SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES ON COBALT COMPLEXES CONTAINING 1, 10-PHENANTHROLINE AS LIGAND

SOWMIYA S

20PCH021

Dissertation work submitted to

Avinashilingam Institute for Home Science and Higher
Education for Women, Coimbatore – 641043,
Tamil Nadu, India.

In partial fulfilment of the Requirements for the Degree of

MASTER OF SCIENCE IN CHEMISTRY

May-2022

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES ON COBALT COMPLEXES CONTAINING 1,10-PHENANTHROLINE AS LIGAND

SOWMIYA S
20PCH021

Dissertation work submitted to
Avinashilingam Institute for Home Science and Higher
Education for Women, Coimbatore – 641043,
Tamil Nadu, India.

In Partial fulfilment of the Requirement for the Degree of
MASTER OF SCIENCE IN CHEMISTRY
May 2022

M. Amurthaselvi.
Signature of the
Supervisor

26/5/2022
Signature of the
Head of the Department

ACKNOWLEDGEMENT

I owe my gratitude to all those who rendered their help for the completion of my work in the form of physical help and the mental strength.

Every work succeeds by the blessings of **Lord Almighty**. Hence, I bow my head at the feet of the Lord Almighty for his blessings rendered with good health and clear mind throughout my work.

I extend my humble thanks to **Dr.S.P.Thyagarajan**, Chancellor of Avinashilingam Institute for Home Science and Higher Education for Women University, Coimbatore for permitting me to carry out my work in this eminent institution.

I would like to thank **Dr. (Mrs.) V.Bharathi Harishankar,** Ph.D., FRSA Vice Chancellor of Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for the encouragement and for providing the opportunity to develop and establish my skills.

I extend my thanks to **Dr. (Mrs.) S.Kowsalya**, M.Sc, M.phil, and Ph.D. Registrar of Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for the encouragement given by her during the investigation.

I am highly thankful to **Dr. (Mrs.) G.Padmavathi,** M.Sc., M.Phil., Ph.D., Dean of School of Physical Sciences and Computational Sciences, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for making all necessary arrangements during the course of the work

I express my heartfelt thanks to **Dr. (Mrs.) R.Saratha**, M.Sc., M.Ed., M.Phil., Ph.D., Professor and Head of the Department, Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore for her constant support and tremendous care rendered for carrying out my thesis successfully.

With deep sense of gratitude and respect I humbly extend my heartfelt thanks to my guide **Dr. M. Amutha Selvi** M.Sc., Ph.D., Asst. Professor, Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women University, Coimbatore for her care, innovative ideas, guidance, encouragement, patience, motivation throughout my thesis.

I owe my respectful thanks to all the faculty members, Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore for their care and support rendered.

I express my deep sense of gratitude to all my friends for their consistent support and inspiration.

At length with deep respect and honour my gratitude highlights on my parents and all my family members without whom there is no glossary to my glory.

Sowmiya S

LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

ABBREVIATION	**EXPANSION**
UV-Vis	Ultraviolet-Visible Spectroscopy
FT-IR	Fourier-Transform Infrared Spectroscopy
TGA	Thermo gravimetric Analysis
Phen	1,10-Phenanthroline
PY	Pyridine
DMP	2,5-dimethylpyrazine
PYS	Pyridine-3-sulfonic acid
CNPY	4-Cyanopyridine

1. INTRODUCTION

Cobalt is sourced from the diets, especially green vegetables and grains, and a common vitamin the cobalt containing blue pigments have been found in Ancient crafts, the metal itself, was not separated until 1735 by the Swedish chemist Brandt as the first elemental metal. It has been known for a long time and has been confirmed only as an element. Despite this late start, the first coordination complex discovered by Tassaert. In 1798 it was Co (III)-hexamine, with a cobalt complexes also being central to Werner's seminal work in 1893.

Cobalt is found in small amounts in alloys, catalysts and pigments Compared to other transition metals in the first column, comprising only 0.0025% of the Earth's crust. By 2000 scientists had carried out lots of experiments related to the synthesis of new cobalt compounds, examination of antibacterial properties of cobalt compounds and cobalt-catalysed reactions.

Nowadays, cobalt and cobalt compounds possess a variety of applications from industry to medicine. This is because of its unique properties such as a high-melting point (1493°C) and retaining its strength to a higher temperature, being ferromagnetic with high thermostability and multivalent. Cobalt is one of the abundant metals in the Earth. Cobalt is an important factor; the body contains about 1 mg of cobalt supplement. Key in his biology Activity is its role in vitamin B12, cobalamin, and is a minority About other cobalt-containing enzymes identified so far. Of other cobalt-containing enzymes identified to date.

Cobalt is an essential metal, it has systemic toxicity, including neurological, cardiovascular and endocrine impairment, attributed largely to free ionic Co (II), with blood concentrations of over 300 mg/L suggested to be of concern. The toxicity of cobalt has been attributed to its redox activity. Beyond the treatment of pernicious anaemia arising from cobalamin deficiency, the use of cobalt in medicine began in 1940 with the first metallic hip replacement, employing a cobalt–chrome alloy in a protocol still widely used today.

In 1951 saw the first Co-60 radiation therapy, which soon superseded X-ray radiation as the primary form of radiotherapy, and is still heavily used in developing countries. Co-60, a beta-emitter with a half-life of 5.3 years, has also been used for brachytherapy, in which a sealed radiation source is implanted close to the tumour, although it has been largely replaced by Ir-192.[51]

In contrast, the study of cobalt coordination complexes for biological applications has flourished only more recently. The above-mentioned applications of cobalt in medicine harness its physical and nuclear properties. In coordination complexes, the cobalt ion also exhibits interesting redox and magnetic properties that make it suitable for a remarkable breadth of applications in biology and medicine. Most importantly, cobalt has a number of possible oxidations states from -1 to +4.

Cobalt in biological systems exists almost exclusively as Co (II) or Co (III), though Co (I) (in cobalamin) and Co (IV) are known2. These two predominant oxidation states exhibit different properties: d6 Co(III) complexes are generally octahedral and may be low spin or high spin. The low spin d6 configuration is diamagnetic and substitutionally inert. d_7 Co (II) ions can form four-, five- or six-coordinate complexes all of which are substitutionally labile and paramagnetic. Based on these various properties, cobalt complexes have demonstrated therapeutic potential as reduction-activated complexes, or can be applied in imaging by MRI or fluorescence. Here we consider recent advances in the application of cobalt coordination complexes in biological systems.[51]

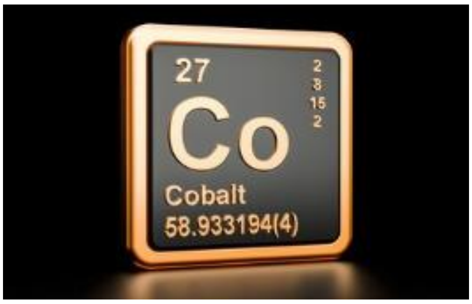


Fig 1.1 Image of Cobalt

Image courtesy: Google Image

In its compounds cobalt nearly always exhibits a +2 or +3 oxidation_state, although states of +4, +1, 0, and −1 are known. The compounds in which cobalt exhibits the +2 oxidation state (Co^{2+}, the ion being stable in water) are called cobaltous, while those in which cobalt exhibits the +3 oxidation state (Co^{3+}) are called cobaltic. Both Co^{2+} and Co^{3+} form numerous coordination_compounds, or complexes. Co^{3+} forms more known complex ions than any other metal except platinum. The coordination_number of the complexes is generally six.[54]

In 1730, chemist Georg Brandt of Stockholm became interested in a dark blue ore from some local copper workings and he eventually proved that it contained a higher to unrecognized metal and he have it the name by which its ore was cursed by miners in Germany, where it was sometimes mistaken for a silver ore. He published his results in 1739. For many years his claim to have uncovered a new metal was disputed by other chemists who said his new element was really a compound of iron and arsenic, but eventually it was recognized as an element in its own right.

The word 'cobalt' is generally accepted as having been derived from Greek medieval German. The earliest recorded use of the archaic form “kobelt” appeared in Agricola’s Bermannus in 1530. However, cobalt colouring of ceramics has been known for 2600 years with evidence in Persia and Egypt, though we are not aware of what it could have been referred to at that time. Colorings from oxides and silicates were the main use of cobalt up to the 20th Century; even in 1916. In 1938, John Livingood and Glenn T. Seaborg discovered the radioisotope cobalt-60. Since cobalt is generally produced as a by-product, the supply of cobalt depends to a great extent on the economic feasibility of copper. Demand for cobalt was projected to grow 6% in 2017.

Cobalt is a ferromagnetic material, hard yet brittle. It has a high melting point and is hard-wearing at elevated temperatures. It has high strength and possesses good conduction properties. It has a hexagonal closed pack crystal structure at temperatures below 417 °C (783 °F) and has 12 radioactive isotopes. Natural cobalt is cobalt 59, which is stable and non-radioactive, but other isotopes 54 to 64 are all radioactive, emitting beta and gamma radiation.[52]

Table 1.1 Other isotopes are listed in the below have short half-lives.

ISOTOPE	HALF LIFE
COBALT 60	5.3 years
COBALT 58	72 days
COBALT 57	270 days
COBALT 56	80 days

1.1 APPLICATIONS

Cobalt has a subject of extensive research and application area due to being ferromagnetic with high thermo stability, multivalent, a high-melting point (1493°C), and retaining its strength to a higher temperature. Some of them are antimicrobial agents in biological systems, biocompatible magnetic-fluids, hybrid super capacitors, magnetic resonance imaging and controlled drug delivery, nanostructured cobalt gas sensors, microwave absorbing paints and catalytic activity in some reactions, active sites for electrochemical applications. Some of these extensive functions and applications can be mentioned.

Cobalt ferrite ($CoFe2O4$) has a great physical and chemical stability and large anisotropy, making it suitable for biomedical applications. It has a magnetic property due to its tetrahedral (Td) and octahedral (Oh) sites, which include cation. Also, it is used to enhance the scope of materials in the biomedical field. Synthesis of $CoFe2O4$ is carried out by the following methods: sol-gel, solid-state reaction method, micro emulsion, combustion, chemical coprecipitation, hydrothermal method, etc. The $CoFe2O4$ is a suitable material in energy harvesting/storage and conversion, pathogen detection, chemo resistive sensor, and dye degradation. Besides these features, it also has applications such as magnetic resonance imaging, magnetic fluid hyperthermia, drug delivery, and tissue repair.

$CoFe2O4$ ferrite nanoparticles can be utilized in various antimicrobial applications that they have good antimicrobial activity against all tested bacteria, especially, Gram-negative bacteria. This feature of theirs can bring a new perspective to future studies in other ferrite and composite structures [10]. Also, the antimicrobial activity of $CoFe_2O_4$ was augmented with the addition of silver. The antibacterial activity of Ag-coated $CoFe_2O_4$ nanocomposites is more efficient than Ag nanoparticles

Cobalt oxide nanostructures have the matchless advantages of high theoretical capacity, highly active catalytic properties, and outstanding thermal/chemical stability. So, they are used as electrode materials for various electrochemical applications. Cobalt oxides are used in many research areas. They are abundant on earth and low cost and have environmental compatibility and excellent thermal stability and exceptional physical and chemical properties. Cobalt oxides have been successfully synthesized and used so far for various applications. These metal oxides stand out in applications of electrochemical energy devices. It will be used in theoretical calculations and simulations in the design of new cobalt oxide-based materials for practical applications in new studies. These studies encourage nanoscience and nanotechnology and the development of materials science, with regard to energy technologies

In addition to all the mentioned properties of cobalt, it is a highly active catalyst for hydrogenation reactions. Supported in most cases, in low-temperature Fischer Tropsch process, Co/Al_2O_3 or Co/SiO_2-ZrO_2 catalysts were used; CoO/SiO_2 and CoO/SiO_2-Al_2O_3 and CoO/ZrO_2-kieselguhr catalysts were used in the hydrogenation of oxoaldehydes, amination of alcohols, and amination of aldehydes and ketones for the production of ethylamine and propyl amines. It was determined that cobalt metal catalysts had higher activity when Ni and Co metal catalysts were compared. Cobalt-based catalysts exhibit high catalytic activity because the tendency of cobalt to react is higher due to its electron configuration. The results of the catalytic hydrolysis reaction of 2Co-1Ni-B/Magnesite catalyst and $NaBH_4$ synthesized by the co-loading of cobalt and nickel metals to the magnesite support material have increased the efficiency of the catalyst by adding Co**.**[57]

1.2 Cobalt 60 has a number of applications.

These include:

- Radiographic inspection

- A gamma ray source
- A tracer
- A Radiotherapeutic agent
- Irradiation of plastics
- A catalyst for the sulphonation of paraffin oil. In this application the gamma rays emitted by the cobalt cause the reaction of sulphur dioxide and liquid paraffin.[53]

1.3 HEALTH EFFECTS OF COBALT

Cobalt is a trace mineral that the human body needs in only small amounts. When trace metals are absent in a diet this leads to health problems. Animals use trace minerals to make essential enzymes which function as catalysts. These enzymes speed up changes that occur in the human body. Enzymes are needed for living cells to function properly For example cobalt is needed for the natural production of B-12 vitamins. B-12 vitamins ensure that enough red blood cells are produced in the human body. Cobalt also affects other animals because of its lack of presence in the soil. For example sheep in Australia become infected with a disease called Coast disease, caused by cobalt deficiency. Excess cobalt can also lead to health problems. People who work around cobalt can inhale its dust which causes vomiting, diarrhoea, or breathing problems. If cobalt is presence on the skin in can lead to an irritation and rash**.**[56]

1.4 CHEMISTRY OF 1,10-PHENANTHROLINE

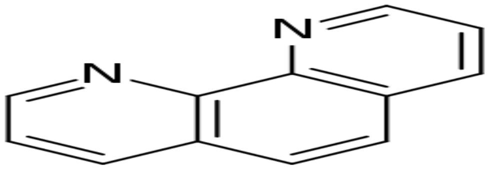


Fig: 1.2 Structure of 1,10-phenanthroline

Image courtesy: Google Image

1,10-Phenantroline (Phen) and its various derivatives are widely used ligands in the different fields of chemical industry. Heteroaromatic group on the Phen provides a binding site for different metal ions. Phen has a rigid structure and has two aromatic nitrogen which contain unshared electron pairs that can bind metal ions. Due to its pi electron deficiency, Phen becomes an excellent pi electron acceptor. Certain derivatives of Phen contain amine groups. Due to this chemical feature, Phen is used as ligand for soft and hard sites.

Most of the research on the Phen derivatives focuses on their catalytic, redox, photo redox, biological activities, and their supramolecular chemistry. Phen and its derivatives have very significant roles in the development of supramolecular chemistry**.**1,10-Phenanthroline is a bidentate planar ligand with a solid structure, hydrophobic, electron-poor, hetero-aromatic compound that is used as a ligand in coordination chemistry and has the property of cation binding to nitrogen atoms. It has a molecular formula $C_{12}H_8N_2.H_2O$ and has a molecular weight 180.2053.

1,10-Phenanthroline and its derivatives can form stable coordination compounds with several transition metals due to their multi-threaded ligand properties.1,10-Phenanthroline (phen) is a classic ligand in coordination chemistry, which couples versatility in metal ion binding with peculiar properties of its complexes. For instance, metal complexes with phenanthroline can be featured by an intense luminescence or can interact with DNA in an intercalative fashion inducing, in some cases, DNA cleavage. For this reason a number of phenanthroline-containing ligands have been recently synthesized by inserting phenanthroline within open-chain or macrocyclic backbone, in order to develop new molecular chemosensors for metal cations and anions, ionophores as well as new intercalating agents for polynucleotides.

Furthermore, phenanthroline is rigid and its insertion within cyclic or acyclic structures can impart to the resulting ligand a high degree of pre-organization, affording selective complexing agents. Luminescence and intercalating and/or DNA cleaving properties as well as on analytical applications of metal complexes with Phenanthroline-based ligands have been discussed. Particular attention will be devoted to macrocyclic receptors or open-chain ligands that, beside the phenanthroline nitrogen atoms, contain other donor atoms able to interact with the metal cations or anions**.**[55]

2. SCOPE OF THE STUDY

- Most of the research work focuses on cobalt ion-containing complexes since it has superior potential for medicinal applications.
- Despite their significant resourcefulness, these cobalt complexes are not famous in the inorganic medicinal field compared to their metals.
- Different ligands could be used to tune the properties of cobalt compounds whose ligand exchange rates become close to those of cellular processes.
- The researchers reported that the metal coordination compounds of 1,10-phenanthroline (phen) and its derivatives could inhibit tumor growth by interacting with DNA.
- In order to obtain more insight into the design of highly sensitive reactive probes, diagnostic reagents and new drugs we developed macrocyclic complexes to study the influence of ligands on the biological activities.

3. REVIEW OF LITERATURE

Mamoni Garai *et al,* (2017) reported a mononuclear cobalt (II) complex, [Co(phen)2Cl2], (phen = 1,10-phenanthroline) has been synthesized and characterized by different spectroscopic methods including single crystal X-ray structural study. Room temperature magnetic susceptibility of this cobalt (II)-Phenanthroline complex in powder state indicates the existence of three-electron high spin state. A comparison of UV–Vis spectrum between our cobalt (II) complexes with other cobalt (II) complexes further confirms the spin state. The cobalt (II) complex has been evaluated as a functional model for phosphatase enzyme by using 4-nitrophenylphosphate (PNPP) as a standard substrate in aqueous DMF medium. This cobalt (II) complex exhibits good hydrolytic phosphoester cleavage efficiency.

