

**SYNTHESIS AND CHARACTERISATION OF  
RUTHENIUM COMPLEXES  
AND ITS APPLICATIONS**

**KEERTHIGA K S  
21PCH011**

**Dissertation work submitted to  
Avinashilingam Institute for Home Science and Higher Education for Women,  
Coimbatore-641043,  
Tamilnadu, India**

**In partial fulfilment of the Requirement for the Degree of  
MASTER OF SCIENCE IN CHEMISTRY  
May-2023**

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## List of Abbreviations

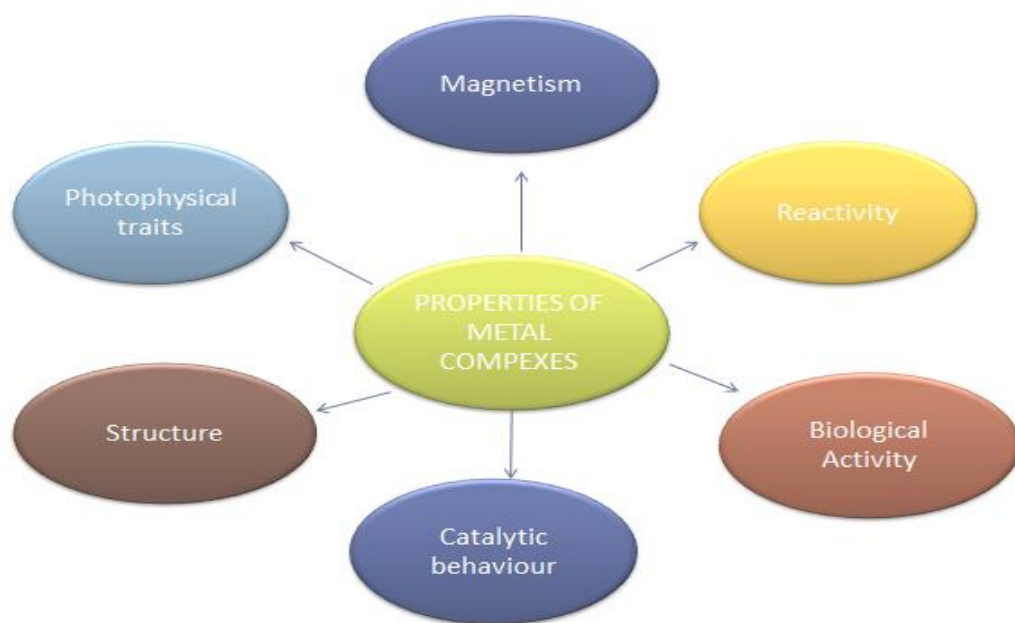
<b>trpy</b>	<b>2,2',6',2-Terpyridine</b>
<b>dmg</b>	<b>Dimethyl glyoxime</b>
<b>dpg</b>	<b>Diphenyl glyoxime</b>
<b>Phen</b>	<b>1,10 phenanthroline</b>
<b>bpy</b>	<b>2,2 Bipyridine</b>
<b>en</b>	<b>Ethelenediamine</b>
<b>FTIR</b>	<b>Fourier transfer Infrared spectroscopy</b>
<b>MLCT</b>	<b>Metal ligand charge transfer</b>
<b>TGA</b>	<b>Thermogravimetric analysis</b>

# INTRODUCTION

## 1.INTRODUCTION

As coordination compounds, which encompass all metal compounds, metal complexes are also classified. A metal complex is a structure made up of anions bound to the metal atom or ion in the centre (ligands). The term "coordination compound" refers to a substance that contains a coordination complex. Metals have a positive charge, which makes them Lewis acids. When they dissolve in water, they produce hydrated compounds [1].

It is recognized that a massive variety of extremely flexible metal-ligand combinations are available. Ten d-block elements (Fe, Ni, Cu, Zn, Tc, Ru, Rh, Ir, Pt, and Au) were reported in these research; however, two studies additionally mention complexes of lanthanides and actinides. Only bismuth complexes were investigated among the key group elements. These contributions utilised a wide variety of ligands, including mono dentate (N-, P-, O-, S), bi dentate (N, N, O, O, N, S-), and multi dentate instances. Some of the experiments also contain chemicals that are organometallic. There are many different properties that metal complexes can have, including colours, photophysical traits, magnetism, reactivity, biological activity, catalytic behaviour, structure, and more shown in figure1[2].



**Figure 1 Properties of Metal complex**

The area of coordination chemistry is one of the most challenging, intellectual, attractive and experimentally demanding frontiers in modern inorganic chemistry. Coordination chemistry has developed a half century from a readily defined and limited area into the most active research field of inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of molecular structure, novel breakthrough in chemical industry and vital insights into the functioning of critical components of biological system. Coordination compounds are one of the most important classes in inorganic chemistry that have been widely studied [3].

Cancers have been treated with platinum (Pt)-based anticancer medications like cisplatin. They do, however, have certain drawbacks, such as poor selectivity, toxicity against normal cells, and rising chemo resistance. The need for innovative metallo-anti cancers has thus gone unmet for decades. There have been several attempts to structurally evolve the ruthenium(Ru) polypyridyl complex in order to increase effectiveness since it was first introduced. Half-sandwich Ru-arene complexes have been the most well-known as an anticancer platform among them. Comparing these complexes to the Pt-based anticancers already available, it is evident that they offer better anticancer characteristics, such as greater selectivity for cancer cells and reduced toxicity against normal cells [4].

