, 3-dimethyl-1-phenyl-3-pyrozolin-5-one(27,28)

Some gramme positive S. aureus and gramme negative E. coli bacteria were tested for the antibacterial activity of tetra-dentate Schiff base ligands (ONNO), which are derived from the condensation of ethylenediamine and o-hydroxyaldehyde/ketone and their VO_3 complexes. However, the ligand is only effective against S. aureus (27, 29).

VII. Anti-fungal activity of Schiff base complexes

Systemic fungal infections are potentially fatal illnesses that have become more common recently. To be regarded as promising antifungal medications, additional potent antifungal drugs must be discovered and developed. For instance, Schiff bases containing sulphur that are generated from derivatives of thiazoles and benzothiazoles have potent antifungal action (29). Since the metal ions in poly-chelates appear to be particularly prone to deactivating enzymes that depend on free hydroxyl groups for their activity, the presence of N and O donors in ligand and its metal chelates suppresses the synthesis of enzymes. Every metal poly-chelate has a higher level of toxicity than the corresponding ligand (27, 29).Additionally, when compared to the ligand and the matching metal salt, Cu (II), Ni (II), and Co (II) complexes have demonstrated superior antifungal activity. A yeast-like fungus called C. albicans was used to investigate two bi-dentate Schiff base ligands: 2-(2-hydroxy-3, 5-dichloro/dibromo) benzaldehyde-[4-(3-methyl-3-mesitylcyclobutyl)-1, 3-thiazol-2-yl] hydrazine, L1H, and L2H together with their metal complexes (27).

2.4: The chemistry of Ethylenediamine

Ethylenediamine, $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ (abbreviated as en when a ligand) is the organic compound with the chemical formula $C_2H_4(NH_2)2$.

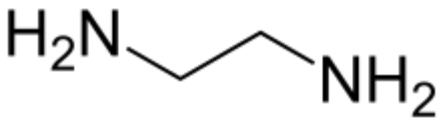


Figure-2: structure of ethylenediamine

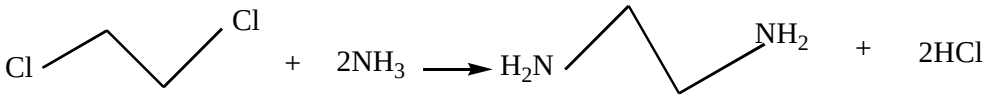
At ambient temperature, ethylenediamine is a colourless liquid with an ammonia-like odour with a melting point of 11.1°C and a boiling point of 116.9°C at 1 atmosphere. It is classified as a basic amine. 1, 2-diaminoethane is entirely miscible in most organic solvents and water. It reacts with water in an aqueous solution to produce the two equilibria that are depicted below.

$$H_2N\_CH_2\_CH_2\_NH_2 + H_2O \longrightarrow H_2N\_CH_2\_CH_2\_NH_3^{+} + OH^{-}$$

$$H_2N\_CH_2\_CH_2\_NH_3^{+} + H_2O \longrightarrow H2N\_CH_2\_CH_2\_NH_4^{+2} + OH^{-}$$

Scheme-5: Ethylenediamine in water

Each nitrogen atom connects a water molecule through a hydrogen bond of the form N-H-O-H in ethylenediamine (en), which has a strong interaction with water molecules. These water molecules, along with others from the metal's first and second hydration spheres, are eliminated during the creation of the metal complexes. Another commercial method for producing ethylenediamine is to subject 1, 2-dichloroethane to ammonia pressure-treated at 180°C in an aqueous media.



Scheme.6: Industrially production of Ethylenediamine from 1, 2-dichloroethane and ammonia

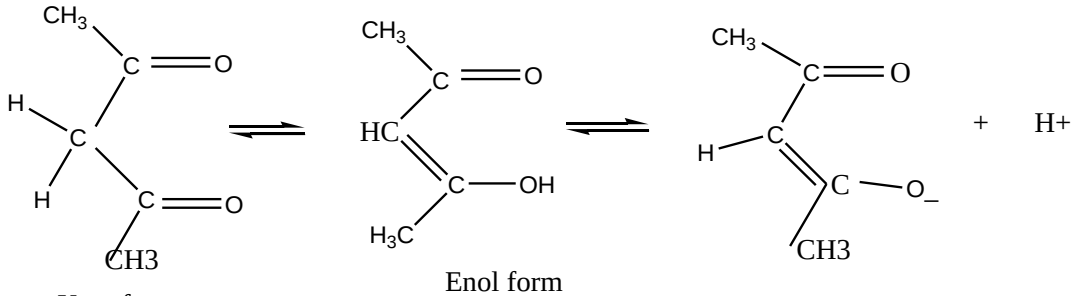
In this reaction hydrogen chloride is generated, which forms a salt with the amine. The amine is liberated by addition of sodium hydroxide. Another industrial route to Ethylenediamine involves the reaction of ethanolamine and ammonia.

Scheme.7: Industrially production of Ethylenediamine

The gaseous reactants are passed across a bed of heterogeneous nickel catalysts throughout this process. It can be made in a laboratory setting through the reaction of urea and ethylene glycol. Distillation can be used to extract water from ethylenediamine after it has been treated with sodium hydroxide. In any case, methylenediamine is a well-known bi-dentate chelating ligand for coordination compounds. When methylenediamine functions as a ligand, the two nitrogen atoms donate their single pairs of electrons. In inorganic chemistry, it is frequently shortened to "en" (31).

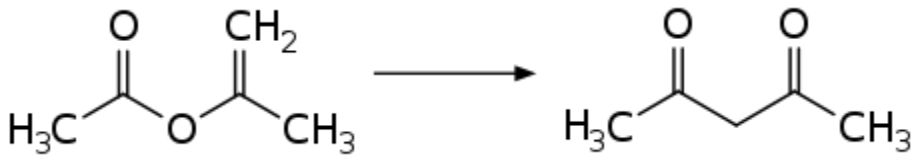
2.5: The chemistry of acetyl Acetone

The chemical formula of acetyl acetone, often known as acac, is $CH_3COCH_2COCH_3$. It is an organic molecule found in 2, 4-pentanedione. Classified as a 1, 3-diketone (a beta-dike tone), it is a very clear, colourless to light yellow liquid that forms the acetyl acetonate anion (often abbreviated acac-) scheme as an equilibrium combination of tautomeric keto and enol.-1.



Scheme.8: keto-enol tautmerism in acetyl acetone and formation of the acetylacetonate anion

When metal ions are present, the acac anion can function as a ligand and the metal will usually form a bi-dentate complex with the two oxygen atoms. Since both keto groups condense, acetyl acetone is a flexible bi-functional precursor to hetero-cycles. Acetyl acetone is miscible in a wide range of organic solvents, and its solubility rises as ionic strength and acidity rise, most likely as a result of an enol-keto shift. Industrial acetyl acetone is made by thermally rearranging isopropenyl acetate.



Scheme.9: Industrially preparation of acac from isopropenylacetate

Laboratory routes to acetyl acetone also begin with acetone. Synthesis of acac from Acetone and acetic anhydride upon the addition of boron tri-fluoride (BF_3), as a catalyst.

$(CH_3CO)_2\ O + CH_3C(O)CH_3 \rightarrow CH_3C\ (O)CH_2C(O)CH_3$

A second synthesis involves the base catalysed condensation of acetone and ethyl acetate, followed by acidifications.

$NaOEt + EtO_2CCH_3 + CH_3C\ (O)\ CH_3 \rightarrow NaCH_3C\ (O)\ CHC\ (O)\ CH_3 + 2EtOH$

$NaCH_3C\ (O)\ CHC\ (O)\ CH_3 + HCl \rightarrow CH_3C\ (O)\ CH_2C\ (O)\ CH_3 + NaCl$ (32, 33)

Scheme.10: Laboratory preparation of acetyl acetone

2.6: The chemistry of some transition metal ions

2.6.1: The chemistry of chromium

Group 6's first element is chromium, which has the atomic number 24 and the chemical symbol Cr. The metallic form of chromium is a hard, brittle, glossy, steely-grey 3d transition metal that melts at 1903.10°C.

Figure.3: sample of pure chromium metal

One crucial trace metal in the diet of humans is chromium (III). It is a crucial nutrient that the body needs to digest specific carbohydrates, proteins, and lipids. It is involved in the metabolism of glucose. Furthermore, the industrial uses of chromium (VI) and chromium (III) include tanning leather, wood preservation, dyes and pigments, and chrome plating. The element's ground state electron configuration is $3d^5 4s^1$, whereas the trivalent Cr (III) has an electron configuration of [Ar] $3d^3$ $4s^0$ for d^3. The element's ground state electron arrangement defies the Aufbau principle. A special focus on colder chromium (III) complex ions with ligands is placed on the chemistry of chromium (major oxidation states +3 and +6).