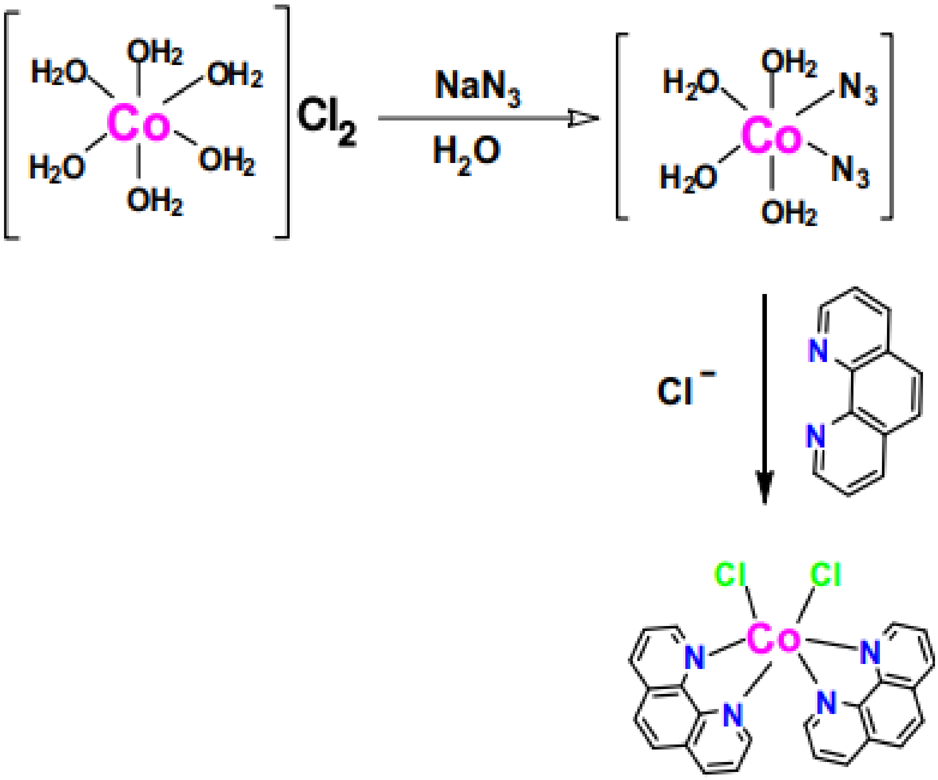


Fig 3.1 Proposed mechanism for synthesis of Co(II) complex

Atakilt Abebe1 *et al*,(2020) reported that three novel mixed ligand complexes of cobalt(II) having the formulae [Co(L1)2(H2O)2]Cl2, [Co(L1)2(L2)(H2O)]Cl2 and [Co2(L1)4(L2)2(L3)]Cl4 (L1 = 1,10-phenanthroline, L2 = adenine, L3 = 1,3-diaminepropane) were synthesized and characterized by elemental analysis, conductivity measurement, infrared, and UV-Vis spectroscopic techniques. y synthesized cobalt(II) complexes are active against gram negative bacteria (Escherichia coli and Klebsiella pneumonia) even though cobalt(II) complexes are well known for their activity against gram positive bacteria.

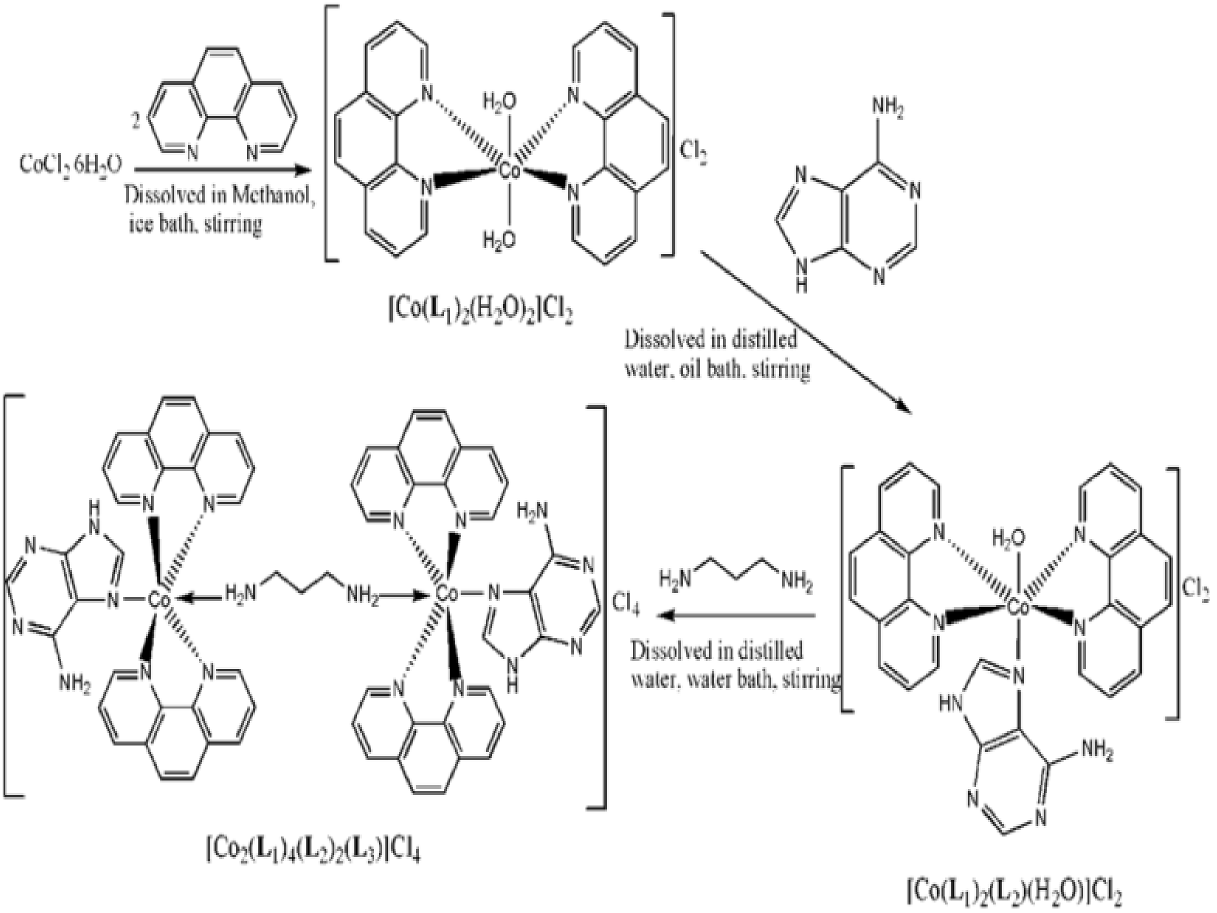


Fig 3.2 Mechanism of complex

Getinet Tamiru1 ***et al*****,(2019)**, reported three new mixed ligand complexes of cobalt (II)viz. mononuclear ($[Co(phen)_2(Act)(H_2O)]Cl_2.H_2O$ and $[Co(phen)_2(Act)(en)]Cl_2$), and binuclear $[Co_2(phen)_4(Act)_2(en)]Cl_4$ which were synthesized and characterized using spectroscopic methods such as ESI-MS, ICP-OES, FT-IR, and UV-Vis, chloride determination as well as melting point and conductance measurement. In vitro antibacterial also tested against the cobalt complex exhibited antibacterial activity. Most Co (II) complexes are known to be active only against Gram-positive bacteria. However, the synthesized complexes showed awide-range of activities even against the Gram-negative bacteria.

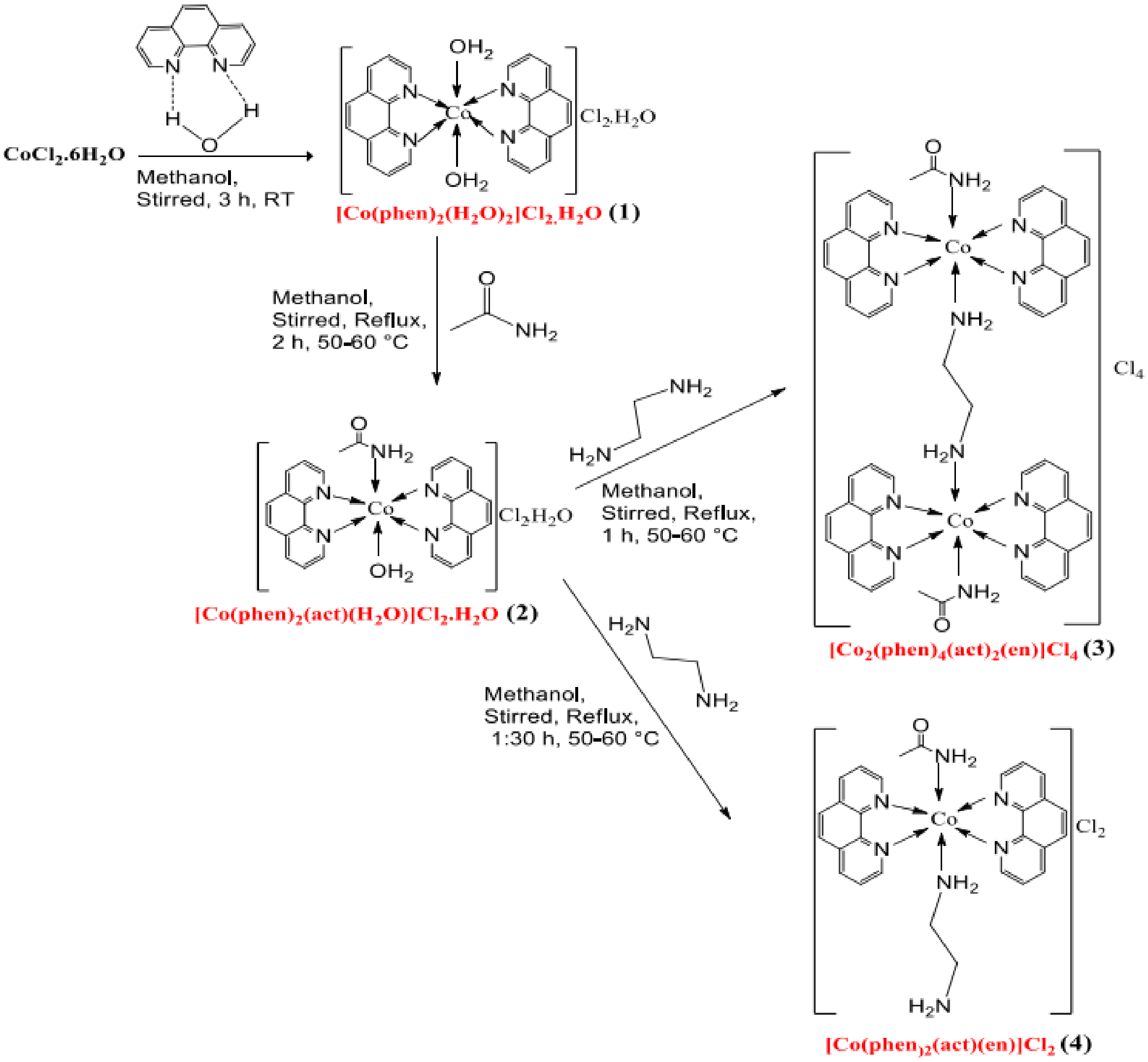


Fig 3.3 Mechanism of the synthesized complex

Atakilt Abebe *et al*,(2018), reported that two complexes were synthesized from 1,10-phenanthroline alone as $[Co(phen)_2\ (H_2O)_2\ ]Cl_2$ and from both 1,10-phenanthroline and cytosine as $[Co(phen)_2(Cyt)H_2O]Cl$. The synthesis was checked using halide test, conductance measurement as well as spectroscopic (AAS, FTIR, Uv-vis) analysis. The complexes into the cell wall and lipid membrane is enhanced which inhibits the growth of the tested gram-positive and gram-negative bacteria. The latter phenomenon demonstrates the wide-range activities of the complexes.

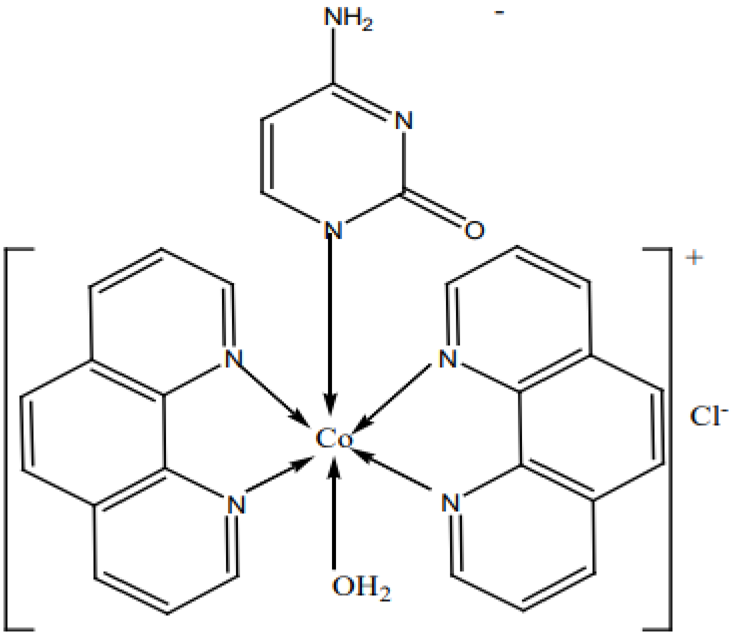


Fig 3.4 Structure of the complex

Atakilt Abebe *et al*,(2016),reported two new complexes; mononuclear $[Co(L_1)_2(L_2)(H_2O)]Cl_2$ and binuclear $[Co_2(L_1)_4(L_2)(H_2O)_2]Cl_4$ using precursor complex, $[Co(L_1)_2(H_2O)_2]Cl_2$, synthesized using the ligand L1: 2,2'-bipyridine and L2: ethylenediamine characterized using the spectroscopic technique (ICP-OES, UV-Vis, FT-IR) and physicochemical methods (chloride determination, thermal analysis, and conductance measurement Their antibacterial activities were also tested against two Gram-negative and two Gram-positive bacteria using the disc diffusion method. The new complexes showed better activities against gram negative bacteria.

Lee Fang Chin *et al*,(2011),reported Metal-based cancer chemotherapeutic agent Co(II) complex of the type{[Co(Me_2Phen)(o-cbiaH) $(H_2O)_2]H_2O$}(1) was synthesized from ligand 5-(2-carboxybenzyloxy)isophthalic acid (o-cbiaH_3) and thoroughly characterized by spectroscopic and single crystal X-ray diffraction method. Complex 1 crystallizes in a slightly distorted octahedral CoN_2O_4 coordination environment. Biophysical techniques revealed that DNA binding sites of ligand and complex 1 of CT DNA while Electronic absorption and fluorescence spectral studies indicated that 1 binds to DNA more avidly as compared to ligand via electrostatic binding mode. The fluorescence spectroscopic technique revealed that affinity of complex 1 towards HSA and 3D scan measurements revealing that 1 quench the fluorescence intensity of HSA more strongly than o-cbiaH_3. The interaction between ligand and complex 1 with HSA can have profound influence on the distribution, free concentration and metabolism of the drug in the blood plasma (as most drugs circulate in plasma) and reach the target tissues by binding to HSA. These studies provide an important rationale for design of new lead anti-cancer drugs and their specific delivery at the active site of action, besides providing the pharmacological profile in vitro.

Ye-Zhong Zhang *et al*,(2009), reported The binding of Co$(phen)_3{}^{2+}$ to BSA by employing different optical techniques was reported by Ye-Zhong Zhang et al, revealed that the binding interaction of the cobalt(II) 1,10-phenanthroline complex (Co$(phen)_3^{2+}$, phen = 1,10-phenanthroline) with bovine serum albumin (BSA) was investigated by fluorescence spectroscopy combined with UV–Vis absorption and circular dichroism measurements under simulative physiological conditions. The fluorescence quenching of BSA resulted mainly from static mechanism and electrostatic interactions, and hydrophobic force played major roles in stabilizing the Co $(phen)_3{}^{2+}$–BSA complex. Results showed that Co $(phen)_3{}^{2+}$ was a strong quencher of the fluorescence of BSA and bound to the protein with high affinity. Conformational investigation suggested that BSA underwent some conformational changes at secondary structure levels, which further indicated that the microenvironments of BSA were changed and its biological activity was weakened in the presence of Co $(phen)_3{}^{2+}$.

Lee Fang Chin *et al*,(2011), reported The synthesis and characterization of two cobalt(II) complexes, Co(phen)(ma)Cl 1 and $Co(ma)_2(phen)_2$, (phen= 1,10-phenanthroline, ma=maltolate or 2-methyl-4-oxo-4H-pyran-3-olate) were reported. Characterizations have been done by various techniques such as FTIR, CHN analysis, fluorescence spectroscopy, UV–visible spectroscopy, conductivity measurement and X-ray crystallography. The two cobalt (II) complexes are found to exhibit different binding affinity and selectivity towards different types of duplex DNA. RE inhibition experiment results showed that the binding of specificity of 1 and 2 are totally different. . Although both cobalt (II) complexes can inhibit Topo I, their inhibitory behaviour is again different the antiproliferative property of both complexes is cell-type dependent, and their potential use as anticancer drug towards MCF7. MDA-MB-231 cancer cells are insensitive towards both cobalt (II) complexes although both have distinctly differential IC50 values

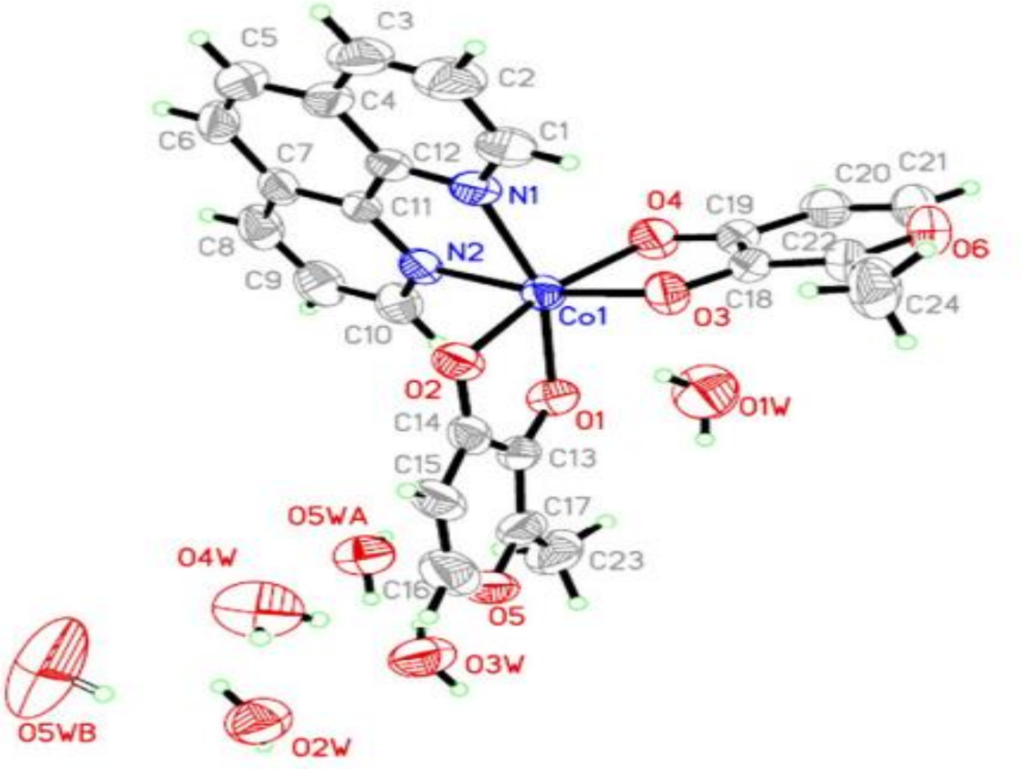


Fig 3.5 ORTEP-Molecular Structure

Dhananjay deya *et al*, (2015), reported the two isostructural mononuclear cobalt (III) complexes [1] $NO3\cdot 3H_2O$ and [1] $NO3\cdot CH_3CO_2H\cdot H_2O$ {$[1]^+$ =

[Co(1,10-phenanthroline)2Cl$_2$] +} and characterized by single crystal X-ray structural analyses. Mass spectral techniques showed that the both the compounds to produce identical cationic species viz., [Co (phen)$_2$Cl$_2$] + in methanol solution. The cationic cobalt (III) complexes, [1]+ exhibits very efficient catalytic activity in saturated oxygen environment towards 3,5-ditertbutylcatechol. Complex 1 induces very efficient cleavage of double-stranded DNA without the requirement of activating agents and exhibits important cytotoxicity against human hepatocarcinoma cell line (HepG2) in terms of damaging the DNA in cancer cells. This activity will help to develop clinically relevant information for possible new anticancer age.