Many Ru complexes are presently undergoing human clinical studies. Ru complexes as photodynamic treatment (PDT) and photo activated chemotherapy (PACT), which can selectively activate pro drug moieties in a specific location, have also been explored for improvement in selectivity and toxicity associated with chemotherapy. It is envisaged that new metallo-anticancer medications would at least partially replace current Pt-based anticancers as a result of all these investigations on these fascinating creatures. An overall view of literature survey Ru-based compounds has anticancer complexes and perspectives [4].

## **1.1 Ruthenium complex**

Ruthenium (II) is a  $d6$  metal ion, whereas polypyridyl ligands are coordinating organic molecules with donor properties brought on by lone pairs of nitrogen atoms, donor properties brought on by electron cloud-rich rings like the five-membered heterocycle imidazole, and donor properties brought on by electron cloud-deficient rings like the six-membered heterocycle pyridine. homoleptic complexes with either bidentate or tridentate ligands or heteroleptic

complexes with an electronic absorption spectrum that includes both an ultraviolet region with absorption bands arising from  $\Pi \rightarrow \Pi^*$  orbital transitions - ligand centred LC - (typically c.a. 240 nm and 300 nm) that arise from polypyridyl moiety and a visible region (400 nm) are characteristics of their complex [5].

In coordination chemistry, ruthenium (II) complexes, in particular ruthenium(II) polypyridine complexes, have been receiving considerable interest during the past two decades. Ruthenium possesses highly adjustable spectroscopic and redox properties that can be used in photocatalysis, molecular devices, and the conversion of solar energy. Each of these characteristics can be modified depending on the ligand type thanks to low lying, intense  $\text{Ru}(\text{d}\Pi^6)$  to ligand( $\Pi^*$ ) MLCT transitions. The resulting distortion of the complexes' octahedral geometry controls their photoactivity. During photoexcitation to the 3MLCT state, this distortion decreases the energy of a dissociative metal-centered triplet state (3MC), allowing for its thermal population. The coordination of ligands that sterically clash with one another can cause the Ru(II) complex's structure to change [6,7].

In addition to having low cytotoxicity and redox stability in biological environments, ruthenium(II) polypyridine complexes have potential use in the creation of novel treatments and bioprobes. Because of the ruthenium center's luminous capabilities, ligands with extended aromatic groups have been devised to intercalate DNA into ruthenium polypyridyl complexes, allowing for the investigation of many elements of DNA's structure. The discipline of phototherapy in particular [7,8].

## **1.2 Application of ruthenium complexes**

### **General application**

Ruthenium is used in both the chemical and electrical industries. It is employed in the electrical sector to produce electronic chips. Chemically, it is utilised as anodes in electrochemical cells to produce chlorine. When ruthenium is combined with other metals to create an alloy, it serves as a hardener. In the creation of palladium jewellery, this property of ruthenium is utilised [9,16]. Ruthenium strengthens titanium's ability to resist corrosion when combined with it to produce an alloy. Ruthenium alloys are used in the creation of jet engine

turbines as well. Ru tips are also found in fountain pen nibs. Ruthenium is used in therapy as well. For instance, the Ru 106 isotope is used in the irradiation of ocular cancer cells [10].

Criminal investigations apply  $\text{RuO}_4$  because it combines with any fat or fatty substance that contains sebaceous pigments to produce ruthenium dioxide pigments that are black or brown in colour. Ruthenium complexes typically absorb visible spectrum light. Manufacturing solar cells for the generation of solar energy uses this feature of ruthenium. On the surface of the substrate, ruthenium vapour is deposited and exhibits magneto-resistive properties. Hard disc drive layers or films are created using this Ru unique [11].

## **Medical applications**

### **Application in diagnosis,**

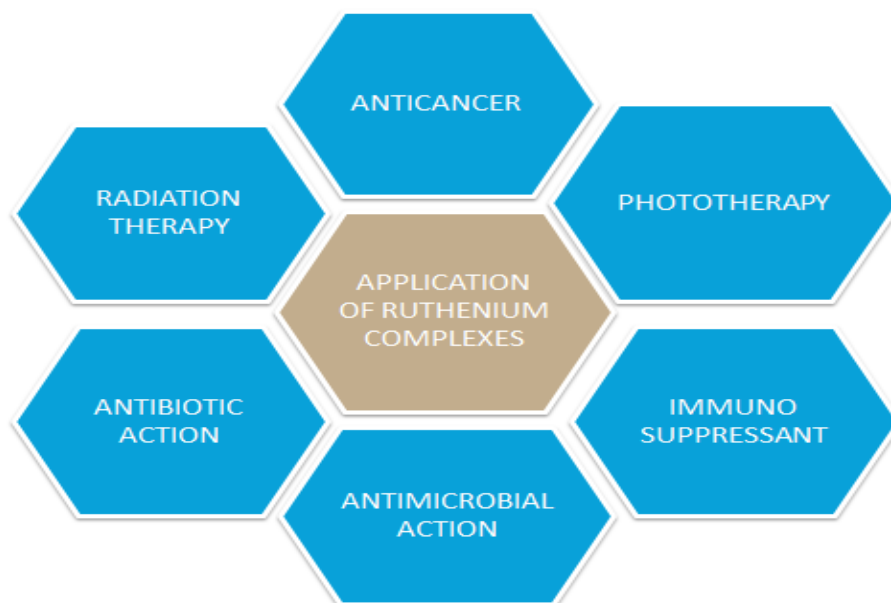
The blood level of calcitonin is measured using ruthenium. This finding is valuable in the diagnosis and management of thyroid and parathyroid gland disorders. Measurement of calcitonin level is crucial in the treatment of medullary thyroid cancer (MTC). The one-step sandwich assay method is used to determine the level of calcitonin. There are two incubation phases in this procedure. Each incubation procedure lasts for nine minutes. 50 microliters of the sample containing the monoclonal human calcitonin specific antibody labelled with ruthenium complex and the monoclonal human calcitonin specific antibody that has been biotinylated are incubated first. When human calcitonin is incubated, a sandwich-like complex is formed that contains both biotinylated and ruthenylated complexes. Following the first stage, the second incubation step is completed with the addition of streptavidin-coated microparticles.