The compounds show a variety of geometries, such as octahedral, tetrahedral, square planar and deformed geometries. All Cr (III) complexes require three unpaired electrons, regardless of the ligand field's intensity. In the high spin state, octahedral Cr (III) complexes with a ^4A_2g ground state should exhibit three spin-allowed transitions (34). Three bands, corresponding to $^4A_2g \rightarrow {}^4T_2g$ (F), $^4A_2g \rightarrow {}^4T_1g$ (F), and $^4A_2g \rightarrow {}^4T_1g$ (P) transitions, are visible in the electronic spectra of Cr (III) complexes at 18880-19120cm-1 (v_1), 24650-25875cm-1 (v_2), and 39900-41055cm-

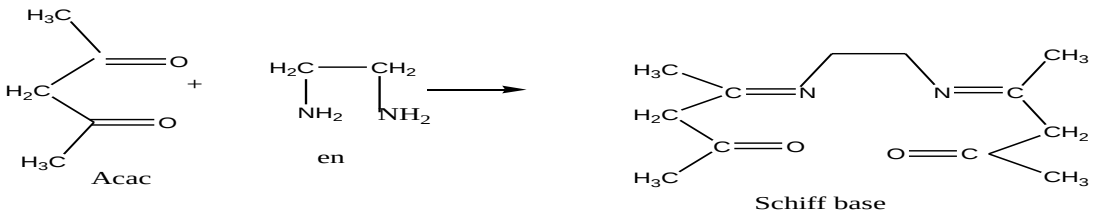
1 (v_3). These bands represent the octahedral geometry surrounding the Cr (III) ion. Two spin forb idden transitions are also possible, $^4A_2g \rightarrow {}^2Eg$ and $^4A_2g \rightarrow {}^2T_1g$. magnetically octahedral Cr (III) complexes have a relative simple behaviour. They all should have three unpaired electrons and thus possess magnetic moments ranging from 3.89-3.98 B.M. Depending on the orbital angular momentum contribution (35).

2.6.2: The chemistry of cadmium

The silver-white, soft, ductile metal cadmium (Cd) is a member of group IIB of the periodic table, along with mercury and zinc. It's melting and boiling temperatures are relatively low, at 320.9 °C and 765 °C, respectively. Divalent Cd (II) ions exhibit flexible coordination properties. Their electron configuration is [Kr] $4d^{10}$. The cadmium (II) ion's coordinative behaviour is somewhat similar to that of zinc (II). For Cd^{+2}, the primary coordination numbers found are 4, 5, and 6. Compared to Zn^{+2}, Cd^{+2} adopts coordination numbers 6 more readily because to its bigger size. Zn^{+2} can be replaced by Cd^{+2} in the active site of Zn-enzymes, which can impact Ca^{+2} metabolisms. Compound containing Cd^{+2} ions that is widely utilised in industry for things like Ni-Cd batteries, pigments in paper, plastic, glass, and ceramics, and materials that are resistant to biological activity and corrosion. The "softness" of cadmium (II) ions and the possibility of obtaining cadmium (II) compounds with chelating ligands that comprise donor atoms from N, S, and O make them appealing (36).

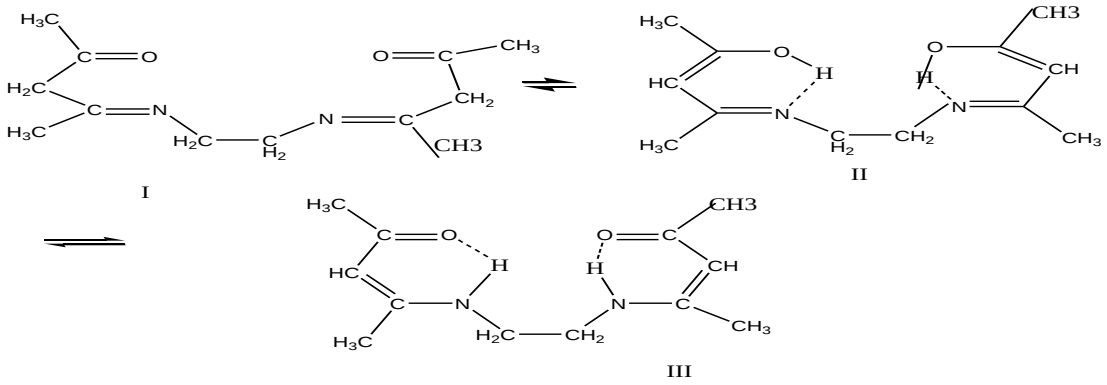
2.7: The chemistry of N, N bis (acetyl acetone) Ethylenediamine

The Schiff base bis (acetyl acetone) Ethylenediamine, H_2acacen obtained from the condensation reaction of Ethylenediamine with acetyl acetone (beta-dike tones) have been used as ligand for the complex formation with a variety of transition metals. It was isolated as colorless needle like crystals from the condensation reaction of en with acetyl acetone (acac) at room temperature.



Scheme.11; A Schiff base was prepared from acac and en

The bis (acac) en liquid has been isolated as stable molecule in its protonated form H_2acacen from the condensation reaction of acac and en (37).This ligand is shown above in scheme. 11. Is in the keto form, but undergoes keto-enol tautomerization like acac, itself.



Scheme.12. Keto-enol tautomerization of bis (acac) en

It is the enol form which coordinates to the metal; this enol form must be deprotonated to enable into coordinate. And this shows the existence of intra-molecular N-H-O hydrogen bonding (38).

2.8: The chemistry of Dithiocarbamates

In the coordination chemistry of metals and main group elements, dithiocarbamates (DTCs) are a type of tiny organic compounds that play a significant role as ligands (39). These soft donor ligands may stabilise both high and low valet metal ions. The two surfer atoms have a strong metal binding property and can form chelates with any transition metal ions (stable metal complexes) due to their resonance.

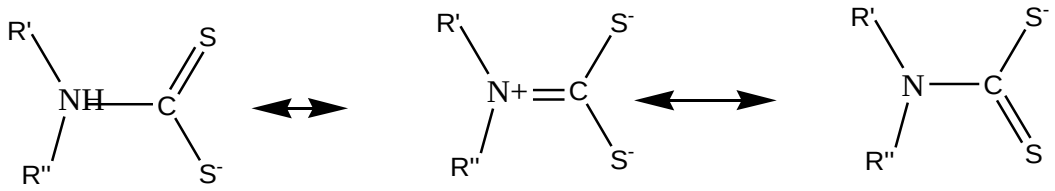


Figure.4: Resonance structure of the dithiocarbamate anion (II)

The binding properties of Dithiocarbamates; could bond as mono-dentate, bi-dentate chelating or anisobi-dentate (chelating or bridging ligands) as present in figure 5. And also stabilize a wide

range of transition metals (even at a varying of metal oxidation states) and adopting a wide range of structural geometry upon coordination to a metal (40).

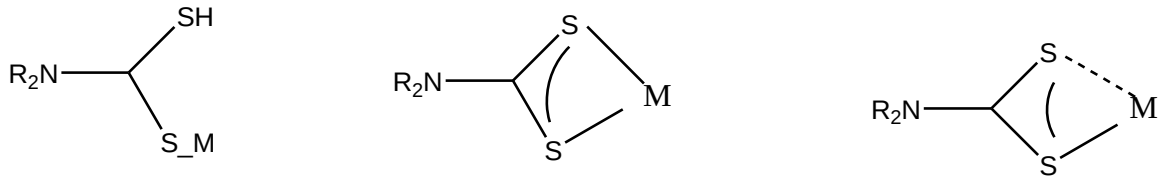


Figure.5: Different coordination modes of dithiocarbamate complex

Dithiocarbamate ligands are more intricate substances made up of sulphur atoms in organic form. This could be because the CSS groups have a low biting angle, which allows them to interact with nearly all of the metals on the periodic table. Furthermore, it contains sulphur atoms, which have the ability to form complexes by joining the central metal atom with a single pair of electrons (39, 40). Structural alterations are possible because the dithiocarbamate group's functional groups are easily changed. The coordination geometry of the resultant complex is mostly determined by the coordination reaction and can be influenced by a number of parameters, including the kind of metal ions, their oxidation state, and the composition of the ligands (40).

As the result, their ligands can form complexes with octahedral, square planar or tetrahedral geometry depending on the type of metal ion and also the ratio of the metal-to-ligand. Both the dithiocarbamate ligands and dithiocarbamate complexes are useful in several applications. However, when both ligands and complexes found relevance in similar applications, the complexes appear to be more potent than the ligands (41). But Dithiocarbamates are essential materials that have been extensively explored in coordination chemistry, medicine, radiopharmaceutical chemistry, sensing engineering, materials science, industry applications and including biological activity (39).

CHAPTER –THREE

3. MATERIALS AND EXPERIMENTAL METHODS

3.1 Chemicals

The chemistry lab chemical store was the source of all the chemicals needed for the production of Schiff bases and complexes. Acetyl acetone and ethylenediamine were the chemicals used to create Schiff base; for complexes, the anhydrous salt of chromium chloride ($CrCl_3$), carbon disulfide, hydrated salt of cadmium nitrate (Cd $(NO_3)_2.4H_2O$), and acetyl acetone were the chemicals utilised.

3.2 Solvents and Reagents

The solvents and reagents ethanol (CH_3CH_2OH), chloroform, dimethyl sulfoxide (DMSO), ethyl acetate, acetonitrile, benzene, distilled water, nitric acid (HNO_3), and silver nitrate ($AgNO_3$) were used for preparing solution, testing, checking the solubility, and washing of the synthesised samples and apparatus. All of them were taken from the laboratory room.

3.3 Apparatus and instruments

3.3.1 Apparatus

Apparatus that are available in the laboratory room and used to accomplish these experiments are a round bottle flask, hot plate, rotary evaporator, beakers, measuring cylinders, volumetric flasks, condenser, funnel, test tube, filter paper, magnetic stirrer, crucible, etc.