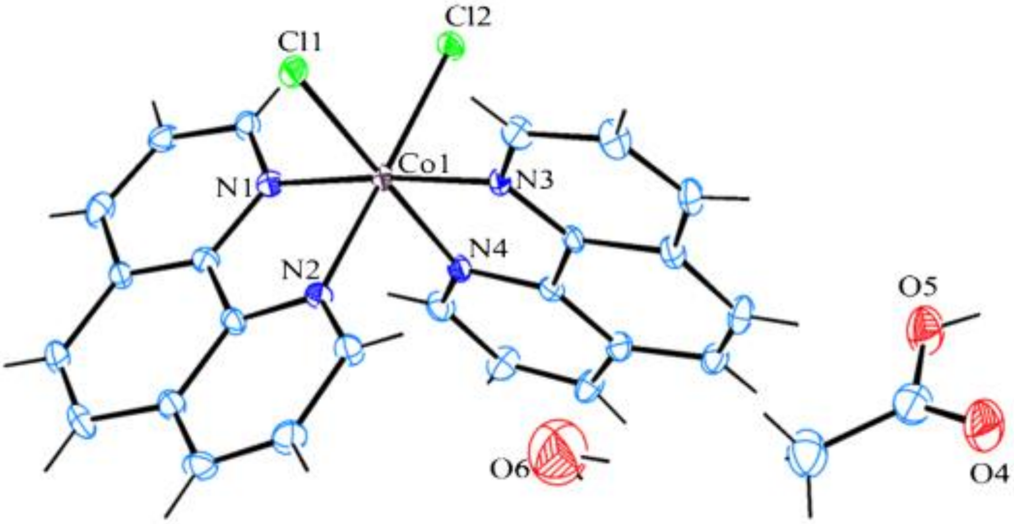


Fig 3.6 Structure of [Co (phen)$_2$Cl$_2$]

M.A. Al-Omair (2018), reported the octahedral Phenanthroline cobalt chlorides, aqua and carbonates complexes have been synthesized and characterized by various techniques. Their antibacterial activity and antioxidant activity were also studied. It was suggested that cobalt phenanthroline carbonate complex possessed highest antibacterial activity, antioxidant activity, degradation effect on DNA and showed moderate cytotoxicity. Complexes have more inhibitory activity towards gram negative bacteria than gram positive bacteria. The complexes were studied under UV spectroscopic which showed the solvent effect on the electronic spectra.

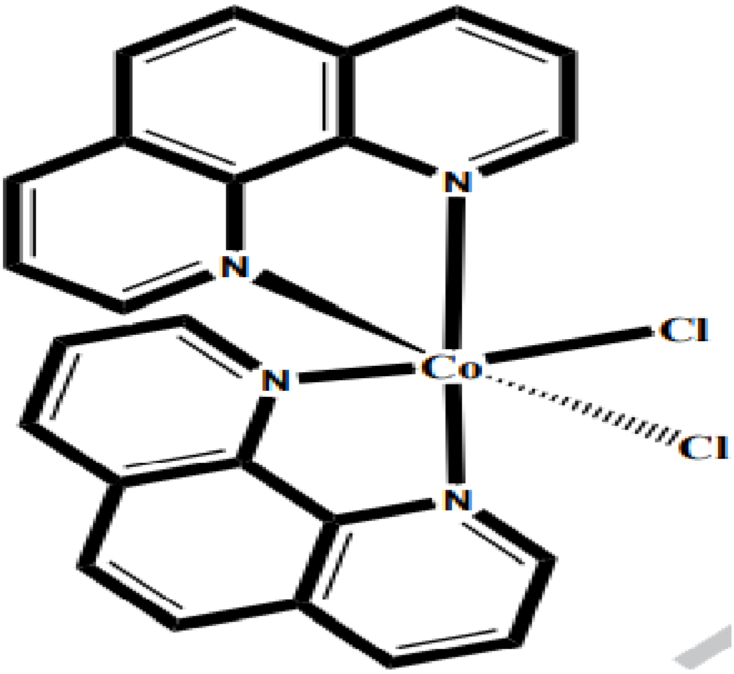


Fig 3.7 Structure of complex [Co (phen)$_2$Cl$_2$]

Jose Parada *et al*,(2017) reported The mononuclear cobalt (III) complex derived from 1,10-phenanthroline with lactose [Co(phen)$_2$ lactose]Cl$_2$ ·3H$_2$O (1) were synthesized and its properties have been compared with the sucrose complex [Co(phen)$_2$sucrose]Cl$_2$·3H$_2$O(2) and the complex without carbohydrate [Co(phen)$_2$Cl$_2$]Cl·3H$_2$O(3). The complexes were characterized using the techniques such as 1 H-NMR, IR, CD and UV-Vis spectral data. The disc diffusion method showed the anti-bacterial activity using the gram negative and positive bacteria which revealed that the complex 1,2and 3 exhibited moderate antibacterial activity. The presence of carbohydrate ligands in the complexes (1) and (2) improves the antibacterial properties over Gram positive in contrast with complex (3). Cytotoxicity assays show that carbohydrate complexes are not cytotoxic to human cells, in contrast with complex (3), which is highly toxic. These results suggest that the use of the lactose ligand would maintain the antibacterial activity and uptake mechanism of the complex at reasonable levels, and would also reduce its toxicity against human cells.

N.N. Golovnev *et al*,(2018) reported Two nickel(II) and cobalt(II) complexes with phenanthroline, $[Ni(Phen)(H_2O)_3Br]Br$ (1) and $[Co(Phen)_2(H_2O)_2](Hba)2·2H_2O$(2), Phen = 1,10-phenanthroline and Hba− = barbiturate anion, were synthesized and characterized by powder XRD, TGA and FT-IR. Their structures were determined by single crystal X-ray diffraction techniques. The compounds 1 and 2 are mononuclear complexes in which Numerous N—H···O, O—H···O and C—H···O hydrogen bonds form a 3D net in $[Co\ (Phen)_2(H_2O)_2](Hba)2·2H_2O$. Lattice water molecules combine the $[Co\ (Phen)_2(H_2O)_2]^{2+}$ cations in an infinite tape by CPhen—H···OW hydrogen bonds. The π–π interaction plays an important role in the stabilization of structures.

Chong-Chen Wang *et al*,(2015) reported Three cobalt-based coordination compounds, $[Co_2(phen)_4(H_2qptb)](H_3qptb)_2$ (1), $[Co_2(phen)_4(H_2dczpb)_2]5H_2O$(2) and $[Co_2(phen)_4(H_2odpa)_2(H_2O)_2]2H_2O$ were synthesized along with 1,10-phenanthroline (phen) by hydrothermal synthesis. Single-crystal X-ray diffraction reveals that complexes 1–3 contain $[Co_2(phen)_4(L)]$ units, further joined into 3D frameworks via hydrogen-bonding interactions All three complexes display considerable thermal stability and exhibit selective absorption in the ultraviolet region, as shown by thermo gravimetric analysis and UV–Vis diffuse reflectance spectroscopy. Both ligands and counterions, increasing the dimensionality of the crystal structures and further helping to extend the crystal structures via intermolecular interactions. The thermo gravimetric analyses showed that the frameworks of all three compounds are stable less than 250 C. All three complexes have nearly identical optical energy gaps, but show different photo catalytic degradation of MB under UV light irradiation, implying that complex 1 can be regarded as a molecular photo catalyst.

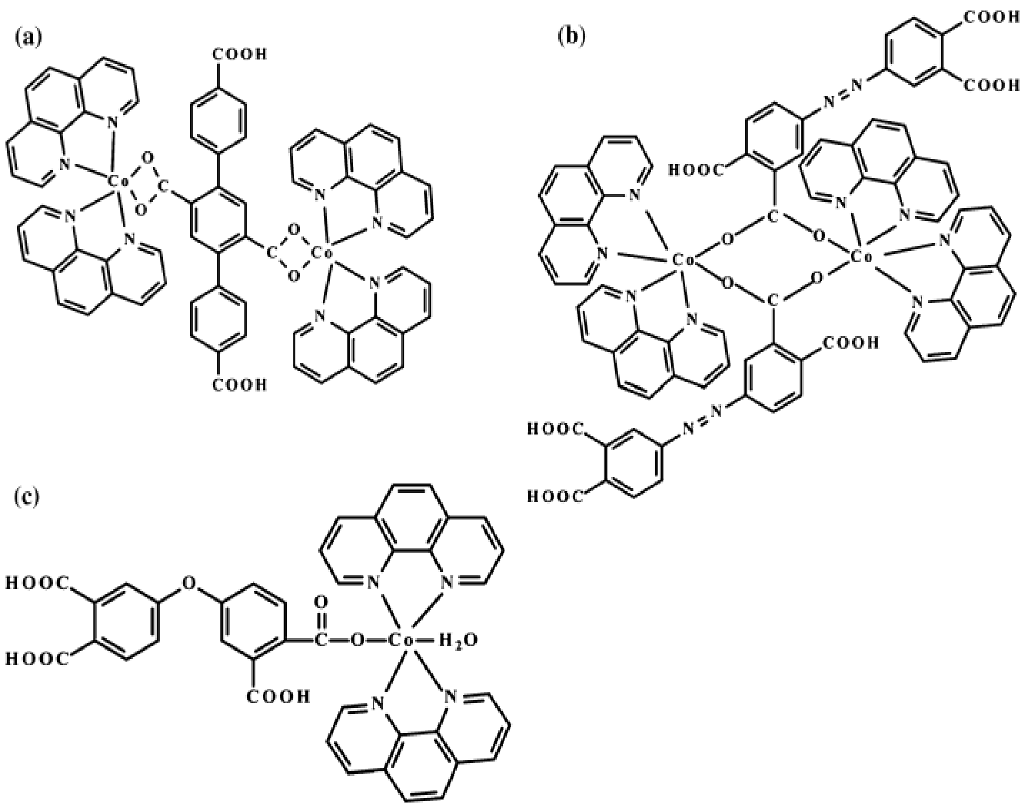


Fig 3.8 Diagram of complexes

M.O. Agwara *et al*, (2010) reported Three new 1,10-phenanthroline and 2,2’-bipyridine mixed-ligand complexes of $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$, $[Cu(bpy)(phen)H_2O)_2]Cl_2.2H_2O$, and $[Zn(bpy)_2(phen)]Cl_2.6H_2O$ were synthesized and characterized by the various techniques such as elemental, IR and visible spectroscopic analyses two molecules of 1,10-phenanthroline and one molecule of 2,2’-bipyridine are coordinated to cobalt(II) giving a six-coordinate complex ion $[Co(bpy)(phen)_2]$ 2+ Antimicrobial studies of these complexes against nine bacteria show that there is increased activity of the metal ions upon coordination to these ligands. There is a decrease in the activities of 1,10-phenanthroline as well as an increase in the case of 2,2’- bipyridine upon coordination. The activity order is $[Cu(bpy)(phen)(H_2O)_2](Cl)_2.2(H2O)$ > $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$ > $[Zn(bpy)_2(phen)]Cl_2.6H_2O$. The very high antimicrobial activities of the copper complex, $[Cu(bpy)(phen)]Cl_2.2H_2O$ and the cobalt complex, $[Co(bpy)(phen)_2](NO_3)_2.2H_2O$.

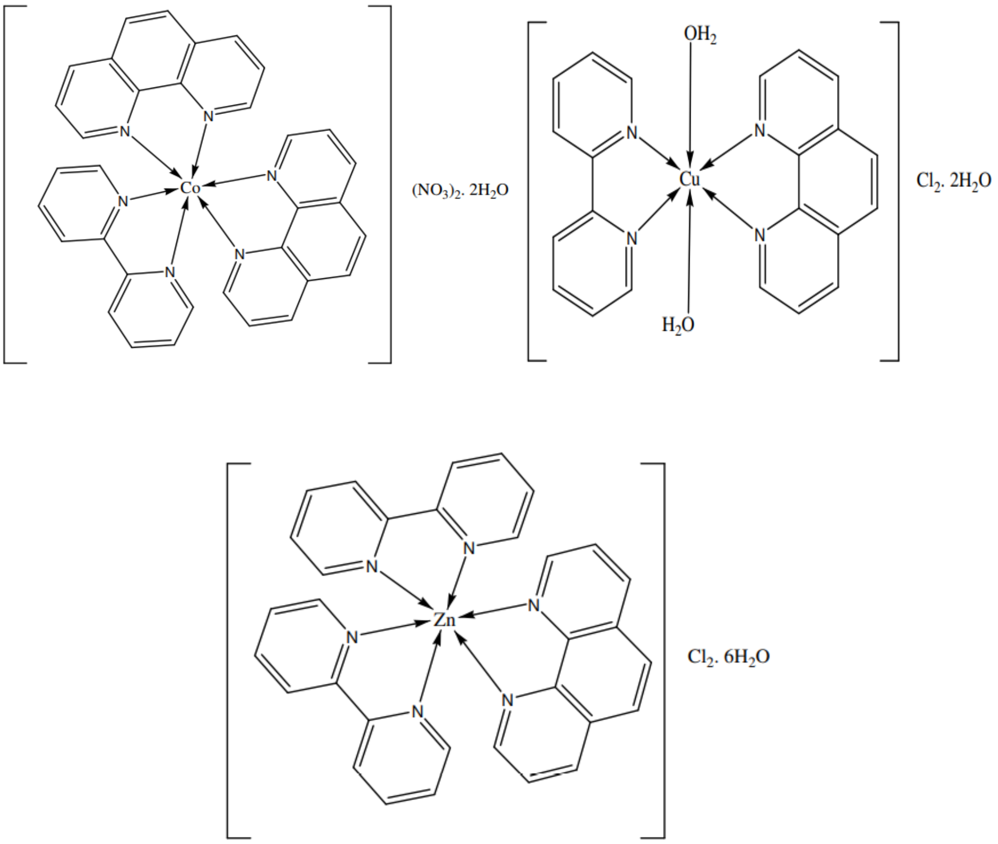


Fig 3.9 Structure of complexes

Donatus B. Eni ***et al*****,(2020)** reported The reaction of 1,10-phenanthroline and dicyanamide ligands with Cu(II) and Co(II) nitrates afforded the complexes [Cu(phen)(BMCA)](NO_3)] (1) and [Co($phen)_2(NO_3$)](dcg-)·(H_2O). The complexes were characterized by elemental analysis, infrared spectroscopy and ultraviolet–visible spectroscopy, magnetic susceptibility measurement and X-ray crystallography. Complex 2 corresponds to octahedral geometry the packing in the unit cell of both complexes was based on intermolecular hydrogen bonding and π–π stacking interactions extending them to interesting 3D structure. Complexes displayed poor antifungal activities as compared to the standard antifungals but higher antibacterial activities as compared to the antibiotic.

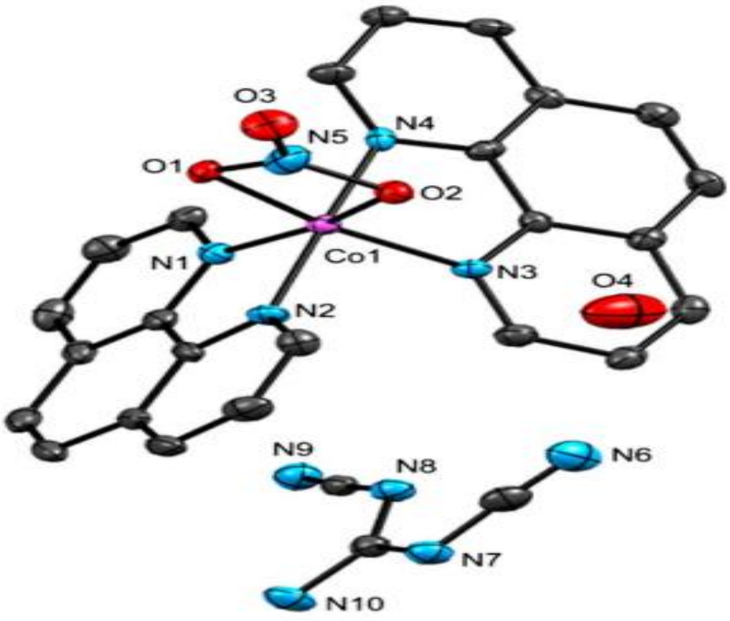


Fig 3.10 Molecular structure of [Co(phen)$_2$(NO$_3$)]

Davut Avcı *et al*,(2019) reported A series of mixed-ligand M(II) complexes containing 1,10-phenanthroline (phen) and 3-methylpyridine-2-carboxylic acid (3-mpaH) or 6-methylpyridine2-carboxylic acid (6-mpaH), namely [Co(3-mpa)2(phen)]3H2O (1), [Hg(6-mpa)2(phen)]2H2O (2), [Mn(6-mpa)2(phen)]2H2O (3), [Co(6-mpa)$_2$(phen)]H$_2$O (4) and [Ni(6-mpa)$_2$(phen)]H$_2$O (5), were synthesized. Characterization was done using spectral studies which shows that complex 2 is a potential α-glucosidase inhibitor candidate and complex 3 could be a significant NLO material. In vitro and docking results are evaluated that, complex 2 can be suggested as a novel strong drug candidate for type 2 diabetes mellitus.