Complexes containing biotin are created via streptavidin-coated microparticles. Measuring is done following the incubation phase. Aspirated into measuring cells for measurement, the incubation mixture's microscopic particles are magnetically drawn to the electrode's surface. The unbound components are then eliminated. Induction of chemi-luminescent emission is carried out by applying voltage to the electrode, and the response is then observed using a photomultiplier [11].

In the Elecsys cyclosporine test, ruthenium is also used to detect cyclosporine. The care of cyclosporine-treated patients undergoing liver, kidney, heart, lung, and bone marrow transplants is highly dependent on the determination of cyclosporine [11].

## Application in treatment

Metals like gold have historically been employed for medicinal purposes, according to medical science history. Metals may have a positive impact on health, but the specific mechanism of action is still understood. Ruthenium has also been used as a medication shown in Figure 1.1.



**Figure 1.1 Application of ruthenium complexes**

### **Immunosuppressant:**

An immunosuppressant is a medication that reduces the immune system's overactivity. An immunosuppressant called Cyclosporin A, which is widely used to treat conditions like anaemia and psoriasis dermatitis, causes adverse effects including nausea, renal problems, and hypertension. Complex created with Ru is used to alter Cyclosporin A's activity (III). A stable substance produced by the ruthenium cyclosporin complex inhibits the growth of T lymphocytes [13].

### **Antimicrobial action**

Drugs with an antibacterial effect prevent microbial growth in the human body. Several parasite infections can be effectively treated with the ruthenium complex. When a certain type of antimicrobial therapy is used on a bacterial strain, the strain develops resistance to the

medication. Because the microorganisms mutate to become resistant to the drug's organic ingredient, resistance eventually arises. Yet, the effectiveness of the medicine rises when a combination with a particular metal forms because the microorganisms cannot digest the metal component of the drug's organometallic complex. When chloroquine is used, Plasmodium species acquire resistance to it, but this does not happen when chloroquine is complexed with ruthenium [14].

### **Antibiotic action**

Antibiotics are medications created from one specific bacteria that work against another microorganism. These days, laboratory-made synthetic antibiotics are also produced. Antibiotics work by entering the cell of microorganisms and concentrating on any important metabolic pathway. If it forms a compound with synthetic antibiotics, ruthenium has the upper hand. Compared to iron, ruthenium has a better potential to bind to cellular components because it is a metal. Sharing or delocalization of cations between the two moieties occurs when an organic moiety binds to a metal ion. The cellular component's permeability to the drug is increased by the drug's component parts' changing charges. For instance, the development of a compound of Thiosemicarbazone exhibits a substantial increase in its activity. For instance, Thiosemicarbazone exhibits a striking increase in activity as a result of Ru complex formation [15].

### **Application of ruthenium in cancer**

#### **Anticarcenogenic activity**

Cancer, also known as carcinoma, is a stage in which body cells proliferate uncontrollably and exhibit invasiveness and metastatic potential. Drug therapy for carcinoma seeks to stop the production of malignant proteins as well as DNA replication. Drugs like Cisplatin, which uses platinum as an anticancer agent, are available on the market. Although platinum has demonstrated improved outcomes in the treatment of cancer, platinum has not been successful in curing all tumors. Ruthenium was a newcomer to cancer treatment due to the disadvantage of platinum. Ruthenium has the capacity to bind to DNA, preventing both protein synthesis and DNA replication. The only disadvantage of ruthenium was that it was poorly soluble in water. By employing ruthenium dialkyl sulfoxide derivative, this flaw was overcome.

Flavonoid acts at the DNA level to drive tumour cells to undergo apoptosis, which is how it combats cancer. Cells undergo a controlled demise process called apoptosis [16].

### **Radiation therapy**

Radiotherapy has also been applied to cancer treatment. Only when applied close to the malignant cell does radiation therapy have a benefit. Radio sensitizers are the substances applied during radiation treatment. Since ruthenium has a strong affinity for DNA binding, it is employed in radio sensitizer complexes to extend the distance to malignant cells [17].

### **Photodynamic therapy**

Chemicals and electromagnetic radiations are utilised in the therapy known as photodynamic therapy. As electromagnetic radiation interacts with the chemicals used in this therapy, the chemicals become cytotoxic and are directed at the malignant cells. Ruthenium is used in this therapy because it improves the accessibility of these compounds to cancerous cells [9,12].