3.3.2 Instruments

- **Digital melting point apparatus**

It is an instrument used to measure, record, and display the melting point temperature of the given solid samples held in glass capillary tubes. The three tubes can be placed in an illuminated

chamber with an aluminium block. The glass capillary tubes were filled with the prepared sample and immersed into the chamber. Observe through an eyepiece and record the temperature at which the entire sample converted into liquid.

Figure 6: Stuart SMP3 Melting point apparatus

- **Magnetic susceptibility balance**

It is a sensitive instrument used to determine the magnetic properties and nature of electrons in solids and liquid samples. It can be used to measure a wide range of paramagnetic and diamagnetic natures of substances. Substances that contain unpaired electrons are paramagnetic, while the absence of unpaired electrons is diamagnetic.

Figure 7: Sherwood magnetic balance

- **Conductivity meter**

A conductivity meter is an electrochemical instrument used for the determination or measurement of the electrical conductance of an electrolyte solution. The electric conductivity of an electrolyte solution depends on the type of ions (cat ions and anions).

Figure 8: HI5521, HI5522- Conductivity bench meter

- **UV-Vis Spectrophotometer**

A UV-Vis spectrophotometer is an instrument that is used to measure the intensity of light transmitted through, absorbed, or reflected by a sample compared to a reference measurement of the incident light source or blank sample across a certain wave length range of UV or visible light [42]. It is important for the identification and determination of chemical compounds.

Figure 9: UV-Vis Spectrophotometer.

- **FT-IR Spectrometer**

A Fourier-transform infrared spectrometer is a largely used technique to identify the functional groups in the materials (gas, liquid, and solid) by using the beam of infrared radiation and structural analysis of the compounds. An infrared spectroscopy measured the absorption of IR radiation made by each bond in the molecule in the range from 4000 cm^{-1} to 400 cm^{-1} (43).

Figure-10 Perkin Elmer spectrum 65FTIR spectrometer

- **NMR Spectrometer.**

In analytical chemistry, nuclear magnetic resonance (NMR) is a spectroscopic tool that is used to determine the content, purity, and molecular structures of a sample. It provides us with details regarding the quantity and kinds of atoms (protons and carbons) that are present in a specific molecule [44]

Figure 11: NMR spectrometer

3.4 Experimental Methods

The Schiff base ligand was synthesized by the condensation process of acetyl acetone with ethylenediamine, and the metal complexes were synthesized by the template method by mixing acetyl acetone and ethylenediamine with hydrated salts of cadmium nitrate ($Cd(NO_3)_2$,$4H_2O$) and acetyl acetone, ethylenediamine, and carbon disulfide with anhydrous salt of chromium chloride, $CrCl_3$, respectively.

3.4.1 Synthesis of Schiff base Ligand

Acetyl acetone (20mmol, 2.056 ml) was dissolved in 20 ml of ethanol, and in another beaker, ethylenediamine (10mmol, 0.667 ml) was dissolved in 15 ml of ethanol. The two solutions were mixed in a round bottom flask and then refluxed over a water bath for 11 hours; a yellow-orange solution with some solids was formed and concentrated with a rotary evaporator. Then, it was washed with cooled ethanol and dried at room temperature. Finally, a yellow-orange solid was collected.

2  + 1  → 

Acetyl acetone Ethylenediamine Schiff base

Scheme 13: Synthesis of Schiff base

The balanced chemical reaction also represented as follow in scheme-14.

$$NH_2\text{-}CH_2CH_2NH_2 + 2CH_3COCH_2COCH_3 \rightarrow C_{12}H_{20}N_2O_2 + 2H_2O$$

Scheme 14: balanced chemical reaction in the Synthesis of Schiff base

3.4.2 Template Synthesis of Cadmium Metal Ion Complex

3.08 g (10mmol) of Cd $(NO_3)_2.4H_2O$ salt, 20mmol (2.056 ml), acetyl acetone, and 10mmol (0.667 ml) of ethylenediamine were taken and dissolved in 10 ml, 20 ml, and 10 ml of ethanol in three different beakers, respectively. The three ethanoic solutions were mixed together in a round bottom flask simultaneously; a colourless solution appeared, and then the solution was refluxed for 13.30 hours; a yellow-orange colour solution with some precipitate was observed. Then, the reaction mixture was concentrated using a rotary evaporator, and after being filtered, washed with cold ethanol, and dried in open air, it changed to a white solid colour. Finally, a white crystalline solid was collected, and the percentage yield was calculated as:

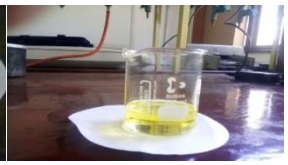
Actual mass = 4.00g

Theoretical yield, which is calculated from the proposed reaction = 4.937 g

$$\% \text{ yield} = \frac{actual\ yield}{theoretical\ yield} \times 100$$

$$\% \text{ yield} = \frac{4.00g}{4.937g} \times 100 = 81\%$$






Acetyl acetone Ethylenediamine Cd (II) metal Cd (II) complex

Scheme 15: Synthesis of Cd (II) complex

The balanced chemical reaction also represented as follow in scheme-16.

$NH_2\text{-}CH_2CH_2NH_2 + 2CH_3COCH_2COCH_3 + Cd(NO_3)_2.4H_2O \rightarrow CdC_{12}H_{22}N_2O4 + 4H_2O + 2HNO_3$

Scheme 16: balanced chemical reaction in the Synthesis Cd (II) complex

3.4.3 Template synthesis of chromium metal ion complex

In this preparation of chromium dithiocarbamate (20mmol, 3.17 g) of anhydrous chromium chloride salt; $CrCl_3$, was dissolved in 20 ml of hot ethanol; a green-black colour was observed. (20mmol, 2.056 ml) of acetyl acetone, (40mmol, 2.67 ml) of ethylenediamine, and (40mmol, 2.41 ml) of carbon disulfide were taken and dissolved each in 10, 15, and 15 ml of ethanol, respectively, in three different beakers, and after mixed together, a white milky precipitate and solution coloured were formed. And, the above solution, including anhydrous chromium chloride in ethanol, was added simultaneously in a round bottled flask and refluxed for 12 hours; a blue-black (brisk) precipitate was formed. The precipitate was filtered and thoroughly washed with cold ethanol to remove the impurities, and the sample was also dried at room temperature. The balanced chemical reaction also represented as follow in scheme-17.

$4NH_2\text{-}CH_2CH_2NH_2 + 2CH_3COCH_2COCH_3 + 4CS_2 + 2Cr\ Cl_3 \rightarrow Cr_2C_{22}H_{36}N_8S_8Cl_2 + 4HCl + 4H_2O$

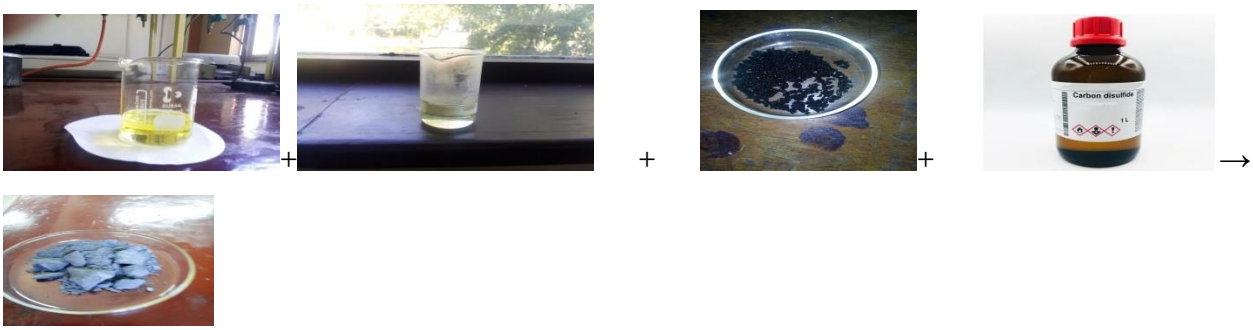
Scheme 17: balanced chemical reaction in the Synthesis Cr (III) complex

Finally, the product (crystal) was weighted with a digital balance and the percentage yield was calculated as;

Actual mass=4.24g

Theoretical yield= 8.43g

% yield = 58%



Ethylenediamine Acetyl acetone Cr (III) metal Carbon-disulfide Cr (III) complex

Scheme 18: Synthesis of Cr (III) complex

3.4.4 Chloride ion test

I. **Qualitative Test**

Qualitatively, when small amounts of synthesised chromium metal complex were dissolved in concentrated nitric acid (HNO_3) and then added to a 0.1 M silver nitrate ($AgNO_3$) solution in the solution, a white precipitate was formed immediately. This confirms that chloride ions are present in the chromium metal complex as a counter ion.

CHAPTE-FOUR

4. Results and discussion

Physical characteristics of the Cd (II) and Cr (III) metal complexes, such as their melting or decomposition temperature, solubility, and spectrum analyses like IR and NMR, will be covered in this section.

4.1 Physical characteristics

A range of at room temperature, the synthesised ligands and their corresponding complexes exhibit stability against moisture and air, displaying colours.

4.1.1 Melting point of complexes

A Stuart SMP_3 Melting Point device was used to determine the melting point of complexes in a capillary tube. The melting points of both complexes are sharp, and they are listed in table -1 below.