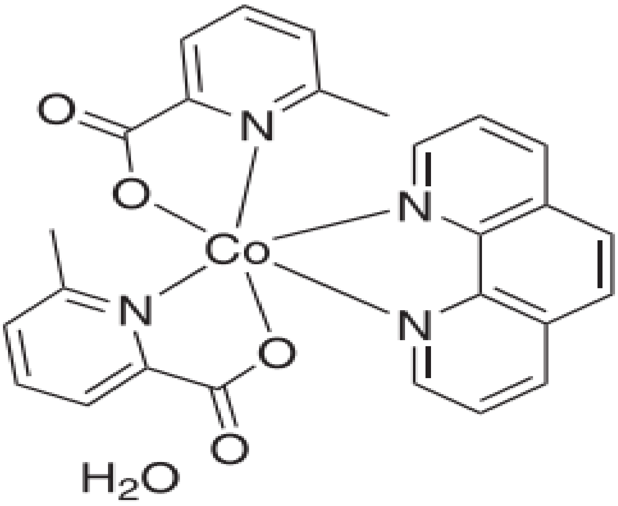


Fig 3.11 ORTEP diagram of complex.

Asia M. Shalash *et al*,(2017) reported Four new Co(II) complexes in the presence of N-donor heterocyclic ligands (2-ampy, 1,10-phen and 2,9-dimephen) have been synthesized and characterized. Magnetic properties, infrared and UV–Vis spectrophotometric techniques were used to study the new complexes in addition to X-ray diffraction of complexes 1 and 4; which reveals distorted octahedral geometry of the Co (II) ion. In complex 1 the cobalt binds two monodentate sulindac groups and in complex 4 cobalt binds two bidentate sulindac groups and one 2,9-dimephen. Te structures of the remaining complexes were proposed depending on IR, UV–Vis results and magnetic properties. Complexes 3 and 4 showed anti-bacterial activity against G+ and G− bacteria. Moreover, complex 4 have demonstrated the highest efficiency against yeast.

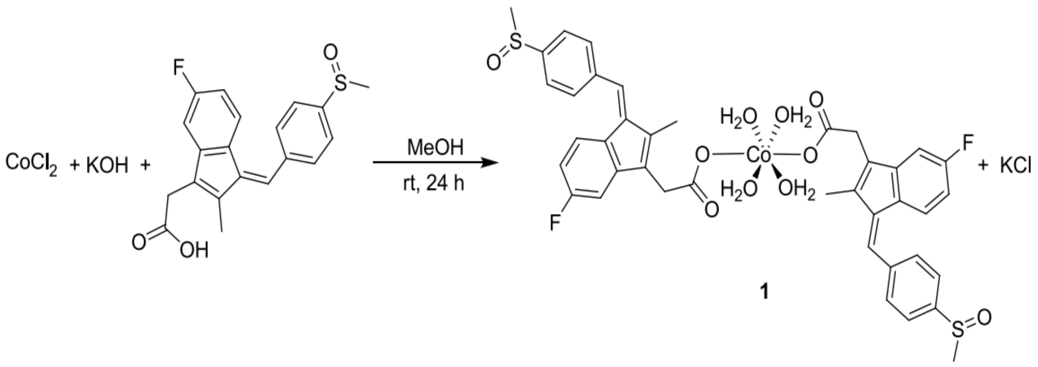


Fig 3.12 Mechanism of the complex

Gui-Lin Wen ***et al,*** **(2016)** reported A new complex, $[Co_2(OH)_2L_2(phen)_2(H_2O)_2]\cdot 2(HL)$ (1) (HL = 2- fluoroisonicotinic acid, phen = 1,10-phenanthroline), has been synthesized using the slow-layered diffusion technique at room temperature. Single crystal X-ray analysis revealed that complex 1 is a dinuclearcobalt (II) complex connected by hydroxyl oxygen. The thermal stability was studied by thermo gravimetric analysis (TGA). In addition, the variable-temperature magnetic property of the complex has been also studied. The two Co(II) centers are linked by μ2- OH−groups and there are uncoordinated HL molecules in the structure. The variable temperature magnetic property of the complex was investigated. Dominant antiferromagnetic interactions are found in it due to the large Co–O–Co angle.

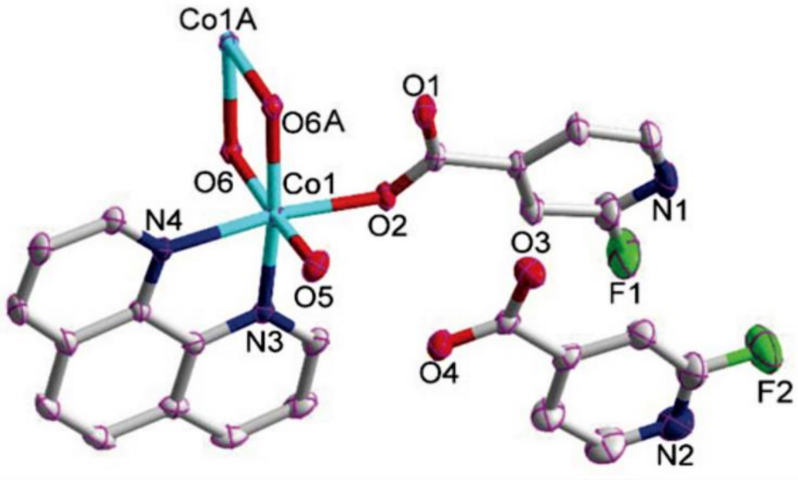


Fig 3.13 A view of coordination of the Co(II) cation

Li Yang *et al,* (2015) reported A new coordination polymer, {[Co (Phen)(HCOO)(H_2O)Cl]H_2O]}n (1) (Phen D 1, 10-Phenanthroline), has been prepared by hydrothermal method and characterized by elemental analysis, IR and single-crystal X-ray diffraction. Complex 1 is orthorhombic; space group. The compound is interlocked by the hydrogen bonding to results in 3D structure.

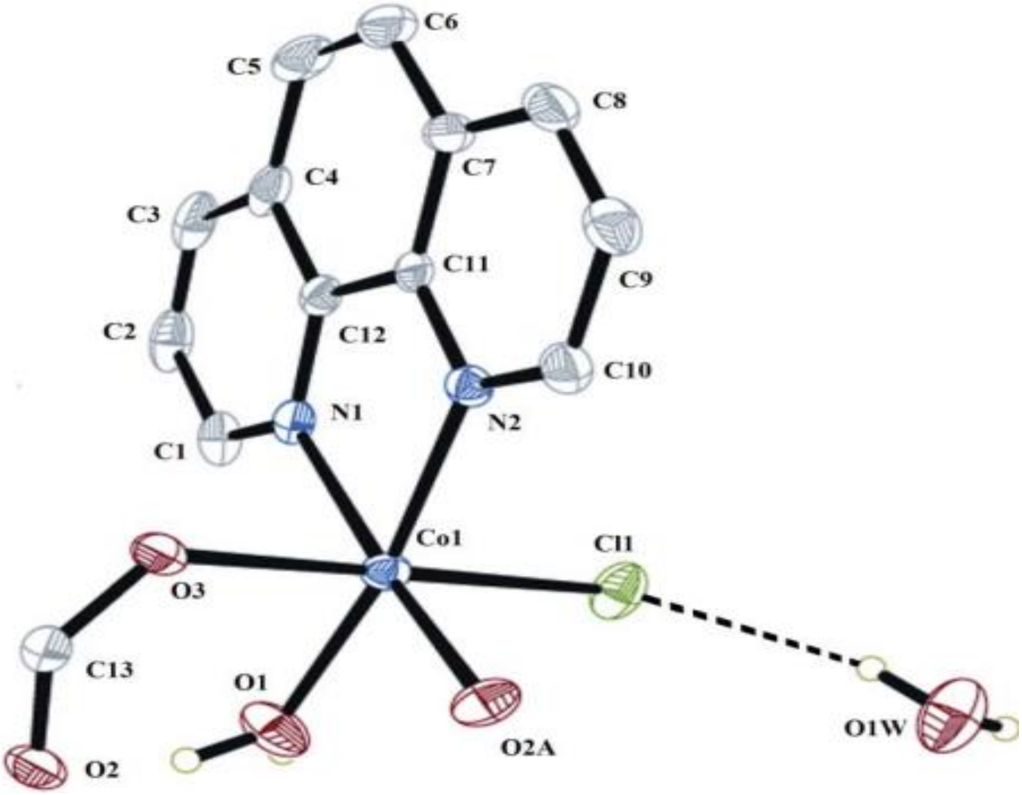


Fig 3.14 Structure of complex

Yueqin Li *et al,* (2017) reported Two novel complexes, $NiL_2phenCH_3CN$ (1) and $CoL_2phenCH_3CN$ (2) (HL ¼ 2-acetonaphthone salicylylhydrazone, phen ¼ 1,10-phenanthroline) were synthesized and characterized by spectroscopy (IR, ESI-MS) and elemental analysis, X-Ray crystallography revealed that the complex are distorted octahedral around the metal. The compounds interacted with HS–DNA through intercalation. Binding of the compounds with bovine serum albumin (BSA) protein investigated using UV-visible, fluorescence and synchronous fluorescence spectroscopic methods indicated that there occurred strong binding of nickel and cobalt complexes to BSA over the ligand HL. The complexes found significant activity against human breast (HeLa) and lung (A549) cancer cell lines, with the best results for Ni (II) complex.

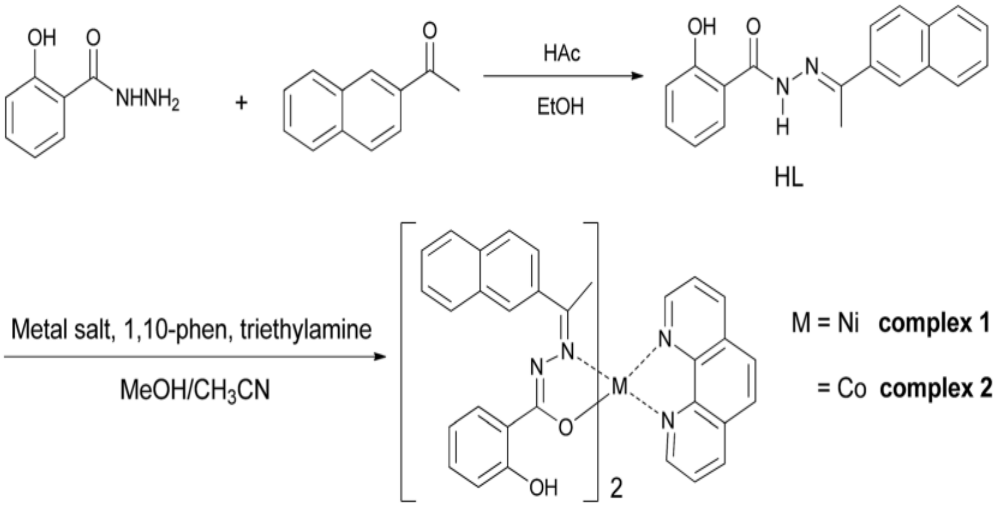


Fig 3.15 Mechanism of synthesized cobalt complex.

Anna Kloska *et al,* (2018) reported two chemical tests—the NBT method and the cyclic voltammetry technique revealed the antioxidant properties of the compounds. Ni(oda)(phen) and Ni(oda)(bipy) exhibit higher antioxidant activity towards the superoxide ion in comparison with the superoxide radical scavenging by L-ascorbic acid. Antioxidant properties of Co (oda)(phen) are similar to the scavenging effect of L-ascorbic acid. In the case of the oxydiacetate complexes of Co^{2+} and Ni^{2+}, the radical scavenging against superoxide ions is higher for the complexes with phen. The presence of bipy or phen in the coordination sphere of cobalt (II) and nickel (II) in the case of oxydiacetate complexes results in increased antioxidant properties of these complexes. The greater basicity of phen as compared to bipy induces an increase of the radical scavenging of the complexes. Co (oda)(phen) causes the highest decrease in the viability of cultured cells and exhibits the most prominent antiproliferative activity and has the highest cytoprotective activity against the hydrogen peroxide effect on the fibroblasts.

Yun Liu *et al,* (2015) reported Polythioantimonate $[Co(phen)_3][Sb4S5(S4)2]$ (1), thioantimonates $[Co(phen)_3]2Sb18S29$ (2), and [H3O][Co(phen)3]SbS4·9H2O (3) were solvothermally prepared using $[Co(phen)_3]^{2+}$ as a structure directing agent in different protic solvents, indicating solvent effects on the solvothermal system of Co/Sb/S/phen. Compound 1 contains a circular anion [Sb8S10 (S4)4] 4− constructed by both sulphide and polysulfide ions. The 3-D [Sb18S294−] ∞ framework in 2 possesses an interpenetrating channel system and the $[Co\ (phen)_3]$ 2+ complexes are enclosed in the channels. Compound 3 contains a water cluster stabilized by O–H···S and O–H···O hydrogen bonding interactions.

Niloufar Akbarzadeh-T *et al*,(2013) reported Two new tetrahedral Co(II) complexes, $Co(dmphen)Cl_2$ (1) and $[Co(ph_2dmphen)Cl_2]2CHCl_3$ (2) were synthesized and characterized by elemental analysis, and by IR, UV–visible and 1 H NMR spectroscopy. Single-crystal X-ray diffraction study of the two compounds revealed analogous tetrahedral arrangements of the ligands around the cobalt (II) ion. Measurement of magnetic susceptibility of 1 and 2 by 1 H NMR spectroscopy (Evans method) revealed their magnetic moments were 4.32 and 4.29 BM, respectively, which also suggests tetrahedral coordination in the two complexes.

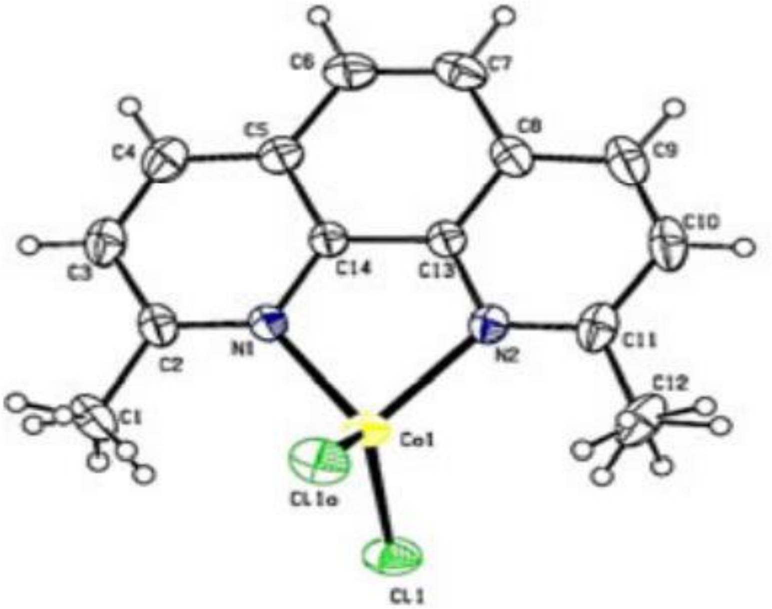


Fig 3.16 Diagram of $Co(dmphen)Cl_2$

Chen-Ming Wu ***et al*****,(2020)** reported Tetrahedral mononuclear Co(II) complex $[CoL_2](ClO_4)^2$ (1) in which L = 2,9- diphenyl-1,10-phenanthroline. Single crystal diffraction revels that structure 1 compound exist in the triclinic space group. Magnetic property studies were con- 1 ducted by reduced magnetization measurements, ab-initio calculations and X-band EPR experiments, the results of which revealed a large zero-field splitting. The Arrhenius equation indicates that the kinetic energy barrier

Peter Bugly ***et al*****,(2020)**,reported the development of new metal based potential drug. A novel ambidentate type hydroxamic acid derivative (phenhaH, 1) containing an (O,O) and a 1,10- phenantroline (phen) based (N,N) donor atom set together with its heterobimetallic complexes incorporating an octahedral and a half-sandwich type entity have been synthesized and characterized using various analytical techniques. The reducibility of the Co(III) is significantly decreased in the bimetallic complex 4, compared to the monometallic complex 2. The antiproliferative activity of compounds 2e4 in various cancer cells (human cervical carcinoma HeLa cells, human breast adenocarcinoma MCF-7 cells, breast carcinoma MDA-MB-231 cells, and human colorectal carcinoma cells HCT116) was tested using the MTT assay. The bimetallic complex 4 was found to be the most active among the tested complexes; it showed activity comparable or better than clinically used cisplatin. Interestingly, 4 is more active than cisplatin against the highly aggressive triple-negative
Breast carcinoma cells, MDA-MB-231.

Lan-Qin Chai ***et al*****,(2018)** reported Two 2-D and 3-D supramolecular zinc(II) complexes, $[Zn(L_1)(phen)(NO_3)^2]$ (1) and $[Zn(L_3)(phen)(NO_3)^2]$ (2), have been synthesized and characterized by IR, UV–Vis, and fluorescence spectroscopy, as well as by elemental analysis. X-ray single crystal analyses reveal that both complexes have penta-coordinated geometry and form an infinite 2-D and 3-D supramolecular frameworks through classical H-bonding and $\pi\cdots\pi$ stacking interactions. The normalized fluorescent spectra show clearly that complexes 1 and 2 have favourable fluorescent emissions in different solvents. Time dependent DFT calculations on the optimized structure of complexes 1 and 2 allowed for the assignment of specific electronic transitions in the UV–Vis spectra.

K. Savithri ***et al*****,(2018)** reported A bidentate (N- and O-) imine-based ligand (L1) and its metal complexes of types were synthesized as potential chemotherapeutic drug. Te prepared complexes were structurally characterized by spectral techniques (NMR, FT-IR, LC-MS, EPR, and electronic absorption), thermo gravimetric analysis (TGA/DTA), magnetic moment, and CHNO elemental analysis. The complexes were screened in vitro for their binding efficacy towards DNA. TGA revealed that the synthesized compounds were thermally stable. Molecular docking study where all the compounds are preferential selective for the groove of DNA. Antimicrobial results in higher antibacterial and antifungal potency of metal complexes than free ligand. Te presence of a planar heterocyclic ligand in Cu (II) and Co (III) drug based mixed-ligand complexes which changes the interaction of complex.

Yiwei Wang ***et al*****,(2015)** reported The crystal structure of a new coordination compound tri(2-(2,6-dichlorophenyl)-1H-imidazo[4,5-f] [1,10]phenanthroline) Co(II) complex ($[Co(dcpip)_3]Cl_2$) was synthesised and characterized using various techniques such as IR and UV-Vis. The ligand binds to Co (II) ions with a Bis-dentate mode and each Co (II) ion with distorted octahedral coordination geometry. Infrared spectrum and the UV-Vis absorption spectrum of the compound show good agreement with the experiment results.