### **Action on cancerous mitochondria**

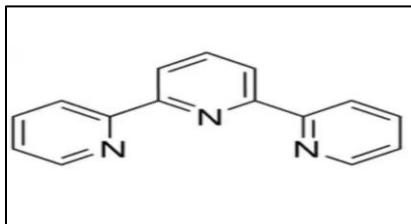
The heart of every cell is its mitochondria. Because of this, it could be a target for cancer treatment. For staining mitochondria, ruthenium red is the type of ruthenium employed. A calcium entity can be seen on the mitochondrial surface. This calcium reacts with the addition of ruthenium red, staining the mitochondria as a result. More tumor-inhibiting features of ruthenium red [9,13].

## **1.3 Nitrogen based Tridentate ligand**

### **Terpyridine**

A major class of aromatic heterocyclic compounds, 2,2':6',2''-terpyridine is a tridentate ligand that contains three coordination sites for N-heteroaromatic rings (figure 1). These ligands can create stable complexes with a variety of different primary groups and transition metal ions due to their strong chelating activity. Terpyridine motifs and their complexes have previously attracted the attention of materials chemists due to their applications in a variety of fields, such

as photovoltaic devices, DNA binders, sensors, photosensitizers, molecular chemistry, medicinal chemistry, and metal-organic framework (MOF) construction [17].



**Figure 1.3 2,2':6',2''-Terpyridine**

Moreover, their complexes with transition metals in particular can provide special photoluminescence, catalysis, sensing characteristics, and extremely promising tumor-inhibiting actions. The development of such molecules for usage in numerous domains, particularly in pharmaceutical and material chemistry, has drawn more interest due to environmental and economic reasons [18]. Constable's group has studied the synthesis of terpyridine derivatives in depth, and they have developed simple and efficient methods for producing a wide range of substituted terpyridine ligands in high yields through the Kröhnke reaction by condensation of 2-acetylpyridine with various substituted aryl aldehydes, followed by oxidation [19].

Due to their numerous/extensive applications in a variety of research fields, including therapeutic uses (such as DNA intercalation and anti-cancer), material sciences (photovoltaics, sensitizers), and catalysis, these ligands exhibit special coordinative capabilities towards transition elements [20]. Another area where 2,2':6',2''-terpyridines and their associated complexes are widely employed and serve as important organic ligands is supramolecular chemistry and material science [21]. The characteristic of the metal-containing assemblies depend on the electronic effects of the terpyridine unit, its substituents, and the metal ion [22].

These molecules offer a chance to investigate how the ligand, the main metal ion, and the coordination geometry affect the binding properties. The remarkable binding affinity of terpyridine and its infrastructure procurement for a wide range of transition metal ions, which led to a variety of metal supramolecular structures with fascinating photophysical and redox properties, was widely recognised [23]. In order to create radiative metallo-supramolecular coordination compounds that accumulate through fibre optics and whose violet-blue emissions

are attributed to fibre optic ligand transfer, have prepared ligands based on terpyridine. A donor-acceptor system has been demonstrated to be an effective method for modifying the optical characteristics of organic-inorganic hybrid materials [24].

Moreover, transition metal complexes offer a variety of benefits, including strong photochemical properties and long-lasting fluorescent excited states. Moreover, fluorescent probes have not yet fully perfected the core-functionalization of terpyridine units with electron-donating/withdrawing substituents. According to the investigations, free terpyridines and their metal complexes' photophysical and oxidation-reduction characteristics can be changed by using electron-accepting and -donating substituents [25].

Thus, a wide range of substituents with various electron-releasing or -accepting behaviours were added to the p-position of the terpyridine rings in order to learn more about the structure-activity interaction (absorption and emission qualities). Moreover, the terpyridine moiety has attracted attention recently due to its intriguing molecular topologies in the design and synthesis of polymers for coordination as well as its potent anti-microbial activity, which may serve as a crucial point of reference for the development of more potent anti-microbial drugs [26].

The cell permeability barrier may break down as a result of this increased lipophilicity, preventing normal cell functions. Bidentate or tridentate ligands with greater lipophilicity had higher anti-microbial activity than monodentate ligands. According to earlier research, tridentate or bidentate ligands with higher lipophilicity had higher anti-microbial activity than monodentate ligands. Additionally, two different types of ligands in complexes had stronger anti-bacterial activity than a single ligand, according to the principle of similarity and inter-miscibility. Finding the structure-property relationship between complex structures and antimicrobial capabilities would serve as motivation and provide theoretical guidance for creating and synthesising complexes with beneficial biological activities [27].

## 1.4 Nitrogen based Bidentate ligands

### [i] Dimethyl glyoxime

Dimethylglyoxime, often known as DMG, is a chemical that appears white powder but is much more soluble in sodium hydroxide solution or methanol than it is in water. Dimethylglyoxime, sometimes referred to as 2,3-Butanedione dioxide, has the chemical formula  $C_4H_8N_2O_2$ . Analytical chemistry uses DMG as a reagent, and its several derivatives have been produced. Apart from nickel, it aids in the detection of several other metal ions. DMGH is the name of the anionic form, and  $DMGH_2$  is the name of the neutral form (here H indicates hydrogen). Palladium and nickel are both identified with  $DMGH_2$ . Moreover, it has two donor arms and is a bidentate ligand. Coordination chemistry currently uses dimethylglyoxime as a ligand. In the chemistry of metal complexation, dimethylglyoxime serves as a potent ligand. One of the few ligands, dimethylglyoxime, does not have a basic dimethylglyoxime 2 deprotonated species[28].