Table 1: melting points of the synthesised complexes

No	Compounds	Mol. Formula	Mol. Weight(g/mol)	Appearance	Color	M.pt (℃)
1	Ligand(L)	$C_{12}H_{20}N_2O_2$	224	Solid	Yellow-orange	-
2	Cd(II) complex	$CdC_{12}H_{22}N_4O_{10}$	494.41	Crystalline solid	White	175
3	Cr(III) complex	$Cr_2C_{22}H_{36}N_8S_8Cl_2$	843	Crystalline	Blue-black	190-200

4.1.2 Solubility of the synthesised ligand and its metal complexes

The ligand's and its complexes' solubility was examined in a few particular solvents. This indicated that the ligand N, N-bis (Acetyl Acetone) ethylenediamine was insoluble in benzene, water, ethylacetate, and DMSO but soluble in DMF, chloroform, ethanol, and acetonitrile. The Cd (II) complex was soluble in DMF but insoluble in all other chosen solvents, including acetonitrile, ethanol, water, and DMSO, chloroform, benzene, and ethyl acetate. On the other hand, the Cr (III) complex was marginally soluble in ethyl acetate but insoluble in acetonitrile, water, DMSO, and benzene. It was soluble in ethanol, chloroform, and DMF. The solubility of synthesised ligands and complexes with specific solvents, as reported in experiments, was compiled in Table- 2.

Table-2: Solubility of the synthesized ligand and complexes (compounds**)**

Compounds	Solvents							
	DMSO	Acetonitrile	Ethanol	Water	DMF	Chloroform	Benzene	Ethyl acetate
Ligand	Insoluble	Soluble	Soluble	In soluble	Soluble	Soluble	Insoluble	Insoluble
Cd(II)complex	Insoluble	In soluble	Insoluble	Insoluble	Soluble	Insoluble	Insoluble	Insoluble
Cr(III)complex	Insoluble	Insoluble	Soluble	Insoluble	Soluble	Soluble	Insoluble	In soluble

4.2 Molar conductance measurements of Cd (II) and Cr (III) complexes

DMF was used to dissolve the complexes, and at room temperature (298k), the specific conductance (K) of 0.001M solutions of Cd (II) and Cr (III) complexes was measured in DMF and found to be 64.5 and 81µS/cm, respectively. Each complex's molar conductance (λ_M) was determined using the formula λ_M =1000k/M, where M stands for 10-3 molarity. The molar conductivities of the Cr (III) and Cd (II) complexes were 81Ω^{-1}.cm^2.mol^{-1} and 64.5 Ω^{-1} cm^2.mol^{-1}, respectively. Because the experimental molar conductance values of the Cr (III) complex was larger than the expected range for an electrolyte, the molar conductance values summarised in Table- 3, show that Cr (III) complex was an electrolyte, but, Cd (II) complex was non-electrolyte.

Table-3: Molar conductance of the synthesized complexes

Complexes	Solvent	λ_M ,(Scm^{2}mol^{-1})	Type of electrolyte	Ratio of electrolyte
Cd (II) complex	DMF	64.5	Non-electrolyte	0
Cr (III) complex	DMF	81.4	Electrolyte	1:1

4.3: Magnetic susceptibility measurement of Cr (III) complex

For the Cr (III) complex, the experimentally measured gram susceptibility (χ_g) was found to be $8.753x10^{-6}$cmg-1 unit's at19^oC (292k). The finding is utilised to determine the number of unpaired electrons of chromium in the synthesised complex and shows that the complex is paramagnetic. The complex's molecular weight was determined to be 843 g/mol, and its magnetic susceptibility (X_M) was computed utilising the following formula:

$\chi_m = \chi_g \times$ Mw.in g/ mole = $8.753x10^{-6}cmg^{-1}$ x 914g/mole=$7378.78x10^{-6}$cm/mol. The effective magnetic moment of the complex was determined from magnetic susceptibility measurements as:

$\mu eff = 2.828(\chi_m \times T)^{1/2} = 2.828\ (7378.778x10^{-6}cm/mole \times 292)^{1/2}$

μeff= 4.1 BM and to know the number of unpaired electros it is possible to use the other way of expression of μeff .

That is, $\mu eff = (n\ (n+2))^{1/2}$

n= 3.2

The experimental value of the μeff of Cr (III) complex was in good agreement with the μeff value of the Cr (III) complex in the literature. Thus, from the electronic configuration of Cr^{+3} ($3d^3$) has three unpaired electrons. The presence of three unpaired electrons and ($0<\chi_m<1$) value indicates paramagnetic nature of a complex. So, the experimental value of the μeff was determined to be 4.1BM which is approximately equal to the spin only magnetic moments of $3d^3$ electron configuration proposed to be distorted octahedral of Cr (III) complex in geometry.

Table 4: magnetic susceptibility of Cr (III) complex

Complex	X_g (cm^3g^{-1})	X_M (cm^3mol^{-1})	μeff (BM)	No of unpaired e-(n)	Magnetic nature
Cr complex	$8.753x10^{-6}$	$7378.78x10^{-6}$	4.1	3.2	Paramagnetic

4.4: Electronic spectra

The electronic absorption spectrum of the complex was recorded in ethanol at room temperature. The electronic absorption spectrum of these complexes was obtained between 300 and 900 nm.

4.4.1: UV-Vis spectrum of Cr (III) complex

The Cr (III) complex's electronic spectrum displays a strong, intense absorption band with a shoulder peak at 321 nm (31153 cm^{-1}), which is related to the complex's azomethine group's $n \rightarrow \pi^*$ transition (C=N). Thus, the nature of the Cr (III) complex was found to be in high spin octahedral geometry.

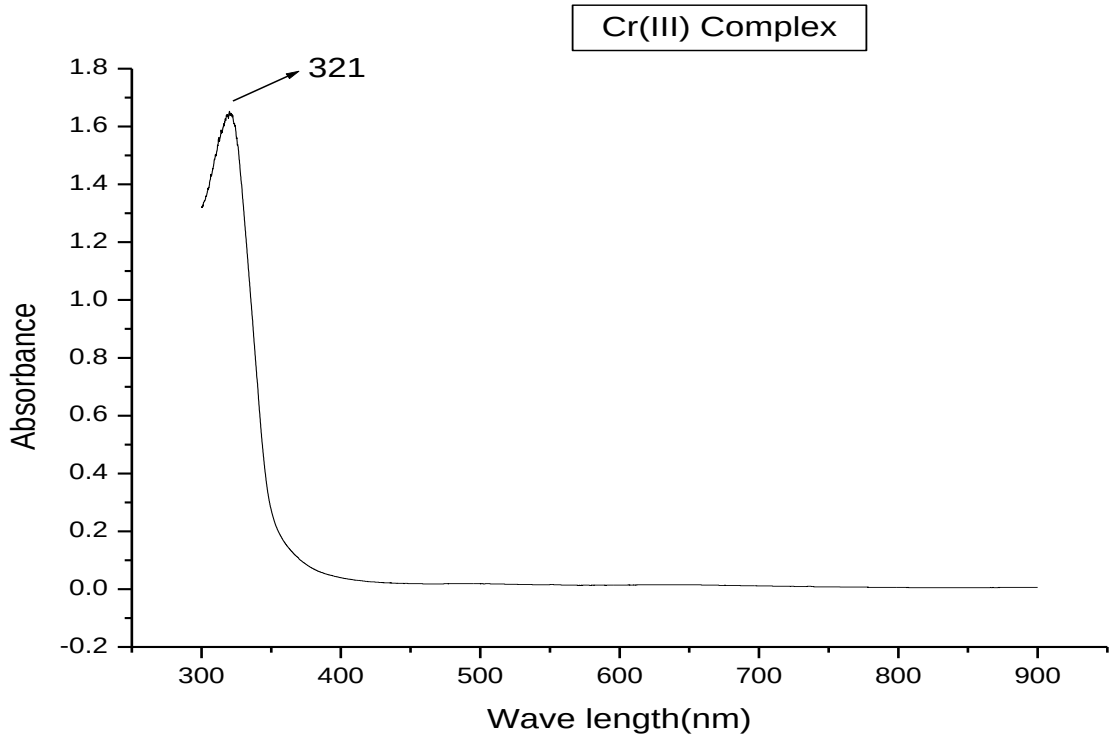


Figure-12: UV-Vis spectrum of Cr (III) complex

UV-Vis spectrum of Cr (III) complex was summarized in (Table-6) below

Table- 5: UV-Vis spectrum data of Cr (III) complex

Complex	Wave length (nm)	Band assignment
Cr complex	321	$n \rightarrow \pi^*$ (charge transfer)

4.5: IR spectra

The main IR data of the synthesized ligand its metal complex are summarized in table 7 and graphs of IR spectra are shown from figure 13 to 15.

4.5.1: The IR spectrum of the ligand

The distinctive locations for the stretching vibration of asymmetric C-H (CH_3) and symmetric C-H (CH_2) in sp^3 hybridised are represented by the medium bands in the IR spectra of the free ligand, L, at 2933 cm^{-1} and 2828 cm^{-1}, respectively. In the Schiff base ligand, the distinctive regions of C=O, C=N, C-C, and C-N stretching vibration are represented by the strong (sharp) bands at 1560, 1511, 1275, and 1004 cm^{-1}. Because of C-H out of plane bending, the absorption bands between 852-498 cm^{-1} are attributed to both symmetric and asymmetric stretching vibration (figure- 13).