Yulia Sotnikova ***et al*****,(2016)** reported Crown-containing phenanthroline derivative 2 the phenanthroline residue is the preferable place for binding as heavy Zn^{2+} as well as alkaline earth Ca^{2+} metal ions. The coordination of metal ions with phenanthroline residue causes the bathochromic shift in absorption and fluorescence spectra. In opposite, the binding of metal ion by macrocyclic moiety results in the hypsochromic spectral shift. Molecular binuclear complexes of the metal–ligand–metal type in their mixed nature are useful systems to study the basic aspects of electron, energy, charge transfer reactions.

Sergey D. Tokarev ***et al*****, (2020)** reported the Reactions of 2-(het)aryl substituted 1H-imidazo[4,5-f]- [1,10]phenanthrolines with Cd^{2+}, Zn^{2+}, Co^{2+} and Fe^{2+} perchlorates afford complexes of 2:1 and 3:1 ligand/metal ratios. Complexes of ligands with Cd^{2+} and Zn^{2+} are luminescent, while Co^{2+} and Fe^{2+} complexes are highly stable, and demonstrate electron transfer from metal to ligand.

Nursabah Sarıkavakli *et al*,(2022) reported 2-amino-4-substituted thiazole derivatives (TH_1-TH_5) and ligands (L_1H and L_2H) were synthesized from the reaction of TH_1 and TH_3 with 2-hydroxybenzaldehyde which were complexed with divalent nickel and cobalt chloride salts to yield complexes: $Ni(L_1H)_2$, $Co(L_1H)_2$, $Ni(L_2H)_2$ and $Co(L_2H)_2$.the complexes were characterized using various techniques such as 1H NMR, 13C NMR and FTIR.

Sujan Shee *et al*, (2018) reported a new phosphine free Co (II) complex catalysed synthesis of various quinoxalines via dehydrogenative coupling of vicinal diols with both the o-phenylenediamines and 2-nitroanilines. This complex was also effective for the synthesis of Quinolines. The practical aspect of this catalytic system was revealed by one-pot synthesis of 2-alkylaminoquinolines.

Spyros Perontsis *et al*, (2020) reported the interaction of cobalt chloride with the NSAID indomethacin led to the formation of the mononuclear-based polymeric complex. In this complex a unique chloride ligand bridges the cobalt. The presence of a nitrogen-donor co-ligand during the interaction results in a variety of complexes. In vitro study of the affinity of the complexes for CT DNA has shown their ability to intercalate to DNA bases. The complexes possess low-to-moderate activity to scavenge DPPH radicals, while the high ability to scavenge the ABTS radicals.

Palanivelu Nithyaa *et al*, (2018) reported a series of mononuclear cobalt and nickel complexes were synthesized and characterized by various techniques such as elemental analysis, infrared, electronic absorption and 1H NMR spectroscopies, single crystal X-ray diffraction. The thermal stability of the complexes was investigated by TG-DTA. The antibacterial activity of the cobalt (II) and nickel (II) complexes was examined against Gram positive and Gram negative bacteria at concentrations between 40-80 μg mL−1.

Ahmed A. Soliman *et al,* (2018) reported Co(II) and Cu(II) complexes were synthesized and characterized using elemental analysis such as DFT , TD-DFTIR and crystal X-ray studies. The ligands and the complexes showed cytotoxic activity and the copper complex was more active compared to the ligand.

Varvara V. Avdeeva *et al*, **(2021)** reported the complexes of $[ML_6]$[B10Cl10] where M = Co, Ni were prepared and characterized using the elemental analysis and IR spectroscopy; single-crystal and powder X-ray diffraction studies.

Xue-Meng Chen *et al,* (2021) reported Cobalt complexes were prepared in a one-pot method by the direct insertion reaction of the [NCN] cobalt with dioxygen or elemental sulphur. These complexes were well characterized by FT-IR and elemental analyses, X-ray crystallographic method. The obtained Cobalt complexes were evaluated as catalysts for isoprene Polymerization with $Al_2Et_3Cl_3$ or $AlEt_2Cl$ as co-catalyst.

Ferdaousse Rhoufal *et al,* (2019) reported two new mononuclear coordination complexes were synthesized and characterized by UV/Vis, FTIR and Raman data. crystallographic studies, shows that the two metals Co(II) and Cu(II), have an octahedral environment in complex 1 and complex 2. The both crystal structures are mainly stabilized by different hydrogen bonds along with the π–π interactions. Three-dimensional Hirshfeld surface analysis and two-dimensional fingerprint maps revealed that the C⋯H/H⋯C contacts represent an important contribution of the Hirshfeld surface result of hydrogen-bonding interactions in the complexes 1 and 2.

Suseelamma *et al,* (2018) reported Cobalt complexes were synthesized and characterized on the basis of elemental analyses, molar conductance, magnetic moment, mass, IR, UV spectral data. Electrochemical behaviour of ligands and complexes has 37. Been investigated by using cyclic voltammetry. Absorption studies reveal that the complexes bind DNA via intercalation involving strong π-stacking interaction of aromatic moiety of the complex between base pairs of DNA. In the presence of H_2O_2, the complexes cleave DNA effectively. It may be due to the reaction of hydroxyl radical with DNA. In the presence of DTT and

H_2O_2, complexes cleave DNA more effectively suggesting that the complexes cleave DNA by oxidative path.

Fatih Sevgia *et al,* (2017) reported the Zinc (II), copper (II), nickel (II), cobalt (II) and iron (III) complexes of Schiff bases were reported and characterized by 1H-NMR, 13C-NMR, elemental analyses, melting point, FT-IR, magnetic susceptibility and thermal analyses (TGA). The compounds were more active against Gram-positive than Gram-negative bacteria and more active towards fungi then bacteria.

M. Moreno-Alvero *et al,* (2021) reported two cobalt (II) complexes have been synthesized and characterized by means of physical measurements. Synthesized compounds were screened for their antimicrobial activity against 6 strains of bacteria. Antimicrobial studies showed more activity against gram-positive bacteria.

K. Rajeshwari *et al,* (2020) reported the Three new water soluble ternary metal complexes, $[Co(metf\ )(en)_2]Cl_2$(1), $[Ni(metf\ )(en)_2]Cl_2$(2), and $[Cu(metf\ )(en)_2]Cl_2$(3), (Metf = metformin,en = ethylenediamine), were synthesized and characterized by various techniques. C, H, and N analysis, molar conductance, TGA, magnetic susceptibilities and spectral data. Kinetic studies gives information regarding nonspontaneous thermal disintegration of complexes indicating its thermal stability. Gel electrophoresis experiment was performed to show complex ability to cleave using H_2O_2 as an oxidant. The docking studies were used to estimate the binding strength of the complexes with DNA and protein molecules.

Michal Gacki *et al,* (2019) reported the cobalt (II) complex and it was synthesized and characterized by various techniques such as elemental analysis, flame atomic absorption spectroscopy (FAAS), infrared spectroscopy (FTIR) and thermal decomposition techniques (TGA). The crystal structure of the complex was determined by single crystal X-ray diffraction technique. The antioxidant activity experiments revealed that 1 showed activity higher than that of sodium diclofenac. The lower activity of sodium diclofenac indicates that unpaired electrons of DPPH are more likely to react to cobalt ions rather, then sodium.

Mohd. Muddassir *et al,* (2020) reported A new four-coordinated high-spin Co(II) complex was synthesized by diffusion method The magnetic properties investigation shows that the single Co^{II} ion properties dominate the magnetic behaviour in the complex. Complex 1 connected to each other through π–π interactions through the sulphur of one of the thiocyanates and one of the nitrogen from the bathocuproine ligand, leading to an infinite one-dimension chain.

Maryam Sedighipoor *et al,* (2018) reported the tetra-coordinated Cobalt (II) and Zinc (II) complexes were synthesized and characterized by elemental analysis and multi-nuclear spectroscopy (IR and 1H and ^{13}C NMR) then, their biological activities including DNA and protein interactions were studied. The molecular docking calculations were performed to explore the interaction of the complexes with DNA and BSA.

Mark R. McClure et al, (2006) reported the compounds -cis [Co (trien)(bipy)]Cl_3 and -cis[Co(trien)(phen)]Cl_3 were synthesized and characterized by one- and two-dimensional NMR spectroscopy. The complexes [Co (trien)(bipy)]Cl_3 and [Co(trien)(phen)] Cl_3 caused the proton resonances to be spread into a wider spectral width and reduced the overlap in the proton spectra. Within each set of geminally related protons, one was found to give rise to a separate multiplet, and the other was lost in a complex multiplet arising from three separate protons. Overall, the degree of separation was not as great as observed previously for [Co (eee)(bipy)]Cl_3 and [Co(eee)(phen)]Cl_3.

Safwan Aroua *et al,*(2017) reported the cobalt(II) complexes were synthesized and fully characterized by elemental analysis, single-crystal X-ray crystallography, mass spectrometry, and UV−vis, 1 H NMR, and Fourier transform infrared (FT-IR) spectroscopy as well as by cyclic voltammetry (CV). Density functional theory (DFT) calculations were performed to investigate the electronic structure of all the Co (II) bis-terpyridyl molecular complexes. terpyridine ligand functionalization allows tuning the redox potentials of the Co(III)/Co(II), Co(II)/Co(I), and Co(I)/Co(I) (tpy) couples over a 1 V

Sebastian Iglesiasa *et al*, (2014) reported the new compounds with antitumor activity, coordination complexes with different metals the synthesis and characterization of six copper complexes with general stoichiometry [Cu (Ldipeptide)(phen)]·nH_2O (were phen=1,10-phenanthroline) and their cytotoxic activities against tumour cell lines. Characterization was done by various techniques such as, analytical and spectroscopic studies (by UV-visible, IR, X-ray diffraction). . The lipophilicity, DNA binding and albumin interaction were also studied. The introduction of phen as a ligand improved the cytotoxic activity as compared to the analog homoleptic Cu-dipeptide complexes. [Cu(Ala-Phe)(phen)] showed the strongest cytotoxic activity against cancer cell lines and therefore, this compound may be a good candidate to test its antitumor activity in vivo.

Suman Sinha *et al*,(2020) reported the three new cobalt complexes were synthesised, characterized and catalytic application of three new cobalt(II)-complexes of redox non innocent arylazo ligands, 2-(phenylazo)-1,10-phenanthroline (L_1a), 2-(4-chlorophenylazo)-1,10-phenanthroline (L_1b) and 2,9-bis(phenyldiazo)-1,10- phenanthroline (L_2). Reaction of L_1a with $Co^{II}Cl_2.6H_2O$ produced a µ-dichloro bridged binuclear cobalt (II)-complex. All these complexes were characterized using available spectroscopic techniques and DFT studies. We further explored the potential of these complexes as catalysts for the synthesis of pharmaceutically important organic compounds via the functionalization of alcohols. Variety of substituted quinazolin-4(3H)-ones were synthesized under aerobic conditions via coupling of alcohols and 2-aminobenzamide using 1b as the catalyst. Mechanistic investigations revealed that both cobalt and the arylazo scaffold act synergistically during catalysis.

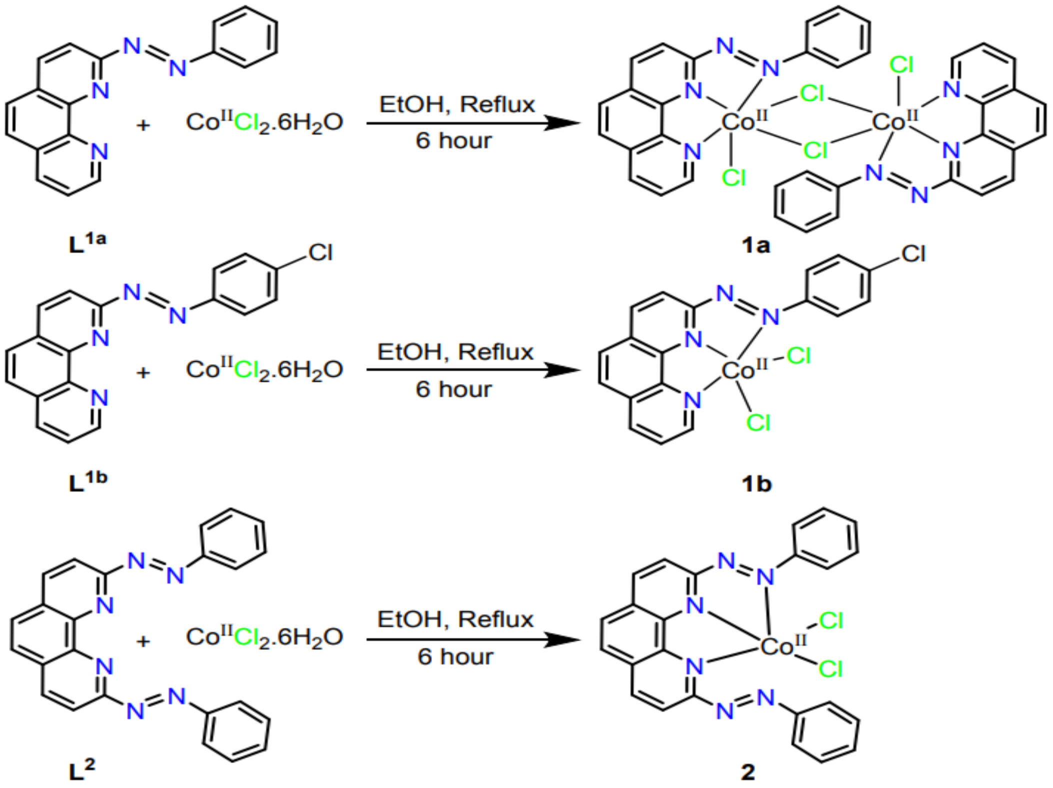


Fig 3.17 Mechanism of the complexes

Magdy Shebl *et al*,(2010) reported the binary complexes of iron(III), cobalt(II), nickel(II), copper(II), zinc(II), cerium(III) and uranyl(VI), have been synthesized by using the organic ligand. Also, ternary complexes were synthesized by using 1, 10-phenanthroline or oxalic acid as a secondary ligand. Characterization and structure elucidation of the synthesized compounds were achieved by elemental and thermal analyses, spectral (IR, electronic, ESR and 1 H and ^{13}C NMR), molar conductivities as well as magnetic measurements. The ligand and some metal complexes showed antibacterial activity towards Staphylococcus aureus and Escherichia coli bacteria and antifungal activity towards the fungi Candida albicans and Aspergillus flavus.

4. MATERIALS AND METHODS

SOLVENTS:

Cobalt Phenanthroline complexes were prepared using the solvent methanol and it was purchased from analytical grade.

CHEMICALS:

1. Cobaltous Chloride. Hexahydrate ($CoCl_2.6H_2O$)
2. 1,10- Phenanthroline
3. Pyridine
4. 4-cyanopyridine
5. 2,5-dimethylpyrazine
6. Pyridine-3-sulfonic acid

All these chemicals were purchased from analytical grade.

4.1 PREPARATION OF COMPLEXES

The Cobalt Phenanthroline complexes were prepared by the following methods are given below:

4.1.1 SYNTHESIS OF $[Co(L_1)_2 L_2]H_2O$

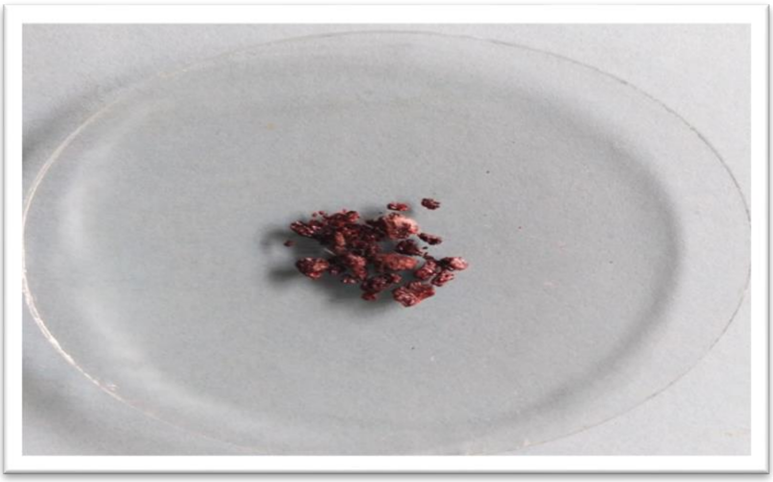


Fig 4.1 Product of $[Co(L_1)_2 L_2]H_2O$

Cobaltous chlorides of 0.6 g were added to the 10ml of methanol and stir the solution till it completely dissolved. To another beaker add 0.9g of 1, 10-Phenanthroline was placed with 10ml of methanol stir the solution till it completely dissolved. Both the solutions were mixed together in a iodine flask, the solution was turned into reddish brown colour and allowed to stirred in a magnetic stirrer in an ice bath for 30mins. To the above solution pyridine was added. The mixture was warmed and stirred for about 3 hrs at 50c. It was then allowed to stand for slow evaporation.

4.1.2 SYNTHESIS OF [Co(L_1)$_2$ L_3]H_2O

Fig 4.2 Product of [Co(L1)2 L3]H2O

Cobaltous chlorides of 0.6 g were added to the 10ml of methanol and stir the solution till it completely dissolved. To another beaker add 0.9g of 1, 10-Phenanthroline was placed with 10ml of methanol stir the solution till it completely dissolved. Both the solutions were mixed together in a iodine flask, the solution was turned into reddish brown colour and allowed to stirred in a magnetic stirrer for 30mins. To the above solution 0.3g of 4-cyanopyridine was added. The mixture was warmed and stirred for about 3 hrs at 50c. It was then allowed to stand for slow evaporation.

4.1.3 SYNTHESIS OF [Co(L1)$_2$ L$_4$]H$_2$O

Fig 4.3 Product of [Co(L1)2 L3]H2O

Cobaltous chlorides of 0.6 g were added to the 10ml of methanol and stir the solution till it completely dissolved. To another beaker add 0.9g of 1, 10-Phenanthroline was placed with 10ml of methanol stir the solution till it completely dissolved. Both the solutions were mixed together in a iodine flask, the solution was turned into reddish brown colour and allowed to stirred in a magnetic stirrer for 30mins. To the above solution 0.65ml of 2,5-Dimethylpyrazine was added. The mixture was warmed and stirred for about 3 hrs at 50c. It was then allowed to stand for slow evaporation.