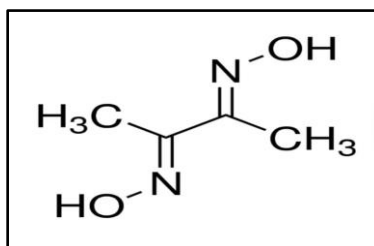
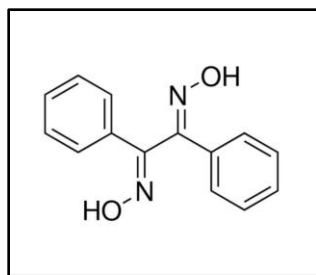


Figure 1.4(a) DimethylGlyoxime

### [ii] Diphenyl glyoxime

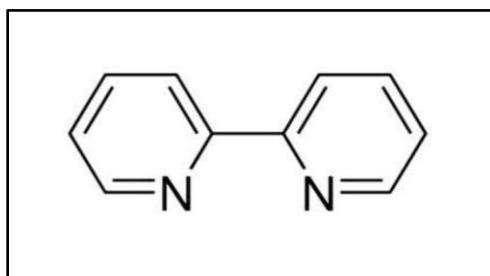
Chemical compound having the formula  $C_{14}H_{12}N_2O_2$  known as diphenyl glyoxime. It is a white, delicate leaf crystal. Easily soluble in sodium hydroxide solution and acetone, but barely soluble in water and ethanol. chelating extractant and the use of analytical reagent. The anionic form is known as DPGH and the neutral form is known as  $DPGH_2$  (here H indicates hydrogen). Moreover, it is a bidentate ligand with two donor arms. Diphenyl glyoxime is now used as a ligand in coordination chemistry. Diphenyl glyoxime functions as a strong ligand in the chemistry of metal complexation [29].



**Figure 1.4(b) Diphenyl Glyoxime**

### **[iii] 2,2-Bipyridine**

An organic substance having the chemical formula  $C_{10}H_8N_2$  is 2,2'-bipyridine. This colourless solid belongs to the class of bipyridines and is an interesting isomer. It forms compounds with numerous transition metals as a bidentate chelating ligand. The strong fluorescence that ruthenium and platinum complexes of bipyridine show may have useful applications. With its strong redox stability and simplicity of functionalization, the 2,2'-bipyridine ligand has been widely employed as a metal chelating ligand. 2,2'-bipyridine is a neutral ligand, as opposed to other ligands like catechol, which is dianionic, and derivatives of the acetylacetonate ion, which are monoanionic. As a result, it can interact chargedly with metal cations, and this characteristic has been used to create and synthesise metal-bipyridine complexes [30].

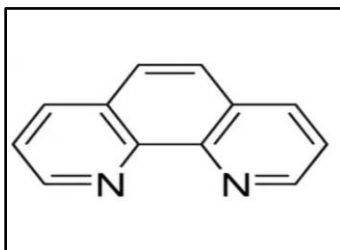


**Figure 1.4(c) 2,2 Bipyridine**

### **[iv] 1,10 Phenanthroline**

A heterocyclic chemical molecule is called 1,10-phenanthroline (phen). It is a whitish solid that dissolves in organic solvents. The 1,10 denotes the position of the nitrogen atoms that replace CH in the hydrocarbon known as phenanthrene. 1,10-Phenanthroline (phen) is a traditional chelating bidentate ligand for transition metal ions and has contributed significantly to the growth of coordination chemistry. It also holds great promise as a flexible starting point for organic, inorganic, and supramolecular chemistry. Phenanthroline is a rigid planar, hydrophobic,

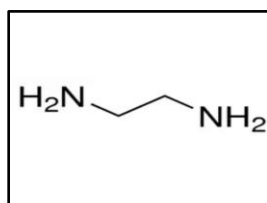
heteroaromatic structure with electron-poor nitrogen atoms that are perfectly positioned to cooperate in cation binding. These structural characteristics control its capacity to coordinate with metal ions [31].



**Figure 1.4(d) 1,10 Phenanthroline**

#### [v] Ethylenediamine

The chemical molecule with the formula  $C_2H_4(NH_2)_2$  is ethylenediamine (abbreviated as en when a ligand). A basic amine is this white liquid with an ammonia-like odour. The earliest member of the so-called polyethylene amines is ethylenediamine. The two nitrogen atoms donate their lone pairs of electrons when ethylenediamine functions as a ligand, making it a well-known bidentate chelating agent for coordination compounds. In inorganic chemistry, it is frequently shortened to "en." A number of different chemical compounds are made from the organic molecule ethylenediamine. In several pharmaceutical formulations, including creams, it serves as an excipient. Importantly, ethylenediamine is a contact sensitizer capable of triggering both local and broad reactions [32].



**Figure 1.4(e) Ethelenediamine**

### **1.5 Scope of the work**

The metal complexes with ligands have been studied because of its potential antifungal, antibacterial, anticancer and industrial applications. The lone pairs of electrons from hetero atoms forming bonds with metal ion and resulting in the formation of ring structure which is the most probable structure of many biological compounds.

Ruthenium complexes are also special interest in photophysical, photochemical and electrochemical studies including photoluminescence and these complexes also exhibit antimicrobial activity against drug resistant pathogenic micro organism which cause malaria and chagas disease.

By competing to find good antimicrobial agents, we studied the ruthenium complexes with different co-ligands such as 2,2 bipyridine,1,10 phenanthroline,dimethyl glyoxime,diphenyl glyoxime and ethylenediamine has been found to be increase the antimicrobial activities.