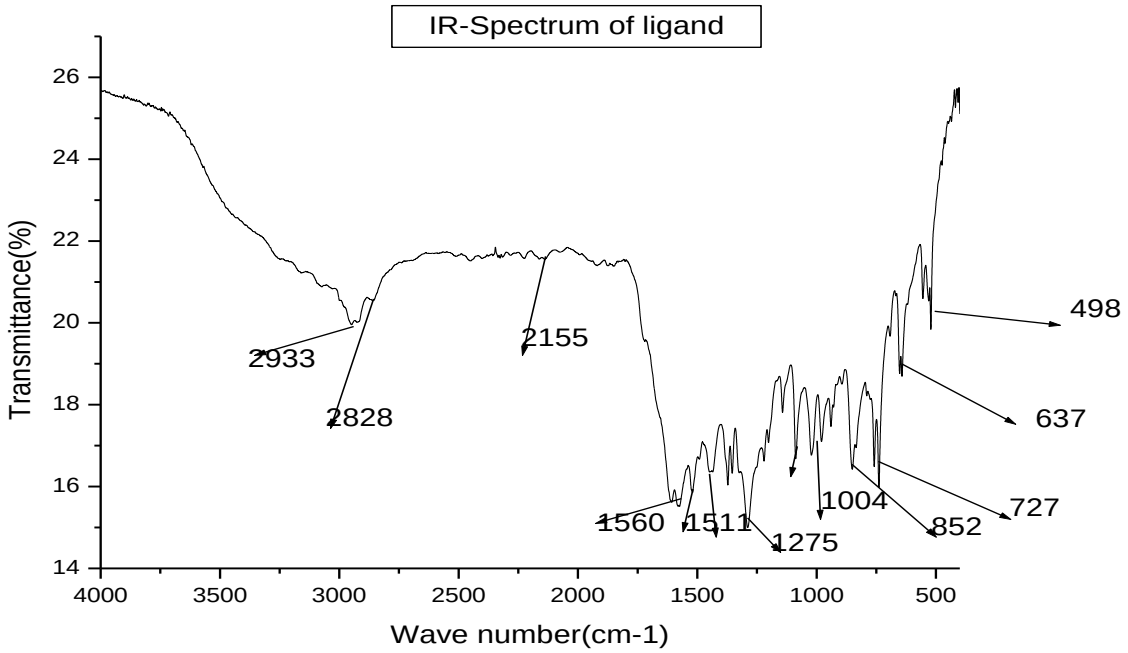


Figure-13: IR-spectrum of NN bis (acac) en ligand

4.5.2: IR spectra of the synthesised complexes

The IR spectra of the complexes were compared with the IR spectrum of the Schiff base ligand in order to describe the coordination sites of the ligand to the metal ion; certain shifts and new bands were found.

4.5.2.1 IR-spectrum of Cd (II) complex

The presence of O-H stretching vibration of coordinated water is shown by the medium broad band that occurred at 3444 cm^{-1} in the Cd (II) complex. The complex's hallmark regions of C-H (sp^2-hybridized), C=C, and C-O stretching vibration are represented by the sharp bands at 3255 cm^{-1}, 1515 cm^{-1}, and 1175 cm^{-1}, respectively. The characteristic regions of C-H (CH_3) and C-H (CH_2) in the sp^3-hybridized stretching vibration are represented by the bands observed at 2933 and 2828 cm^{-1} in the Schiff base ligand, which shifted to higher frequencies at 3085 and 2935 cm^{-1} in the complex. This suggests that the ligand is involved in the complex. The strong bands observed at 1511, 1004 and 1275 cm^{-1} were assigned for C=N, C-C and C-N stretching vibration

frequencies in the ligand, these vibrations were shifted to higher frequencies of 1595, 1005 and 1375 cm^{-1} respectively, in the IR spectrum of the Cd (II) metal complex. This observation suggested that the nitrogen and oxygen atoms on the ligand formed a coordinate bond during the complexation. The weak bands in the regions at 736 and 346 cm^{-1} are assignable to Cd-O and Cd-N stretching vibrations, respectively (figure- 14).

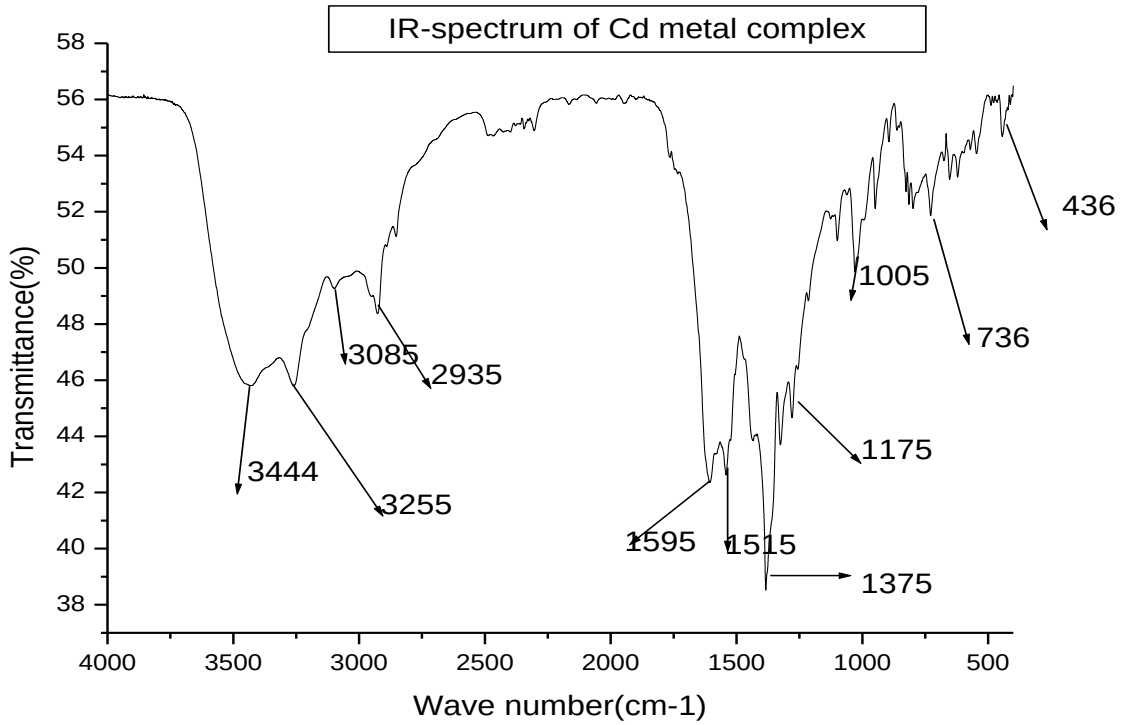


Figure-14: IR spectrum of Cd (II) metal complex

4.5.2.2. IR-spectrum of Cr (III) complex

The broad bands that appeared at 3418 cm^{-1} in the Cr (III) complex indicate the presence of N-H stretching vibration due to 2^0amine of the aliphatic group. The bands observed at 2933 and 2828 cm^{-1} in the Schiff base ligand shifted to a higher frequency at 3189 and 2933 cm^{-1} in the complex are the characteristic regions of C-H (CH_3) and C-H (CH_2) in sp3-hybridized, stretching vibration, respectively, which indicates the involvement of ligand in the complex. The sharp bands observed at 1511, 1004 and 1275 cm^{-1} were assigned for C=N, C-C, and C-N stretching

vibration frequencies in the ligand; these vibrations were shifted to a lower frequency of 1504 and a higher frequency of 1317 and 1372 cm^{-1}, respectively, in the IR spectrum of the Cr (III) metal complex. This observation suggested that the nitrogen and oxygen atoms on the ligand formed do not form a coordinate bond during the complexation. The medium band at 1039cm^{-1} was assigned for C-S stretching vibration, and the weak bands at 539 and 437 cm^{-1} were indicated for Cr-S and Cr-Cl cm^{-1} stretching vibration of the Cr (III) complex (figure -15).