4.1.4 SYNTHESIS OF [Zn(L$_1$)$_2$ L$_3$]H$_2$O

Fig 4.4 Product of [Zn(L$_1$)$_2$ L$_3$]H$_2$O

Zinc nitrate of 0.74 g was added to the 10ml of methanol and stir the solution till it completely dissolved. To another beaker add 0.9g of 1, 10-Phenanthroline was placed with 10ml of methanol stir the solution till it completely dissolved. Both the solutions were mixed together in a iodine flask, the solution was turned into reddish brown colour and allowed to stirred in a magnetic stirrer for 30mins. To the above solution 0.26g of 4-Cyanopyridine was added. The mixture was warmed and stirred for about 3 hrs at 50c. It was then allowed to stand for slow evaporation.

4.1.5 SYNTHESIS OF $[Co(L_1)_2 L_5]H_2O$

Fig 4.5 Product of $[Co(L_1)_2 L_5]H_2O$

Cobaltous chlorides of 0.6 g were added to the 10ml of methanol and stir the solution till it completely dissolved. To another beaker add 0.9g of 1, 10-Phenanthroline was placed with 10ml of methanol stir the solution till it completely dissolved. Both the solutions were mixed together in a iodine flask, the solution was turned into reddish brown colour and allowed to stirred in a magnetic stirrer for 30mins. To the above solution 0.3g of pyridine-3-sulfonic acid was added. The mixture was warmed and stirred for about 3 hrs at 50c. It was then allowed to stand for slow evaporation.

5. RESULT AND DISCUSSION

The formation of the complexes can be expressed by the following equation

$$CoCl_2.6H2O + 2L_1 + L_2 \rightarrow [Co(L_1)_2\ L_2]H_2O$$

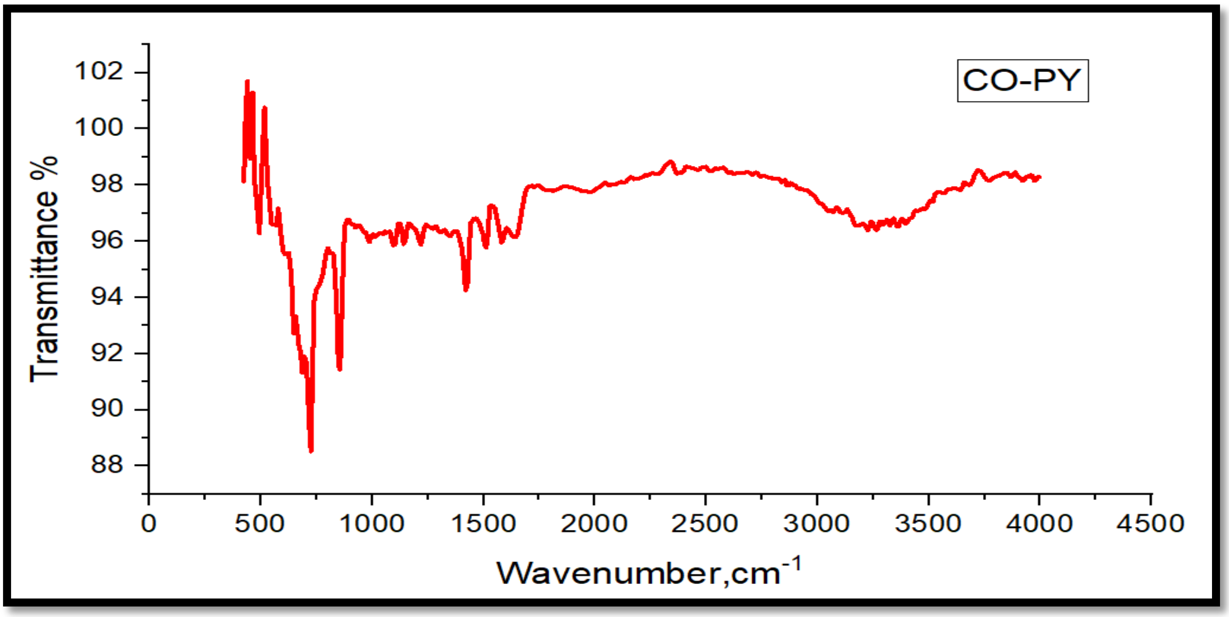
Where L_1 – 1,10-Phenanthroline monohydrate, L_2 - Pyridine, 4-Cyanopyridine, 2,5-Dimethylpyrazine, Pyridine-3-sulfonic acid.

5.1 FT-IR SPECTRA

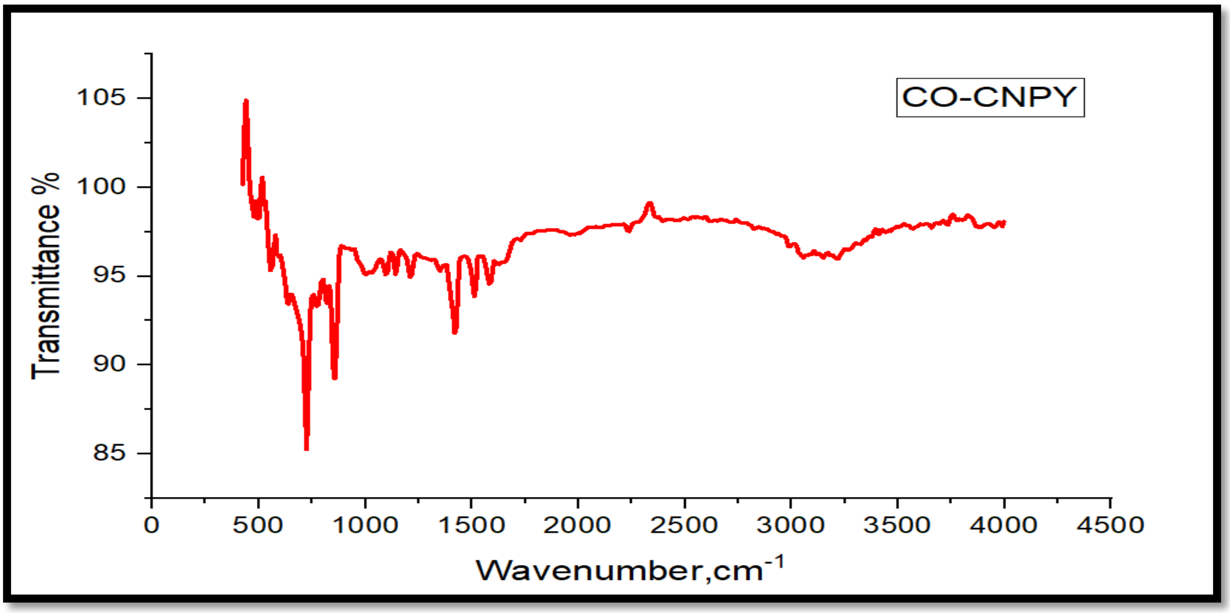
IR spectra have played an important role in the structural study of the class of complexes. The IR spectrum of the complexes revealed that the N atom of ligands are coordinated with the metal. The bands at 1405cm^{-1} and 1584cm^{-1} peaks corresponds to ʋC=C and ʋC=N for 1,10-phenanthroline monohydrate shifted to 1643cm^{-1} and 1581cm^{-1} in the complexes. The bands at 3263cm^{-1} indicates the ʋO-H stretching vibrations. They also appeared at 1521cm-1 (w), 1725cm-1 (w), 686cm-1(w), 1095cm-1(w) characteristics for ʋC=C , ʋC=N , ʋC-H, ʋC-N respectively in $[Co(phen)_2(py)]H_20$. Similarly the co-ordination between pyridine and metal ions is evident in the appearance of strong sharp peaks at 570cm^{-1}. The additional absorption bands appeared in the Table 4.1 for the mixed ligand complexes could be assigned to the metal to ligand. **Atakilt Abebe1 *et al*, (2020).**

Table 5.1 : Characteristics IR absorption (cm-1) of ligands and complexes

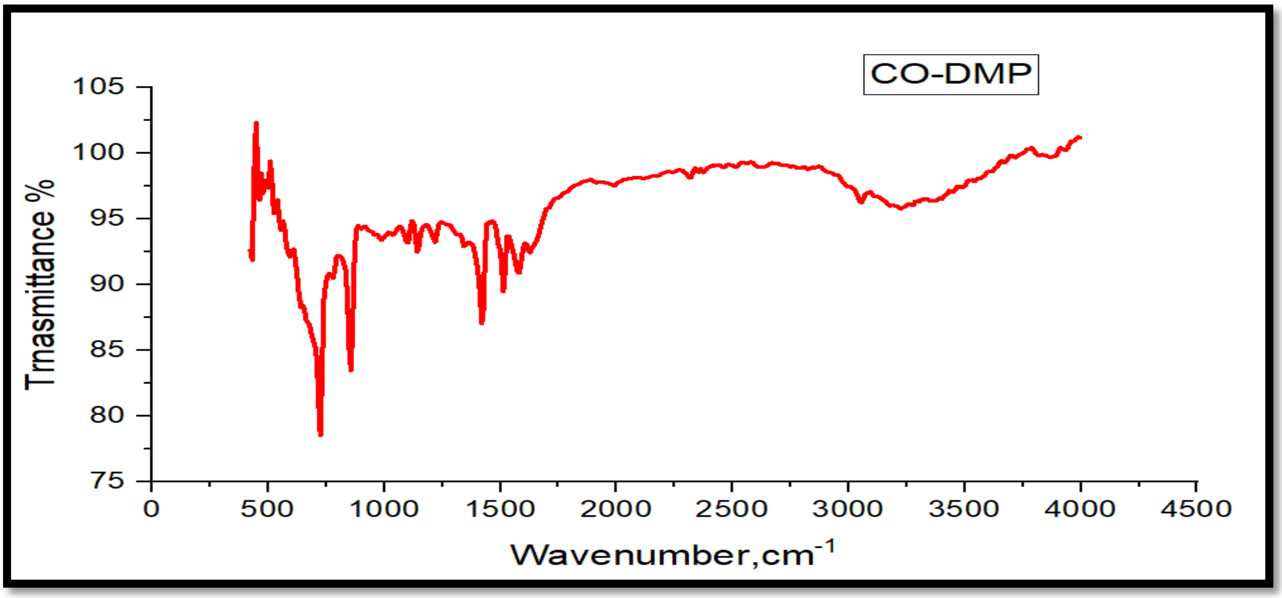
COMPOUND	C=C	C=N	C-H	C-N	O-H	C≡N	C-CH3	Co-N	CH3	SO_2	S-OH
$[Co(L1)_2L2]H_2O$	1512	1725	686	1095	-		-	570	-		
$[Co(L1)_2L3]H_2O$	1512	1725	686	1095	-	2237	-	555	-		
$[Zn(L1)_2L3]H2O$	1566	1519	640	1033	-	2376	-	555	-		
$[Co(L1)_2L4]H2O$			856				432	594	1342		
$[Co(L1)_2L5]H2O$	1512	1725	686	1095				555		686	925


CO-PY
Transmittance %
102
100
98
96
94
92
90
88
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Wavenumber,cm^{-1}

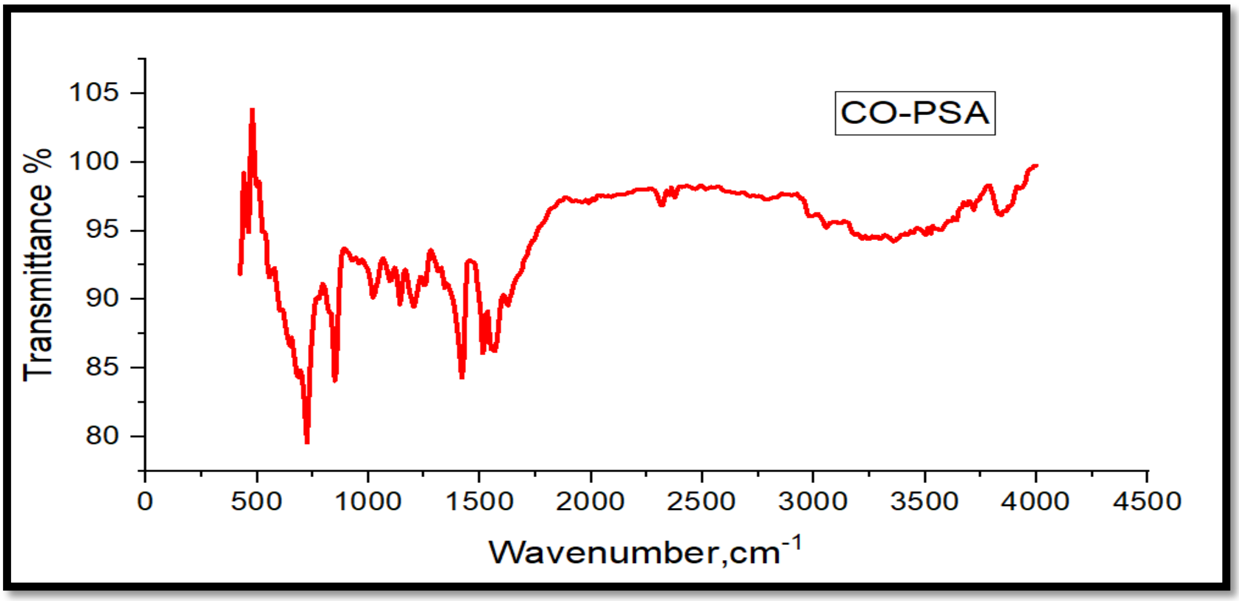
(a)


CO-CNPY
Transmittance %
105
100
95
90
85
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Wavenumber,cm^{-1}

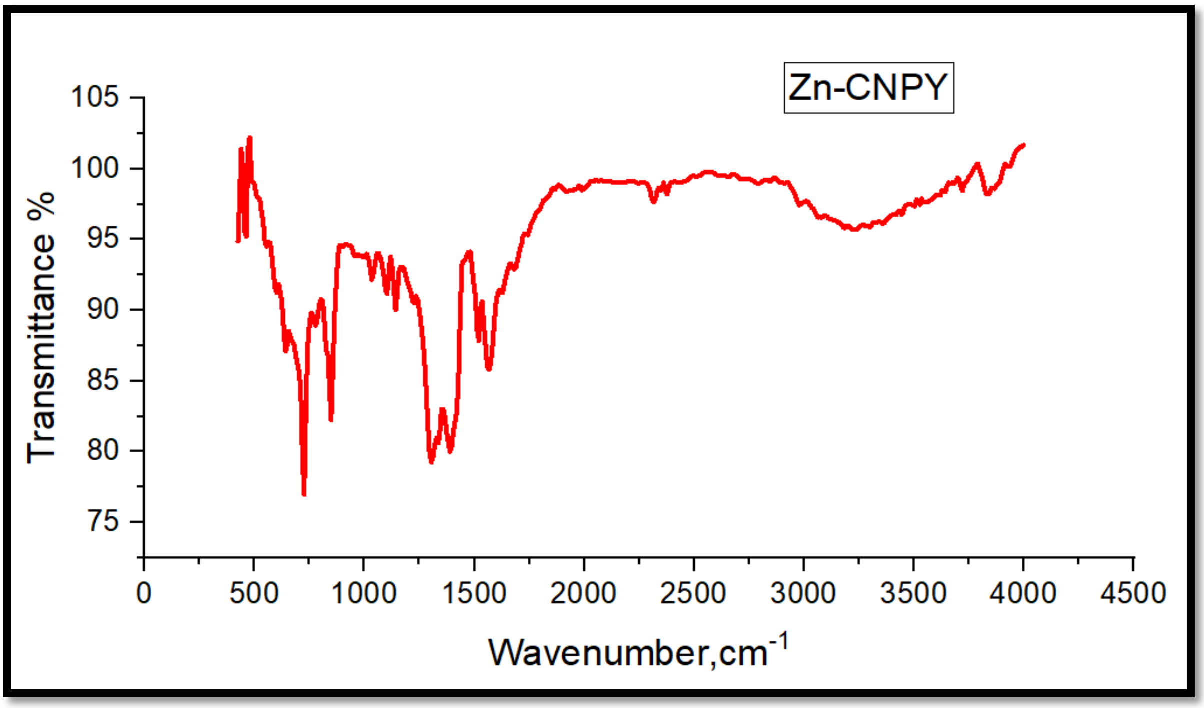
(b)


CO-DMP
Trnasmittance %
105
100
95
90
85
80
75
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Wavenumber,cm-1

(c)


CO-PSA
Transmittance %
105
100
95
90
85
80
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Wavenumber,cm-1

(d)



(e)

Fig 5.1 Infrared spectra of **(a)** $[Co(L_1)_2\ L_2]H_2O$ **(b)** $[Co(L_1)_2\ L_3]H_2O$ **(c)** $[Co(L1)_2\ L_4]H_2O$ **(d)** $[Co(L_1)_2\ L_5]H_2O$ **(e)** $[Zn(L_1)_2\ L_3]H_2O$ where L_1 – 1,10-Phenanthroline monohydrate, L_2- Pyridine, L_3- 4-Cyanopyridine, L_5 – Pyridine-3-sulfonic acid.

5.2 THERMO GRAVIMETRIC ANALYSIS

TGA curve for cobalt Phenanthroline complexes are shown in figure4.2. Cobalt Phenanthroline complexes showed three-step thermal degradation behaviour. The higher the value of Temperature higher will be the heat stability of complexes.

5.2.1 FIRST STAGE OF THERMAL DECOMPOSITION

The first step of thermal decomposition of Co(II) Phenanthroline complexes were started at 100 ◦C and is marked with a regular loss in mass up to 150◦C. The initial mass loss for the complexes were started with 7.1% and agreed well with the theoretically expected loss of 6.5–7.3%. This is mainly due to the elimination of molecule of coordinated water.

5.2.2 SECOND STAGE OF THERMAL DECOMPOSITION

The weight loss of about 16% occurred in second step degradation process in the temperature range 350–510◦C. The weight loss in this step is due to partial decomposition of organic ligand Phenanthroline.