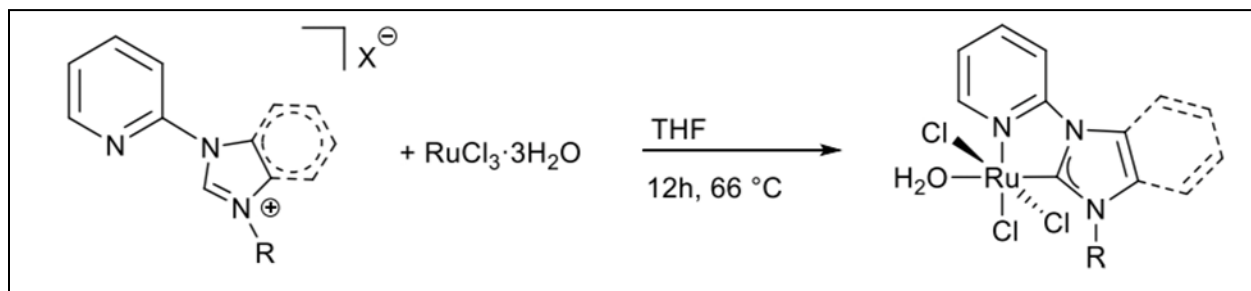
# REVIEW OF LITERATURE

## 2. REVIEW OF LITERATURE

### 2.1 Ruthenium complexes review

[33] **Konstantinos Ypsilantis et.al (2023)** have reported Ruthenium compounds with the typical formulas  $[\text{Ru}(\text{L}_1)(\text{L}_2)](\text{PF}_6)_2$  are mononuclear heteroleptic, were synthesized and characterized by means of NMR spectroscopic techniques, elemental analysis, and high-resolution mass spectrometry. Moreover, the complexes photophysical properties were investigated. Terpyridines have been shown to function as tridentate chelating ligands, generating incredibly stable metal complexes. Because of these complexes special abilities as photoluminescence chemicals, DNA binders, sensors, tumour inhibitors, and photosensitizers in PDT, researchers are interested in them.

[34] **NidaShahid et.al (2023)** have synthesized Ru(III)-NHC complexes,  $[\text{RuIII}(\text{PyNHCR})(\text{Cl})_3(\text{H}_2\text{O})]$  have been created, starting from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and travelling in a base-free manner. The Lewis acidic Ru(III) centre generates carbene through an electrophilic C-H activation with halide assistance. The rare paramagnetic Ru(III)-NHC complexes are structurally easy-to-make and moisture- and air-stable. Furthermore, it was demonstrated that these bench top stable Ru(III)-NHC complexes make excellent metal precursors for the synthesis of brand-new  $[\text{RuII}(\text{PyNHCR})(\text{Cl})_2(\text{PPh}_3)_2]$  and  $[\text{RuII}(\text{PyNHCR})(\text{CNCMe})]\text{PF}_6$  complexes. Using spectroscopic techniques, all the complexes have been described, and single-crystal X-ray diffraction has been used to identify their structures. The investigation of novel properties and potential applications is made simple by this work's easy access to new Ru-NHC complexes.



**Figure 2.1(a) synthesis of Ru –Py-NHC**

[35] **Han et.al (2023)** have synthesized four Ru(II)-terpyridine complexes, C1–C4, that were sumanene-ligated. Upon excitation at the ligand-centered band, all of the complexes displayed more emission ability than typical terpyridyl phenyl complexes. Particularly, the ones

with phenylene components displayed the dual emission associated with the TICT, which was brought on by a rapid intramolecular rotation due to the low rotation barrier of sumanene and the following terpyridine in the excited state. The complexes at the sumanene cores susceptibility to  $\text{Li}^+$  trapping was also demonstrated by the cation recognition studies. Our research will help to clarify the bowl-shaped effect of curved-based emissive materials. These will also increase the range of applications for sumanene-based sensing materials.

[36] **Marta Chrzanowska et.al (2023)** have reported at how a variety of ruthenium(II) complexes with the general formula  $[\text{RuII}(\text{terpy})(\text{N-N})\text{Cl}]\text{Cl}$ , where terpy is 2,2':6',2''-terpyridine and N-N is a bidentate ligand, behaved when substituted in aqueous solutions. We have demonstrated that, due to various electronic effects supplied by the bidentate spectator chelates, the most and least reactive complexes of the series are  $[\text{RuII}(\text{trpy})(\text{en})\text{Cl}]\text{Cl}$  (en = ethylenediamine) and  $[\text{RuII}(\text{trpy})(\text{phen})\text{Cl}]\text{Cl}$  (phen = 1, 10-phenanthroline), respectively. Model systems can be used to track heterogeneous multiphase ligand substitution processes at the solid-liquid interface using characteristics of polypyridyl Ru(II) complexes behaviour in aqueous solutions. Ru(II)-aqua derivatives of the initial chlorido complexes were used to create colloidal coordination compounds in the submicron range, which were then stabilised by a surfactant shell layer.

[37] **S.Behera (2022)** have reported For the past few decades, antibiotic, antibacterial, and antifungal resistance in pathogenic microbes has been growing, and it has recently become a widespread threat to public health. To effectively treat antibiotic-resistant epidemics, alternative nontoxic powerful antibiotic medicines are thus required. Two terpyridine ligands, 4-(4-N,N-dimethylaminophenyl)-2,2':6',2''-terpyridine (L1) and 4-(4-tolyl)-2,2':6',2''-terpyridine (L2), have been designed, prepared, and their structures have been confirmed by spectral studies in an effort to combat the challenges posed by the co-occurrence of multidrug resistance. After that, gram positive and negative bacteria as well as fungal strains were tested using an antimicrobial assay. At Minimum inhibitory concentration values of 6.25 and 3.125 mg/ml, respectively, both compounds L1 and L2 demonstrated impressive inhibitory activity against the microorganisms *Escherichia coli* and *Staphylococcus aureus*. In addition, bacterial DNA was used in in silico molecular docking research.