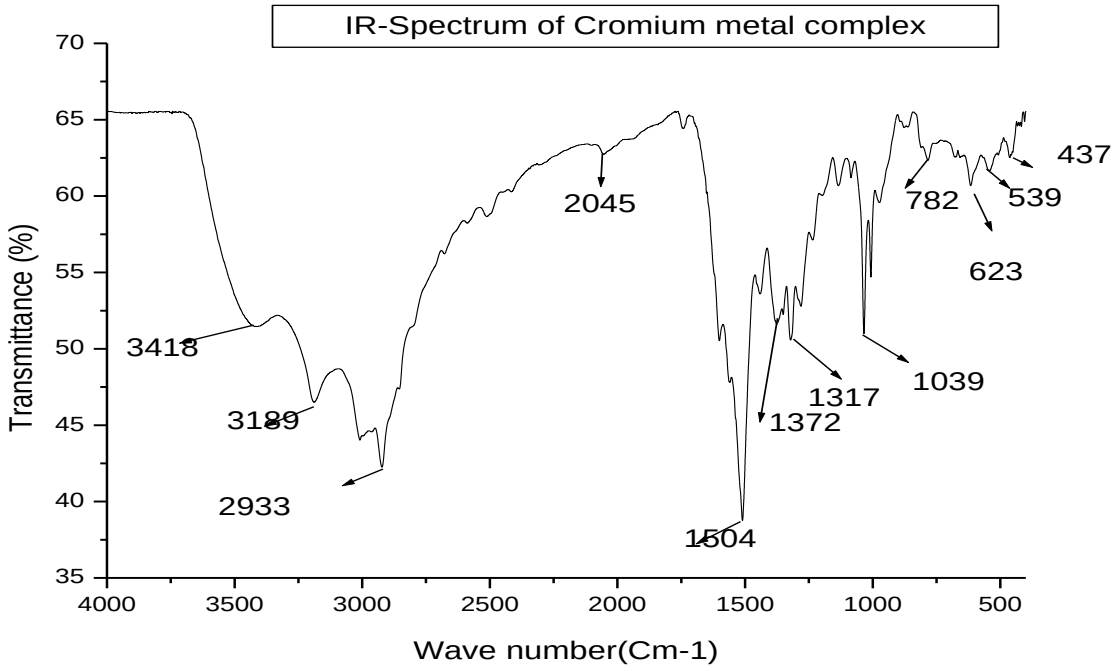


Figure-15: IR spectrum of Cr (III) metal complex

Table-6: Synthesized IR complexes spectra results of synthesized Schiff base ligand and their metal complexes

IR assignments	N,N bis(acac)en (cm^{-1})	Cd-complex (cm^{-1})	Cr-complex (cm^{-1})
ν (-OH)	_	3444	-
ν(N-H) 2^o amine	-	-	3418
ν(C-H) sp^2	_	3255	-
ν(C-H) of CH_3, CH_2	2933, 2828	3085, 2935	3189, 2933
ν(C=N, C-C, C-N)	1511, 1004, 1275	1595, 1005, 1375	1504, 1317, 1372
ν(C=O,C=C, C-O)	1560	1515, 1175	
ν(M-N,O)	-	436, 736	-
ν(C-S, M-S, Cl)	-	-	1039, 539, 437

Where; M-metal

4.6. NMR spectrum of the NN bis (acac) en ligand

NMR spectra of the sample were recorded using $CDCl_3$ as a solvent, and the chemical shift (δ) is represented in parts per million (ppm).

4.6.1 ^{1}H NMR of the Schiff base ligand

NN bis (acac) en's ^{1}H NMR spectra were obtained using $CDCl_3$, a deuterated chloroform solvent. The solvent protons are responsible for the singlet signal seen in the spectrum between δ 7.3 and δ 7.5 ppm. The singlet signal at δ 2.0 ppm and at δ 1.8- δ 1.9 ppm in the ^{1}H NMR spectra of the Schiff base NN bis (acac)en ligand is caused by the three protons of the $–CH_3$, which are present in the (CH_3-CO-) (C_1) and (CH_3-CN) (C_3), respectively. The two protons in the CH_2 group in (-CO-CH_2) are responsible for the singlet peak at δ 3.8 ppm, whereas the peaks between δ 3.3 and δ 3.5 ppm are caused by the CH_2 group in (-CO-CH_2-CN) (C_2), respectively. The other triplet signals at between δ 4.6 and δ 4.9 ppm are assigned to the two protons in the CH_2 group of the methylene carbon bonded to the azomethine nitrogen atom (C_4).

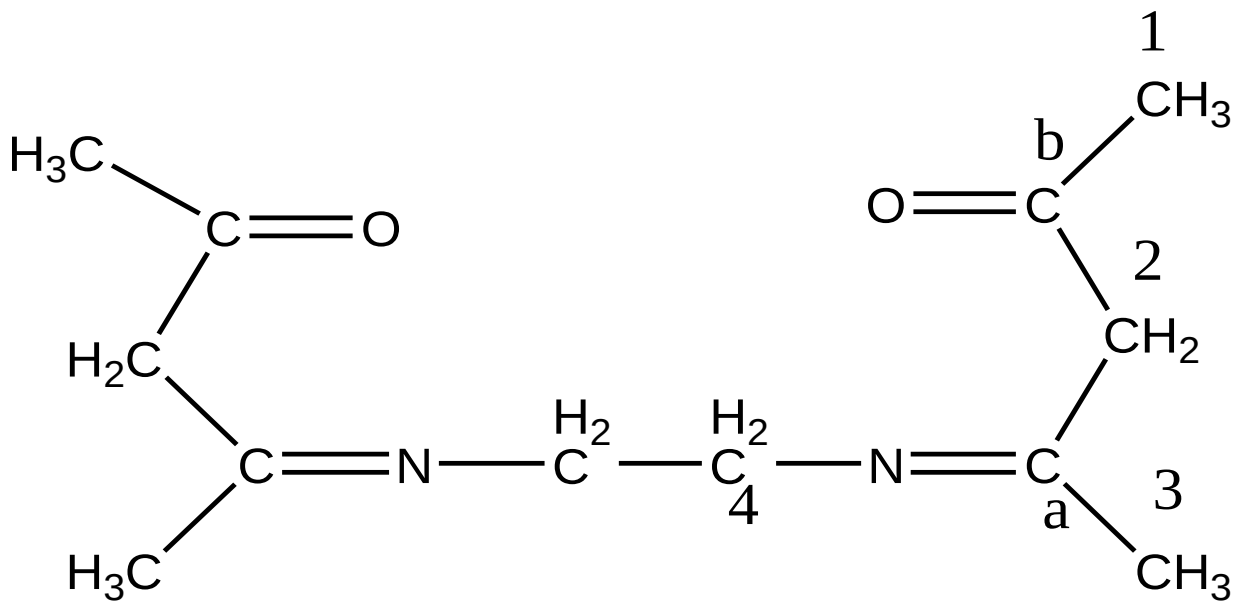


Figure.16: The structure of NN bis (acac) en ligand

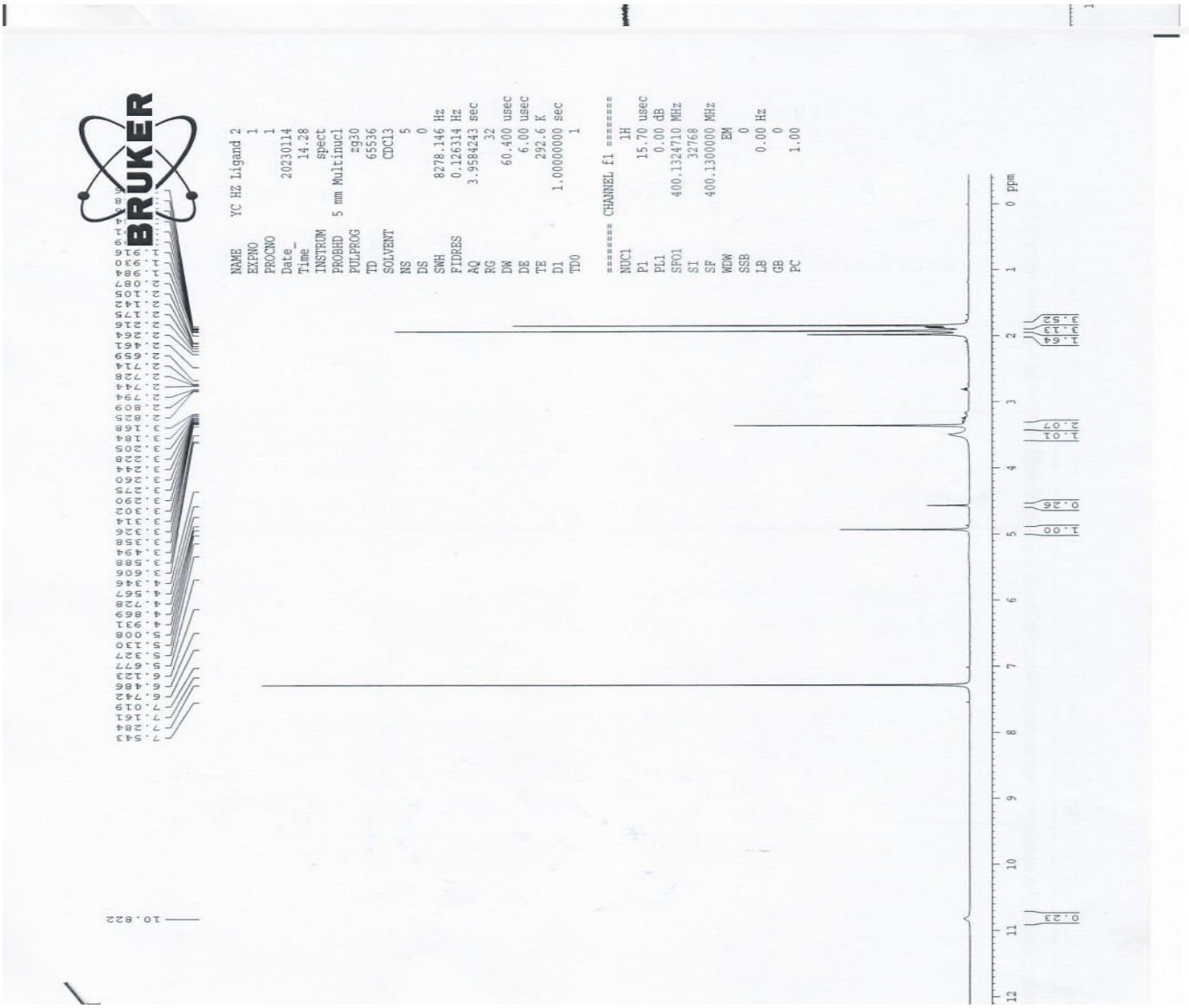


Figure-17: ^{1}H NMR spectrum of the Schiff base ligand

Table-7: ^{1}H NMR spectra data of NN bis (acac) en Schiff base ligand

Types of protons	Number of protons	^{1}H NMR shifts (δ) of the ligand	Solvent
3H in C**H**$_3$ (C_1)	6	2.0 (s)	
2H in C**H**$_2$ (C_2)	4	2.8 and 3.3-3.5 (s)	$CDCl_3$
3H in C**H**$_3$ (C_3)	6	1.8-1.9 (s)	
2H in C**H**$_2$ (C_4)	6	4.6-4.9 (t)	