5.2.3 THIRD STAGE OF THERMAL DECOMPOSITION

The mass loss in the temperature range 780-950◦C corresponds to third step degradation process of complexes. The weight loss in this step is about 36%. The weight loss in this step is due to the elimination of inorganic ligand. **Gui-Lin Wen *et al,* (2016)**

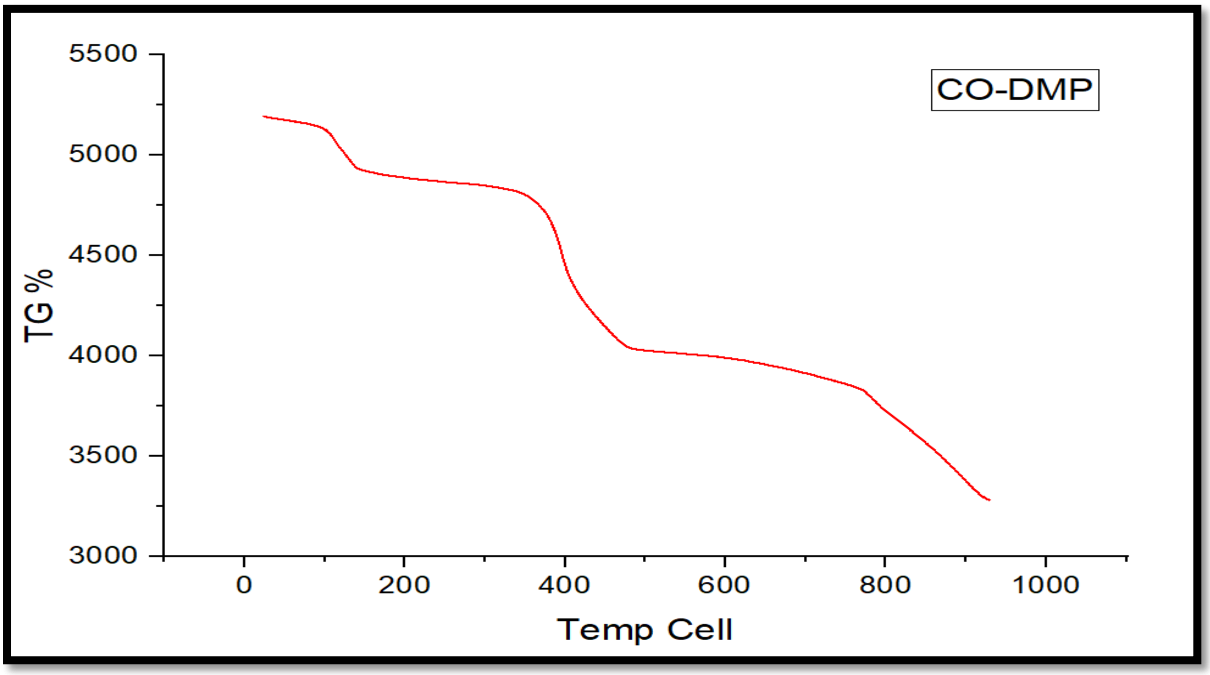
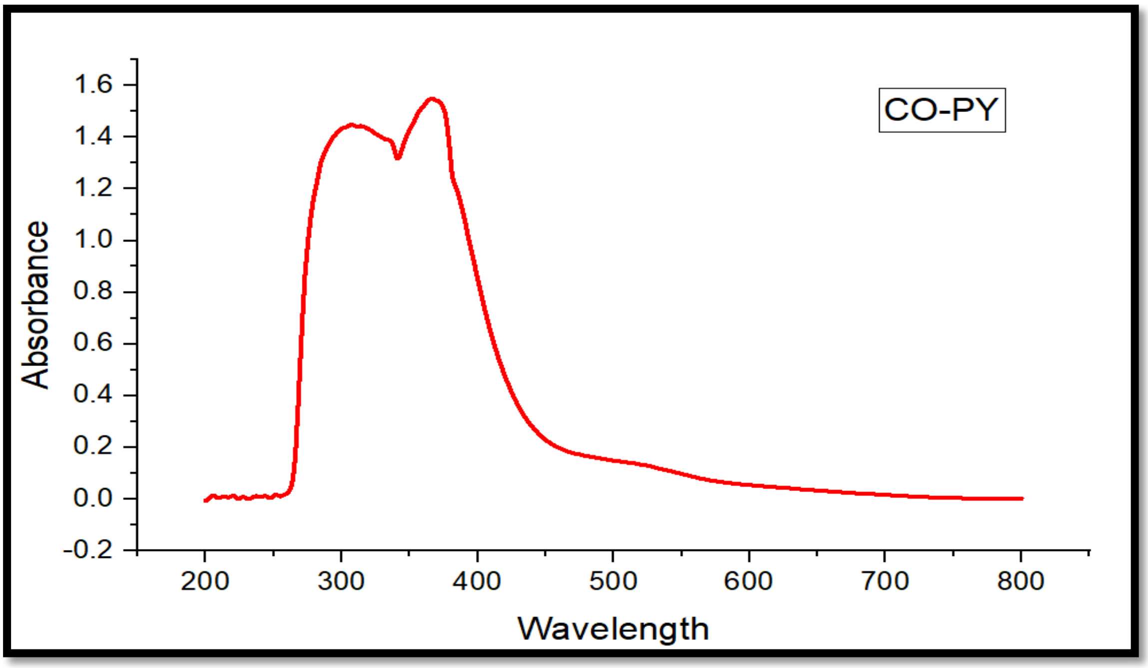


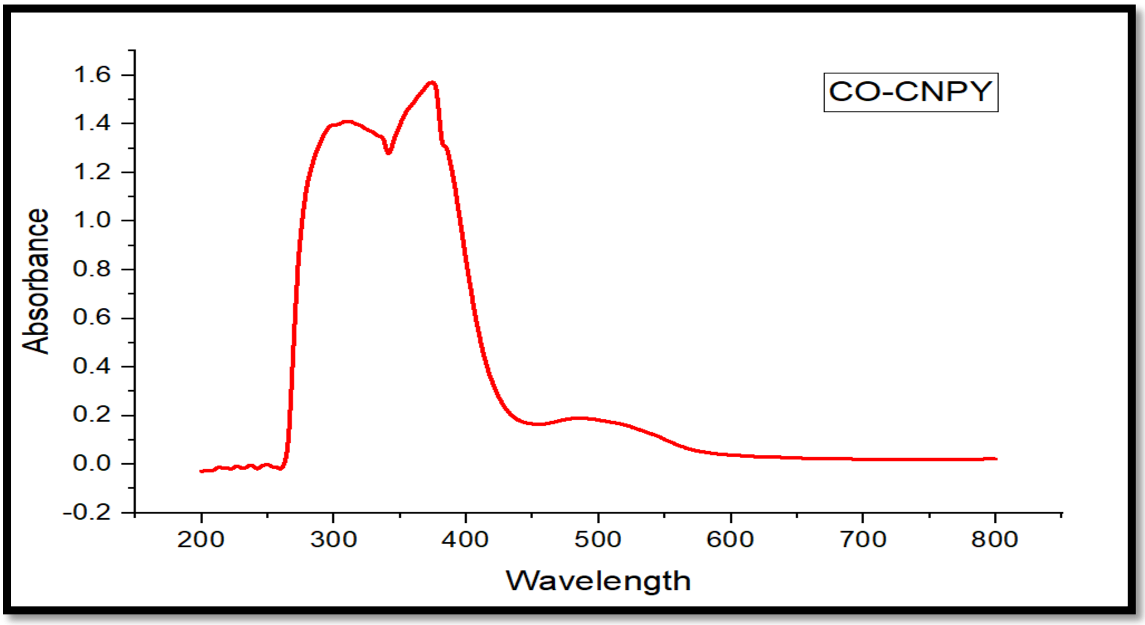
FIG 5.2 TGA curve for $[Co(L1)_2\ L_4]H_2O$ where L_4-2,5-Dimethylpyrazine

5.3 UV-VIS SPECTRA

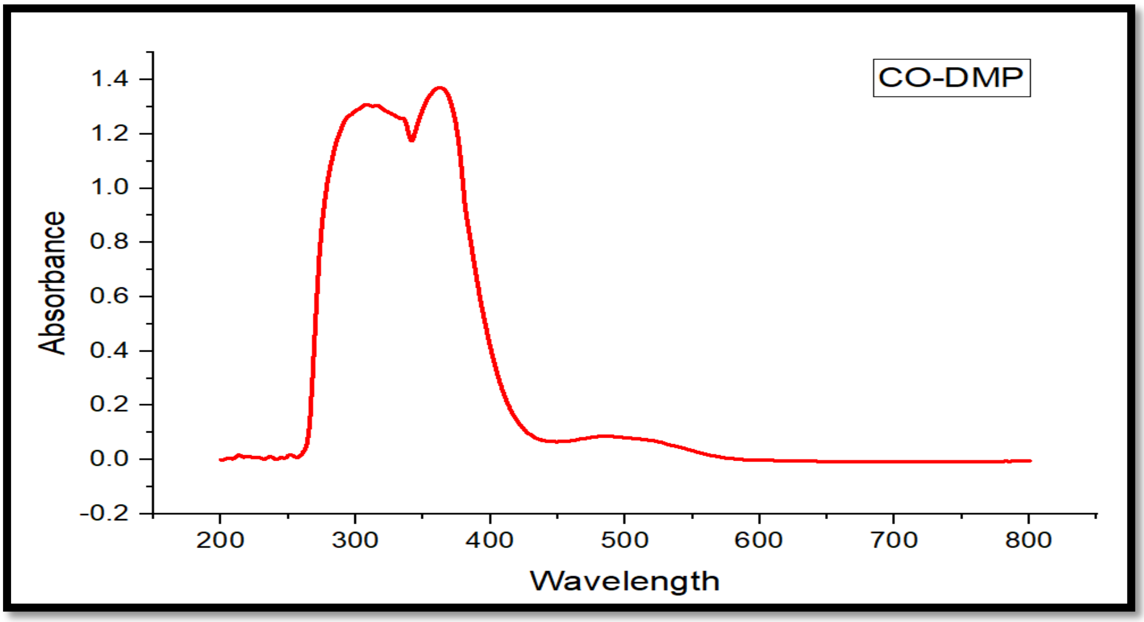
The absorbance of complexes were measured by UV-Visible spectrophotometer. Three types of electronic transitions have been observed for coordination compounds: Metal to ligand (MLCT) or ligand to metal (LMCT) charge-transfer absorption bands, d–d transition bands and intra-ligand (LC) transition bands. . Co (II) metal ion with low spin d7 electronic configuration showed two low intensity bands in the visible region. The source of these two bands is due to the d–d transition. In this study the maximum absorption took place at the wavelength of 270-450 nm for the metal complexes are due to the d-d transition in cobalt ions. The complexes showed π-π* transition appearing in the region 370nm. The weak d-d transition appearing in the region 440-580nm. **Asia M. Shalash *et al*,(2017)**



(a)



(b)



(c)

Fig 5.3 UV-Vis spectra of (a) $[Co(L_1)_2 L_2]H_2O$ (b) $[Co(L_1)_2 L_3]H_2O$ (c) $[Co(L1)_2 L_4]H_2O$ where L_1 – 1,10-Phenanthroline monohydrate, L_2-Pyridine, L_3- 4-Cyanopyridine.

5.4 ANTIBACTERIAL STUDIES

The antibacterial effect can be explained via the complex's diffusion across the lipid membrane of cells, where it interacts with the cells' normal activity. This can be modified by creating complexes with lipophilic properties. Complexes can interact with target cells by altering them such that their components have covalent binding qualities or interact with non-covalent binding capabilities, and by using in vivo delivery agents to deliver active ligands towards biological targets. **Atakilt Abebe1 *et al*,(2020)**.

The ligands 1,10-phenanthroline, pyridine , 2,5-dimethylpyrazine , Pyridine-3-sulfonic acid ,4-cyanopyridine, 2,5-dimethylpyrazine and their metal complexes(1),(2),(3),(4) and (5) were evaluated for in vitro antibacterial activities against strains of Gram-positive bacteria Staphylococcus aureus (S.aureus) and Gram-negative bacteria E.coli. They were investigated by Growth method. Kanamycin as a positive control for Gram positive and Gram negative bacteria. It has been observed that complex 4 [Co-CNPY] showed better biological activities than the other complexes against Gram-positive bacteria *Staphylococcus aureus* and complex 5 [Zn-CNPY] showed a better biological activities against Gram-negative bacteria E-coli.

Table 5.2 Antibacterial activity of metal salt, ligand and its metal complexes

SAMPLE	**Zone of Inhibition (mm)**	
	Staphylococcus aureus	***Escherichia coli***
Positive Control (Kanamycin)	18mm	24mm
Negative Control	0mm	0 mm
Co-PY	15mm	18 mm
Co-DMP	20mm	16 mm
Co-PYS	16mm	16 mm
Co-CNPY	25mm	16 mm
Zn-CNPY	17mm	24 mm

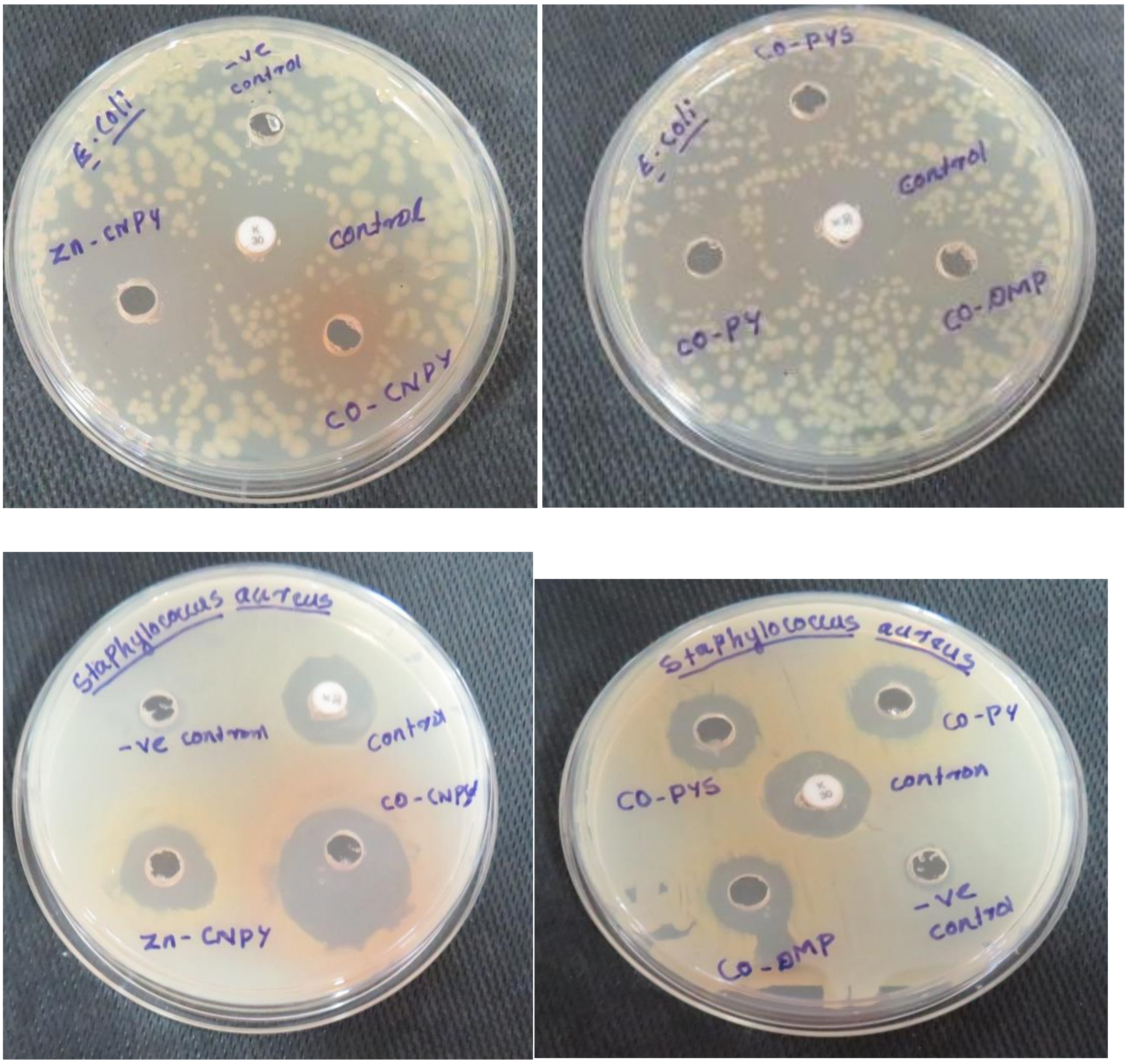


Fig 5.4 The inhibition observed by the action of complexes on Gram-positive bacteria (S. aureus) and Gram-negative bacteria (E.coli) where CO-PY, CO-DMP, CO-PYS, CO-CNPY and Zn-CNPY stand for complexes (1),(2),(3),(4) and (5) respectively.

6. SUMMARY AND CONCLUSION

6.1 PREPARATION OF THE COMPLEXES

The preparation of cobalt Phenanthroline complexes containing Pyridine , 4-Cyanopyridine ,2,5-dimethylpyrazine,Pyridine-3-sulfonic acid based ligands are used in the synthesized complexes,

$$[Co\ (phen)_2L_2]H_2O$$

Where, L_2 = Pyridine, 4-Cyanopyridine, 2,5-dimethylpyrazine, Pyridine-3-sulfonic acid.

6.2 CHARACTERIZATION OF THE COMPLEXES

6.2.1 IR SPECTRA

The cobalt Phenanthroline complexes showed the co-ordination between ligand and metal ions is evident in the appearance of peak at 570cm-1 which confirms the co-ordination of ligand to metal centre. The characteristics peaks around 3000 cm^{-1} , which can be attributed to the water molecules. The other spectral band observed in the range 1521cm-1 (w), 1725cm-1 (w), 686cm-1(w), 1095cm-1(w) corresponds to the υC=C , υC=N , υC-H, υC-N bonds in the complexes.

6.2.2 THERMOGRAVIMETRIC ANALYSIS

TGA curve for the cobalt phenanthroline complexes showed a three stage of thermal degradation. The first step of thermal decomposition of Co (II) phenanthroline complexes starts at 100 ◦C with 7.1% due to water molecules. The Second stage of thermal decomposition in the temperature range 350–510◦C with 16% was due to partial decomposition of organic ligand Phenanthroline. The mass loss in the temperature range 780-950◦C corresponds to third step degradation process of complexes. The weight loss in this step is about 36%. The weight loss in this step is due to the elimination of inorganic ligand.

6.2.3 UV-VISIBLE SPECTRA

The maximum absorption took place at the wavelength of 270-450 nm for the metal complexes are due to the d-d transition in cobalt ions. The complexes showed π-π* transition appearing in the region 370nm. The weak d-d transition appearing in the region 440-580nm.

6.2.4 ANTIBACTERIAL STUDIES

The ligands 1,10-Phenanthroline, Pyridine , 2,5-Dimethylpyrazine , Pyridine-3-sulfonic acid ,4-Cyanopyridine, 2,5-Dimethylpyrazine and their metal complexes were evaluated for antibacterial activities against strains of Gram-positive bacteria Staphylococcus aureus (S.aureus) and Gram-negative bacteria E.coli. Kanamycin as a positive control for Gram positive and Gram negative bacteria. It has been observed that complex 4 [Co-CNPY] showed better biological activities than the other complexes against Gram-positive bacteria Staphylococcus aureus and complex 5 [Zn-CNPY] showed a better biological activities against Gram-negative bacteria E-coli.