[38] **Nandisiwe Ghandi Sibongile Mateyise et.al (2022)** reported showed a series of substituted terpyridine ligands, demonstrating that reduction generally occurs below 2V relative

the redox potential of ferrocene. Numerous substituted oligo (aza)pyridine ligands, including terpyridine, bipyridine, and phenanthroline, have theoretically calculated energies and reduction potentials that are related to experimentally measured reduction potentials. These are calculated using density functional theory (DFT). Numerous chemistry-related fields, including supramolecular chemistry, molecular electronics, homogeneous and redox catalysis, fluorescence, photochemistry, biomedical applications, light-emitting devices, nonlinear optical (NLO) materials, and photosensitizers in dye-sensitized solar cells, use these oligo(aza)pyridine ligands and their metal complexes.

[39] **Sheida Rajabi et.al (2022)** have synthesized Two mononuclear ruthenium(II) complexes based on di anionic ligands and with axial pyridines. These complexes are positively charged, however their neutral N-donor ligands, which typically results in greater redox potentials and frequently encourages the harmful leaching of immobilised catalysts into an aqueous solution. UV-vis spectro electrochemistry (SEC) experiments were conducted using a quartz cell with Pt mesh as a working electrode, Pt wire as a counter electrode in a mixed solution of aqueous triflic acid

[40] **Antoine Bohn et.al (2022)** have synthesized a pyrazole-based ligand substituted with terpyridine groups at the 3 and 5 positions. This complex electro catalytically converts carbon dioxide (CO<sub>2</sub>) to carbon monoxide (CO) in the presence of Bronsted acids in DMF. Studies conducted in an inert atmosphere using chemical, electrochemical, and UV-vis spectro-electrochemical methods reveal paired reduction processes of complex . An electro reduced CO-containing di cobalt complex is consistent with infrared spectro-electrochemical experiments conducted in CO<sub>2</sub> and CO atmospheres.

[41] **According to Yuanwei Liang et.al (2022)**, a [Ru(tpy-CM)<sub>2</sub>]Cl<sub>2</sub> complex can be produced by chelating RuCl<sub>3</sub> with a relatively small-sized aryl nitrogen mustard-conjugated terpyridine in just two stages. Against a variety of tumour cells, this compound has strong anti proliferative action. Further research unequivocally demonstrates that the compound inhibits human renal clear cell carcinoma cells by triggering G1 phase cell cycle arrest and apoptosis. The research presented here offers a model for the synthesis and treatment of metal complexes containing nitrogen mustard.

[42] **Miaomiao Wa and others (2022)** have reported One of the most helpful technologies for the in situ, real-time detection and imaging of tiny biomolecules and ions is a

luminescence chemosensor. In recent years, there has been an increase in interest in the development of ruthenium (II) complex-based chemosensors due to the distinct photo-physical/chemical properties of these complexes. As a result, numerous Ru(II) complexes have been designed and synthesized for the detection of ions and small biomolecules in biological and environmental samples. The development of Ru(II) complex-based chemosensors for the detection of ions and small biomolecules, such as anions, metal ions, reactive biomolecules, and amino acids, is summarised in this work. A particular emphasis is placed on binding/reaction-based chemosensors for the investigation of intracellular analytes evolution through luminescence analysis and imaging.

[43] **Jiang et.al (2022)** have synthesized Ruthenium(II) polypyridyl complexes have been used for a variety of purposes because of their optical and electrochemical characteristics. The construction of new Ru(II) complexes as light-up probes for certain areas of DNA has been thoroughly investigated since the discovery of the  $[\text{Ru}(\text{bpy})_2\text{dppz}]_2$  light-switch +s ON effect when interacting with DNA. G-quadruplexes (G4s) are particularly interesting among them. Many biological events may be linked to these structures, which are created by guanine-rich regions of DNA and RNA. It has been difficult to find them and comprehend their effects on biological circuits, nevertheless. Using photo probes that can mark these G4s either irreversibly or reversibly is one of the more elegant ways to approach this problem

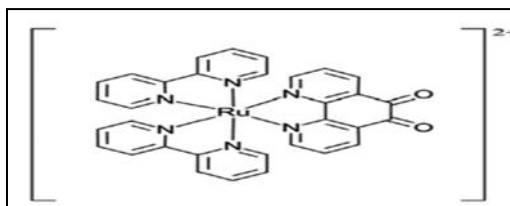
[44] **Oscar Filevich and Roberto Etchenique (2022)** have synthesized Polypyridine-containing ruthenium coordination complexes have been researched for a long time. It was learned a great deal about their photo physics and photochemistry while working on energy harvesting systems. A adaptable scaffold that can release a molecule upon light absorption was recently made using this understanding for a somewhat different use. When developing new applications and as instruments in biological research, this scaffold's structural variety, photochemical tunability, and clean photochemistry are huge advantages. In this chapter, we discuss the initial developments in the realm of Ru-based phototriggers as well as the theory guiding their creation.