Where; s-singlet and t-triplet

4.6.2 ^{13}C NMR and DEPT-135 spectra of NN bis (acac) en

The Schiff base ligand's 13C NMR was measured with a solution of deutrated chloroform ($CDCl_3$). The quaternary carbonyl carbon (C=O) at peak at δ 195.46 was discovered to pair with carbon showing at δ 195.51 ppm (C_b), and the quaternary azomethine carbon (C=N) at peak at δ 161.93 and δ 162.96 ppm (C_a). Due to alkyl carbon bound to carbonyl carbon (C=O), a peak at δ 28.88 ppm was seen, wherein carbons were found to couple with carbons showing at δ 28.83 ppm (C_1). Due to carbons bound to carbonyl carbon (C=O) and nitrogen group, respectively, there is a signal at δ 43.45 ppm that couples with δ 43.34 ppm and δ 41.77 ppm (C_2) and peaks at δ 49.95 ppm (C_4), due to carbons bonded to carbonyl carbon (C=O) and nitrogen group, respectively. Peaks at δ 18.66 ppm and δ 24.69 ppm (C_3), due to methyl carbon bonded to carbon of the azomethine group (CH_3-C=N).

This is also confirmed by the DEPT-135 spectrum (figure-19) of the Schiff base ligand. But the peaks formed at the carbonyl carbon (C_b) and azomethine carbon (C_a) have disappeared because they were due to quaternary carbons.

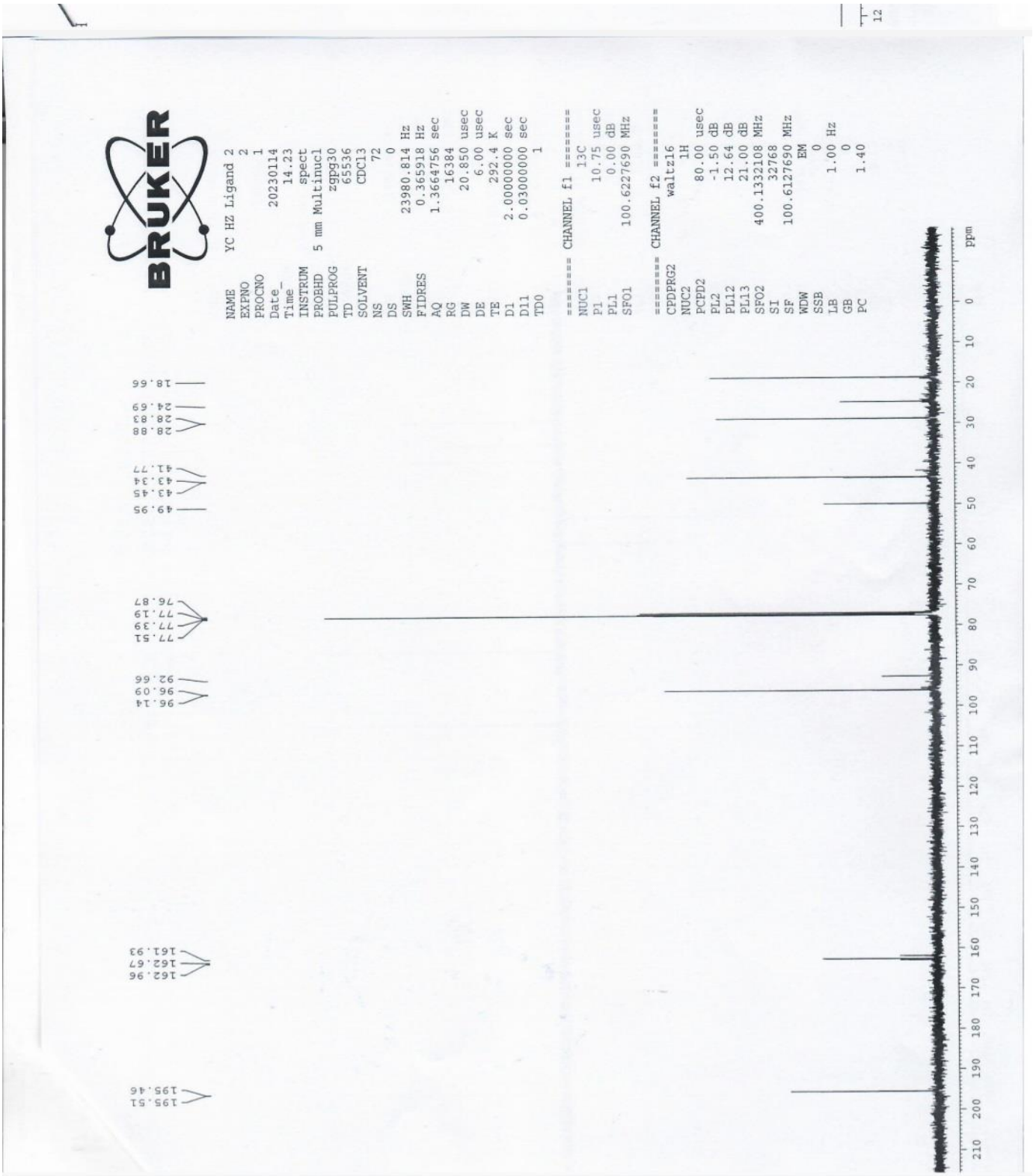


Figure-18: ^{13}C NMR spectrum of the Schiff base ligand

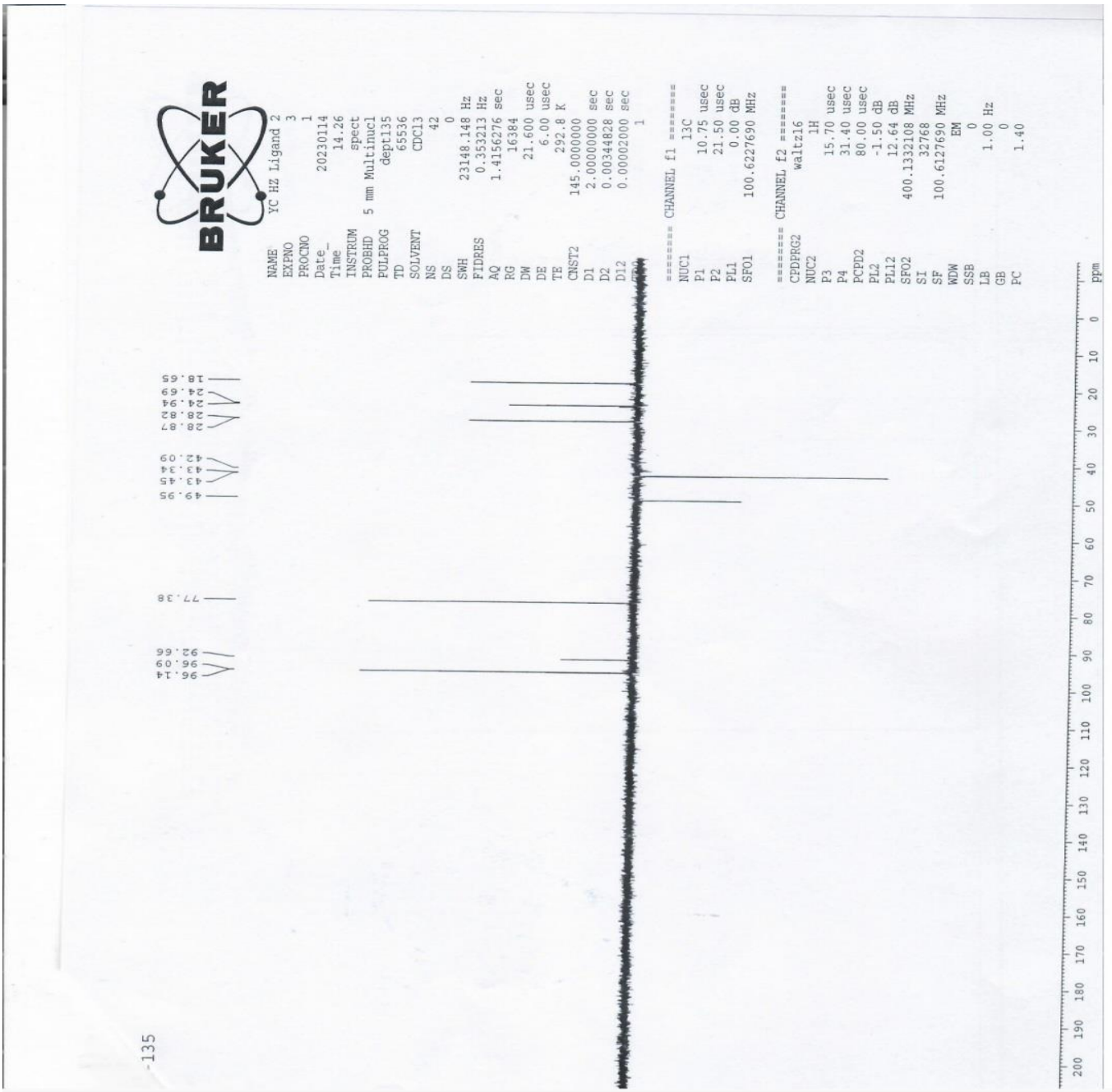


Figure-19: Dept-135 NMR of NN bis (acac) en ligand

Table-8: ^{13}C NMR and Dept-135 spectra of NN bis (Acac) en

Type of carbons	^{13}CNMR shift **(δ)**	No of carbon atoms	Dept-135 data	Assigned
C_a	161.93-162.96	2		Q
C_b	195.46-195.51	2		Q
C_1	28.83-28.88	2	28.82-28.87	C-H in CH_3
C_2	41.77-43.45	2	41.77-43.45	C-H in CH_2
C_3	18.66, 24.69	2	18.66, 24.69	C-H in CH_3
C_4	49.95	2	49.95	C-H in CH_3