- In this work, Cobalt Phenanthroline complexes were synthesized.
- The synthesis brought about Co(II) and the ligands in a rigid configuration. we have designed and synthesized a new Co(II) Phenanthroline complexes $[Co(L_1)_2\ L_2]H_2O$, $[Co(L_1)_2\ L_3]H_2O$,$[Co(L1)_2\ L_4]H_2O$, $[Co(L_1)_2\ L_5]H_2O$ and $[Zn(L_1)_2\ L_3]H_2O$ derived from ligand 1,10-phenanthroline which was characterized by spectroscopic studies.
- Investigation into the biological activities of this class led to discovery of their antibacterial ability. In vitro antibacterial tests revealed that all the synthesized complexes exhibited antibacterial activity.
- Most Co (II) complexes are known to be active only against Gram-positive bacteria. However, the synthesized complexes showed awide-range of activities even against the Gram-negative bacteria.

7. BIBLIOGRAPHY

1. Garai, M., Dey, D., Yadav, H. R., Maji, M., Choudhury, A. R., & Biswas, B. (2017). Synthesis and phosphatase activity of a Cobalt (II) phenanthroline complex. *Journal of Chemical Sciences*, *129*(10), 1513-1520.
2. Abebe, A., Bayeh, Y., Belay, M., Gebretsadik, T., Thomas, M., & Linert, W. (2020). Mono and binuclear cobalt (II) mixed ligand complexes containing 1, 10-phenanthroline and adenine using 1, 3-diaminopropane as a spacer: synthesis, characterization, and antibacterial activity investigations. *Future Journal of Pharmaceutical Sciences*, *6*(1), 1-9.
3. Tamiru, G., Abebe, A., Abebe, M., & Liyew, M. (2019). Synthesis, structural investigation and biological application of new mono-and binuclear cobalt (II) mixed-ligand complexes containing 1, 10-phenanthroline, acetamide and ethylenediamine. *Ethiopian Journal of Science and Technology*, *12*(1), 69-91.
4. Atakilt, A., Bayissa, G., Sendek, A., & Kibret, M. (2018). Cobalt (II) complexes with 1, 10-phenanthroline alone and mixed with cytoside: Synthesis and antibacterial activities. *Ethiopian Journal of Science and Technology*, *11*(2), 79-96.
5. Abebe, A., Kendie, M., & Tigineh, G. T. (2021). Mono-and Binuclear Cobalt (II) Mixed Ligand Complexes of 2, 2'-Bipyridine and Ethylenediamine: Synthesis, Characterization and Biological Application. *Biointerface Research in Applied Chemistry*, *12*(2), 1962-1973.
6. Tabassum, S., Ahmad, M., Afzal, M., Zaki, M., Faizi, M. S. H., & Ali, A. (2016). Synthesis and crystal structure determination of cobalt (II) mixed-ligand complex containing 1, 10-phenanthroline and 5-(2-carboxybenzyloxy) isophthalic acid: Their biological evaluation viz. DNA/protein binding profile, pBR322 DNA cleavage activity. *Inorganica Chimica Acta*, *451*, 216-226.
7. Zhang, Y. Z., Li, H. R., Dai, J., Chen, W. J., Zhang, J., & Liu, Y. (2010). Spectroscopic studies on the binding of cobalt (II) 1, 10-phenanthroline complex to bovine serum albumin. *Biological trace element research*, *135*(1), 136-152.

8. Chin, L. F., Kong, S. M., Seng, H. L., Khoo, K. S., Vikneswaran, R., Teoh, S. G., ... & Ng, C. H. (2011). Synthesis, characterization and biological properties of cobalt (II) complexes of 1, 10-phenanthroline and maltol. *Journal of inorganic biochemistry*, *105*(3), 339-347.
9. Dey, D., Roy, A. B., Ranjani, A., Gayathri, L., Chandraleka, S., Dhanasekaran, D., ... & Biswas, B. (2015). Synthesis and bio-catalytic activity of isostructural cobalt (III)-phenanthroline complexes. *Journal of Chemical Sciences*, *127*(4), 649-661.
10. Al-Omair, M. A. (2019). Biochemical activities and electronic spectra of different cobalt phenanthroline complexes. *Arabian Journal of Chemistry*, *12*(7), 1061-1069.
11. Parada, J., ATRIA, A., Baggio, R., Wiese, G., Lagos, S., Pavón, A., ... & Corsini, G. (2017). Antibacterial activity and human cell cytotoxic of cobalt (III) complexes with 1, 10-phenanthroline and carbohydrate ligands. *Journal of the Chilean Chemical Society*, *62*(4), 3746-3751.
12. Golovnev, N. N., Molokeev, M. S., Sterkhova, I. V., & Lesnikov, M. K. (2018). Two novel mixed-ligand Ni (II) and Co (II) complexes with 1, 10-phenanthroline: Synthesis, structural characterization, and thermal stability. *Chemical Physics Letters*, *708*, 11-16.
13. Wang, C. C., Jing, H. P., Zhang, Y. Q., Wang, P., & Gao, S. J. (2015). Three coordination compounds of cobalt with organic carboxylic acids and 1, 10-phenanthroline as ligands: syntheses, structures and photo catalytic properties. *Transition Metal Chemistry*, *40*(5), 573-584.
14. Agwara, M. O., Ndifon, P. T., Ndosiri, N. B., Paboudam, A. G., Yufanyi, D. M., & Mohamadou, A. (2010). Synthesis, characterisation and antimicrobial activities of cobalt (ii), copper (ii) and zinc (ii) mixed-ligand complexes containing 1, 10-phenanthroline and 2, 2'-bipyridine. *Bulletin of the Chemical Society of Ethiopia*, *24*(3).
15. Eni, D. B., Yufanyi, D. M., Nono, J. H., Tabong, C. D., & Agwara, M. O. (2020). Synthesis, characterization and thermal properties of 1, 10-phenanthroline mixed-ligand complexes of cobalt (II) and copper (II): metal-mediated transformations of the dicyanamide ion. *Chemical Papers*, *74*(9), 3003-3016.

16. Avcı, D., Altürk, S., Sönmez, F., Tamer, Ö., Başoğlu, A., Atalay, Y., ... & Dege, N. (2019). Novel Cu (II), Co (II) and Zn (II) metal complexes with mixed-ligand: Synthesis, crystal structure, α-glucosidase inhibition, DFT calculations, and molecular docking. *Journal of Molecular Structure*, *1197*, 645-655.
17. Shalash, A. M., & Abu Ali, H. I. (2017). Synthesis, crystallographic, spectroscopic studies and biological activity of new cobalt (II) complexes with bioactive mixed sulindac and nitrogen-donor ligands. *Chemistry Central Journal*, *11*(1), 1-11.
18. Wen, G. L., Hua, M. R., Wang, X. L., Liang, X., Tian, D., & Zhao, X. (2016). Synthesis, crystal structure, and magnetic property of a cobalt (II) complex constructed from symmetrical 2-fluoroisonicotinate. *Molecular Crystals and Liquid Crystals*, *631*(1), 154-163.
19. Yang, L., Guo, J. J., Zhang, C. L., & Zhang, S. H. (2015). Syntheses, Crystal Structure, and Properties of a New Co (II) Coordination Polymer Constructed from 1, 10-Phenanthroline. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, *45*(8), 1112-1115.
20. Li, Y., Yang, Z., Zhou, M., & Li, Y. (2017). Synthesis and crystal structure of new monometallic Ni (II) and Co (II) complexes with an asymmetrical aroylhydrazone: Effects of the complexes on DNA/protein binding property, molecular docking, and in vitro anticancer activity. *RSC advances*, *7*(78), 49404-49422.
21. Piotrowska-Kirschling, A., Drzeżdżon, J., Kloska, A., Wyrzykowski, D., Chmurzyński, L., & Jacewicz, D. (2018). Antioxidant and cytoprotective activity of oxydiacetate complexes of cobalt (II) and nickel (II) with 1, 10-phenantroline and 2, 2′-bipyridine. *Biological trace element research*, *185*(1), 244-251.
22. Liu, Y., Lu, J., Wang, F., Shen, Y., Tang, C., Zhang, Y., & Jia, D. (2015). Solvothermal syntheses and characterizations of polysulfido-thioantimonate and thioantimonate templated by Co-phen complex cation. *Journal of Coordination Chemistry*, *68*(13), 2334-2346.
23. Akbarzadeh-T, N., Rezvani, A., Saravani, H., Kondori, T., Amani, V., & Khavasi, H. R. (2015). Synthesis, characterization, and crystal structure of

new four-coordinated cobalt (II) complexes containing phenanthroline derivatives. *Research on Chemical Intermediates*, *41*(3), 1247-1256.

24. Wu, C. M., Tsai, J. E., Lee, G. H., & Yang, E. C. (2020). Slow magnetization relaxation in a tetrahedrally coordinated mononuclear Co (II) complex exclusively ligated with phenanthroline ligands. *Dalton Transactions*, *49*(46), 16813-16820.
25. Nagy, I., Farkas, E., Kasparkova, J., Kostrhunova, H., Brabec, V., & Buglyó, P. (2020). Synthesis and characterization of (Ru (II), Co (III)) heterobimetallic complexes formed with a 1, 10-phenanthroline based hydroxamic acid conjugate. *Journal of Organometallic Chemistry*, *916*, 121265.
26. Chai, L. Q., Hu, Q., Zhang, K. Y., Zhou, L., & Huang, J. J. (2018). Synthesis, structural characterization, spectroscopic, and DFT studies of two penta-coordinated zinc (II) complexes containing quinazoline and 1, 10-phenanthroline as mixed ligands. *Journal of Luminescence*, *203*, 234-246.
27. Savithri, K., Kumar, B. V., Vivek, H. K., & Revanasiddappa, H. D. (2018). Synthesis and Characterization of Cobalt (III) and Copper (II) Complexes of 2-((E)-(6-Fluorobenzo [d] thiazol-2-ylimino) methyl)-4-chlorophenol: DNA Binding and Nuclease Studies—SOD and Antimicrobial Activities. *International Journal of Spectroscopy*, *2018*.
28. Wang, Y., Zhang, Y., Zhu, D., Ma, K., Ni, H., & Tang, G. (2015). Synthesis, structural characterization and theoretical approach of the tri (2-(2, 6-dichlorophenyl)-1H-imidazo [4, 5-f][1, 10] phenanthroline) cobalt (II). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *147*, 31-42.
29. Sotnikova, Y., Lukovskaya, E., Bobylyova, A., Fedorov, Y., Novikov, V., Peregudov, A., ... & Fedorova, O. (2016). Cation-dependent structural diversity of zinc (II), calcium (II) mono-and binuclear complexes of aryl-imidazo-1, 10-phenanthroline derivatives. *Inorganica Chimica Acta*, *445*, 103-109.
30. Tokarev, S. D., Fedorov, Y. V., & Fedorova, O. A. (2020). Imidazo [4, 5-f][1, 10] phenanthroline complexes with Fe2+, Cd2+, Co2+ and Zn2+ ions. *Mendeleev Communications*, *30*(4), 445-448.

31. Sarıkavaklı, N., Söyleyici, H. C., Erol, F., & Omara, T. (2022). Synthesis, characterization and computational studies of 2-amino-4-substituted thiazoles, their divalent nickel and cobalt complexes and molecular docking studies of their ligands as potent μ-opioid receptor agonists.
32. Shee, S., Ganguli, K., Jana, K., & Kundu, S. (2018). Cobalt complex catalyzed atom-economical synthesis of quinoxaline, quinoline and 2-alkylaminoquinoline derivatives. *Chemical Communications*, *54*(50), 6883-6886.
33. Perontsis, S., Geromichalou, E., Perdih, F., Hatzidimitriou, A. G., Geromichalos, G. D., Turel, I., & Psomas, G. (2020). Synthesis, structural determination, in vitro and in silico biological evaluation of divalent or trivalent cobalt complexes with indomethacin. *Journal of inorganic biochemistry*, *212*, 111213.
34. Nithya, P., Rajamanikandan, R., Simpson, J., Ilanchelian, M., & Govindarajan, S. (2018). Solvent assisted synthesis, structural characterization and biological evaluation of cobalt (II) and nickel (II) complexes of Schiff bases generated from benzyl carbazate and cyclic ketones. *Polyhedron*, *145*, 200-217.
35. Soliman, A. A., Amin, M. A., Sayed, A. M., Abou-Hussein, A. A., & Linert, W. (2019). Cobalt and copper complexes with formamidine ligands: synthesis, crystal X-ray study, DFT calculations and cytotoxicity. *Polyhedron*, *161*, 213-221.
36. Avdeeva, V. V., Vologzhanina, A. V., Ugolkova, E. A., Minin, V. V., Malinina, E. A., & Kuznetsov, N. T. (2021). Synthesis and structures of compounds [ML6][B10Cl10](M= Co, Ni; L= CH3CN, DMF, DMSO) as precursors for synthesis of cobalt (II) and nickel (II) complexes with organic L ligands. *Journal of Solid State Chemistry*, *296*, 121989.
37. Chen, X. M., Huang, L. C., & Gao, W. (2021). One-pot synthesis of cobalt complexes with 2, 6-bis (arylimino) phenoxyl/phenthioxyl ligands and catalysis on isoprene polymerization. *Dalton Transactions*, *50*(15), 5218-5225.
38. Rhoufal, F., Laachir, A., Guesmi, S., Jouffret, L., Sergent, N., Obbade, S., ... & Bentiss, F. (2019). New Cobalt (II) and Copper (II) Thiocyanate Complexes of 2, 5-Bis (pyridin-2-yl)-1, 3, 4-oxadiazole Ligand: Synthesis,

Crystal Structures, Spectral Properties and Hirshfeld Surface Analysis. *ChemistrySelect*, *4*(26), 7773-7783.

39. Suseelamma, A., Raja, K., & Reddy, K. H. (2018). Synthesis, characterization, DNA binding and nuclease activity of cobalt (II) complexes of isonicotinoyl hydrazones. *Iran. J. Chem. Chem. Eng. Research Article Vol*, *37*(4).
40. Sevgi, F., Bagkesici, U., Kursunlu, A. N., & Guler, E. (2018). Fe (III), Co (II), Ni (II), Cu (II) and Zn (II) complexes of schiff bases based-on glycine and phenylalanine: Synthesis, magnetic/thermal properties and antimicrobial activity. *Journal of Molecular Structure*, *1154*, 256-260.
41. Moreno-Alvero, M., Luna-Giles, F., Barros-García, F. J., Viñuelas-Zahínos, E., & Fernández-Calderón, M. C. (2021). Cobalt (II) complexes derived from a 2-aminobenzimidazole-thiazoline ligand: Synthesis, characterization, crystal structures and antimicrobial activity studies. *Polyhedron*, *207*, 115390.
42. Rajeshwari, K., Anantha Lakshmi, P. V., Archana, J., & Sumakanth, M. (2021). Ternary Cobalt (II), Nickel (II), and Copper (II) complexes containing metformin and ethylenediamine: Synthesis, characterization, thermal, in vitro DNA binding, in silico molecular docking, and in vivo antihyperglycemic studies. *Applied Organometallic Chemistry*, *35*(2), e6100.
43. Gacki, M., Kafarska, K., & Wolf, W. M. (2019). A supramolecular polymeric chain in the cobalt (II) complex with diclofenac: Synthesis, crystal structure, spectroscopic, thermal and antioxidant activity. *Journal of Coordination Chemistry*, *72*(22-24), 3481-3494.
44. Muddassir, M., & Song, Y. (2020). Synthesis, Crystal Structures and Magnetic Properties of Mononuclear High-Spin Cobalt (II) Complex. *Crystals*, *10*(2), 87.
45. Sedighipoor, M., Kianfar, A. H., Sabzalian, M. R., & Abyar, F. (2018). Synthesis and characterization of new unsymmetrical Schiff base Zn (II) and Co (II) complexes and study of their interactions with bovin serum albumin and DNA by spectroscopic techniques. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *198*, 38-50.

46. McClure, M. R., & Holcombe, J. (2004). Synthesis and NMR characterization of cobalt (III) complexes with triethylenetetramine, 2, 2-bipyridine and 1, 10-phenanthroline. *Journal of Coordination Chemistry*, *57*(11), 907-915.
47. Aroua, S., Todorova, T. K., Hommes, P., Chamoreau, L. M., Reissig, H. U., Mougel, V., & Fontecave, M. (2017). Synthesis, characterization, and DFT analysis of bis-terpyridyl-based molecular cobalt complexes. *Inorganic Chemistry*, *56*(10), 5930-5940.
48. Iglesias, S., Alvarez, N., Torre, M. H., Kremer, E., Ellena, J., Ribeiro, R. R., ... & Facchin, G. (2014). Synthesis, structural characterization and cytotoxic activity of ternary copper (II)–dipeptide–phenanthroline complexes. A step towards the development of new copper compounds for the treatment of cancer. *Journal of Inorganic Biochemistry*, *139*, 117-123.
49. Sinha, S., Das, S., Mondal, R., Mandal, S., & Paul, N. D. (2020). Cobalt complexes of redox noninnocent azo-aromatic pincers. Isolation, characterization, and application as catalysts for the synthesis of quinazolin-4 (3 H)-ones. *Dalton Transactions*, *49*(25), 8448-8459.
50. Shebl, M., Khalil, S. M., & Al-Gohani, F. S. (2010). Preparation, spectral characterization and antimicrobial activity of binary and ternary Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Ce (III) and UO2 (VI) complexes of a thiocarbohydrazone ligand. *Journal of Molecular Structure*, *980*(1-3), 78-87.
51. Renfrew, A. K., O'Neill, E. S., Hambley, T. W., & New, E. J. (2018). Harnessing the properties of cobalt coordination complexes for biological application. *Coordination Chemistry Reviews*, *375*, 221-233.
52. https://www.hmpgloballearningnetwork.com/site/thederm/site/cathlab/event/review-cobalt
53. https://www.azom.com/article.aspx?ArticleID=596
54. https://www.britannica.com/science/cobalt-chemical-element
55. Bencini, A., & Lippolis, V. (2010). 1, 10-Phenanthroline: A versatile building block for the construction of ligands for various purposes. *Coordination Chemistry Reviews*, *254*(17-18), 2096-2180.

56. https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_%28Inorganic_Chemistry%29/Descriptive_Chemistry/Elements_Organized_by_Block/3_d-Block_Elements/Group_09:_Transition_Metals/Chemistry_of_Cobalt
57. Renfrew, A. K., O'Neill, E. S., Hambley, T. W., & New, E. J. (2018). Harnessing the properties of cobalt coordination complexes for biological application. *Coordination Chemistry Reviews*, *375*, 221-233.