Where Q; Quaternary

CHAPTER-FIVE

5. CONCLUSION

In conclusion, the reflux synthesis method was used to create N,N bis (acac) en Schiff base ligand, Cd (II), and Cr (III) complexes from the reactions of acac with en, acac, en with $Cd(NO_3)_2.4H_2O$ salt and en, acac, CS_2 with $CrCl_3$ salt for Schiff base, Cd(II) complex, and Cr(III) complex, respectively, in chosen molar ratios. Using this approach, the produced products' structural analysis was based on conductivity tests, IR, NMR, magnetic susceptibility testing, and electronic spectrum data. Cd (II) and Cr (III) complexes proposed that octahedral geometries were based on these results. The suggested building plans were displayed below.

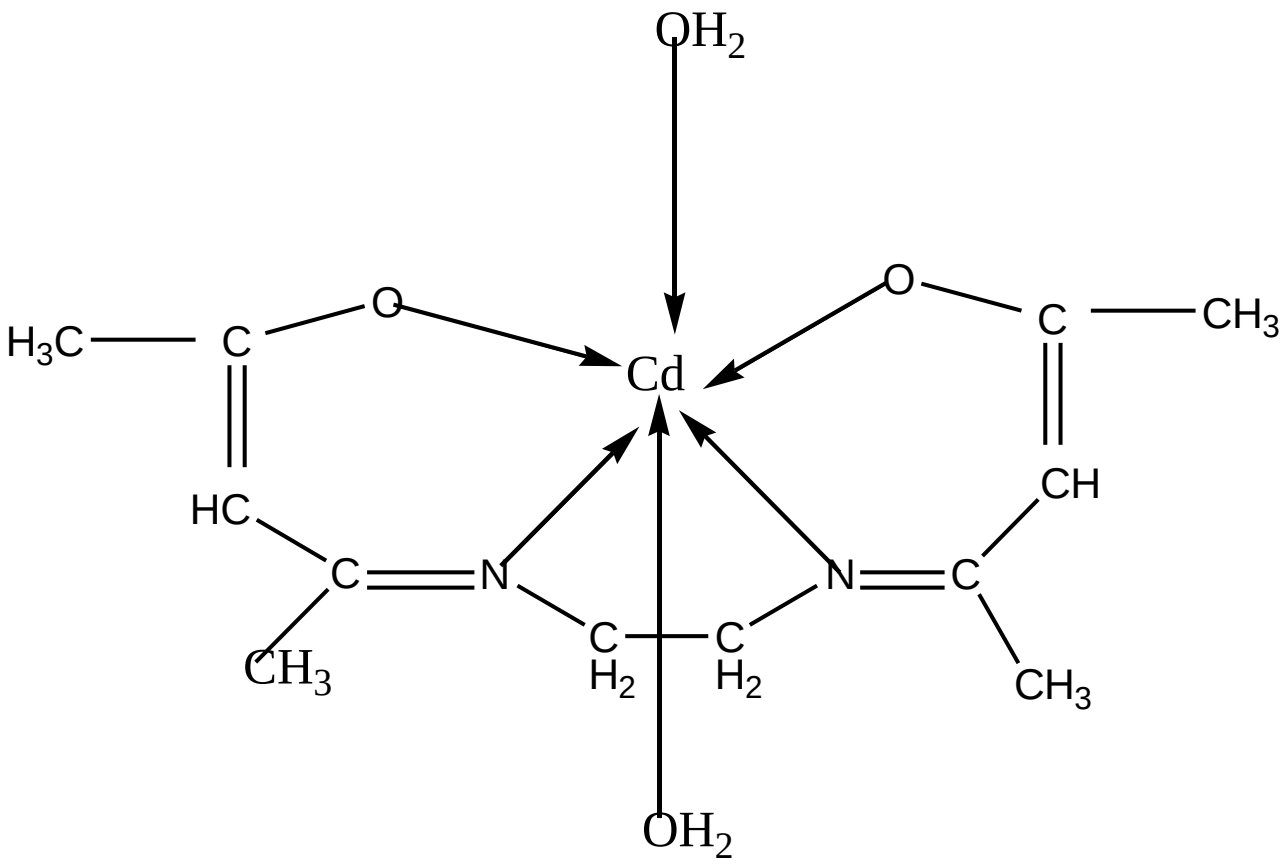


Figure-20: Proposed structure of Cd (II) complex

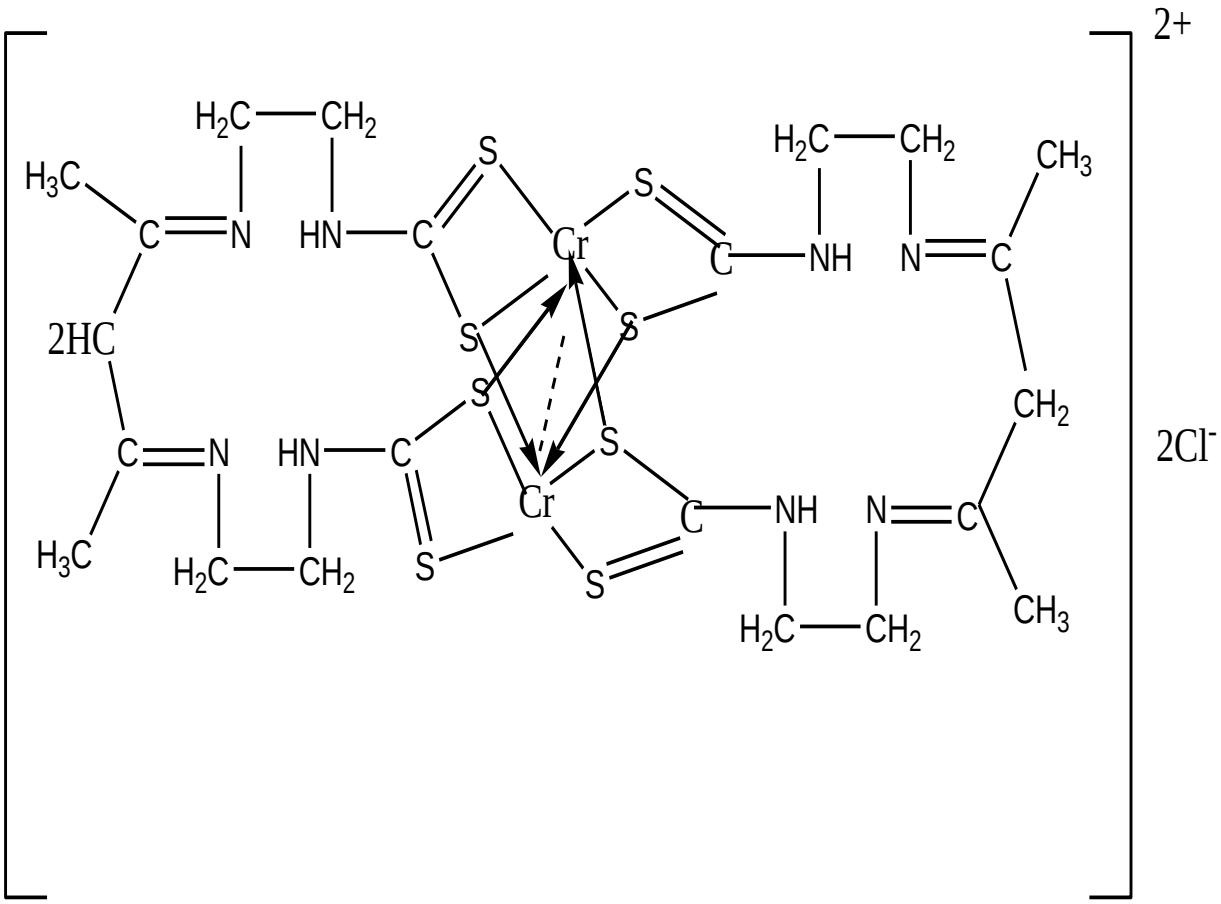


Figure-21: Proposed structure of Cr (III) complex

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