[45] **Ben J. Pages et.al (2022)** have reported Using biophysical, spectroscopic, and genomic techniques, more and more DNA structures are being uncovered. The unique contributions that transition metals make to the overall structure of metal complexes depend on the different coordination numbers, geometries, physiologically relevant redox potentials, as well

as kinetic and thermodynamic properties. As a result, the diversity of transition metal complexes is also increasing. The wide variety of ligands that can be used must also be taken into account. A wide range of biological interactions are not surprising given this diversity. In particular, interactions with negatively-charged DNA can be brought about by covalent/coordinate or subtle non-coordinate interactions such as electrostatic attraction, groove binding, and intercalation, as well as mixtures of all of these modes.

[46] **Max Mennicken et.al (2021)** have reported functional units used in nanoelectronic and molecular electronic devices and their addressability, which is frequently a matter of suitable interfaces and device design, are crucial to the functioning of these devices. In this article, we contrast two viable ideas for creating solid-state electrical devices that share a functional unit. Optically addressable Ru-terpyridine complexes were integrated into supramolecular wires or used as gold nanoparticle ligands and in contact with nanoelectrodes. The resulting tiny area nano devices underwent extensive electrical characterization in relation to temperature and light exposure. Different device designs and their associated transport mechanisms, such as sequential tunnelling in nanoparticle-based devices or thermally induced hopping conduction in the case of devices based on Ru-terpyridine wires, may result in differences in the device conductance.

[47] **Avijita jain et.al (2021)** have reported One of the most pressing issues in public health today is antibiotic resistance. Antibiotic photodynamic therapy (aPDT) is an effective treatment for the rising problem of antibiotic resistance. The aPDT produces reactive oxygen species by combining a photosensitizer with light in order to cause bacterial inactivation. The significance of ruthenium polypyridyl complexes stems from the fact that they have special photo physical characteristics that enable them to create reactive oxygen species following photo irradiation, which causes cytotoxicity. By damaging the DNA and cytoplasmic membrane, these antimicrobial chemicals kill bacteria. This article provides a thorough analysis of the photoactive antimicrobial characteristics of photoactive ruthenium nanoparticles, photoactive kinetically inert and labile ruthenium complexes, and nanoparticles linked photoactive ruthenium complexes.



**Figure 2.1(b) structure of [Ru(bpy)<sub>2</sub>phendione]**

[48] According to **Houria Asri et.al from 2020**, active and recyclable supported catalysts that use molecular Ru-terpyridine complexes to encourage the transfer hydrogenation of nitroarenes in 2-propanol were made and characterized. The system is based on the development of unique pyrene-tagged terpyridine ligands, either monomeric "1tpy" or multivalent "5tpy" (one pyrene tag for five terpyridines), that can interact with the graphene surface of commercially available cobalt magnetic nanoparticles (MNPs) through  $\pi$ -stacking interactions. For the first time in an organic medium called 2-propanol, fluorescence spectroscopy was used to determine whether there were non-covalent contacts between the pyrene-tagged terpyridines and the MNPs surface at 20 °C.

[49] **Mira T. Rupp et.al (2020)** have prepared a number of peripheral pyridine substituents in different places on nonsymmetric 2,6-di(pyridin-2-yl)pyrimidine ligands, together with the associated ruthenium(II) complexes. All four compounds exhibit longer excited-state lifetimes and higher luminous quantum yields than similar terpyridine complexes. Also, compared to the previously described bis(terpyridine) complexes utilized as Photosensitizers, all compounds are simpler to decrease. According to an evaluation of the driving forces, electron transfer to the catalyst might be more difficult due to a drop in driving force, whereas reductive quenching by the Sacrificial electron donor should be more successful. These complexes had significantly higher activity in hydrogen evolution studies due to efficient reductive quenching than the previously reported ruthenium(II) bis(terpyridine) complexes.

[50] **Ehsan Ullah Mughal et.al (2020)** developed By using the Krohnke process, a variety of terpyridine(tpy)-based ligands. They were complexed with Co(II), Fe(II), and Zn(II) ions to examine their binding behaviour, which produced unusual coordination compounds with the formulas  $[\text{Zn}(\text{tpy})_2]\text{PF}_6$ ,  $[\text{Co}(\text{tpy})_2](\text{PF}_6)_2$ , and  $[\text{Fe}(\text{tpy})_2](\text{PF}_6)_2$  with fascinating spectroscopic features. Because the functional groups in each compound have diverse properties, each compound exhibited amazing photo luminescent characteristics and different maximum emission peaks. Furthermore, docking analyses were performed to look into the binding affinity of terpyridine-based ligands and associated proteins. This allowed for the evaluation of the anti-microbial potential of ligands and complexes

[51] **Maja Savic et.al (2020)** have synthesized  $[\text{Ru}(\text{Cl-tpy})(\text{en})\text{Cl}][\text{Cl}]$  ruthenium(II) terpyridine complexes. Ru-1, (en = ethylenediamine, tpy = terpyridine), and  $[\text{Ru}(\text{Cl-tpy})(\text{dach})\text{Cl}][\text{Cl}]$  (dach = 1,2-diaminocyclohexane, Ru-2) were evaluated in vitro, in vivo, and in comparison to oxaliplatin, the most widely employed chemotherapeutic drug against colorectal cancer. Due to their low toxicity and effectiveness against platinum drug-resistant tumours, ruthenium compounds have garnered significant interest as potential anticancer agents over the past 20 years. This interest is reflected in encouraging results from various preclinical to early clinical studies. Furthermore, the high expectations placed on ruthenium compounds are justified by the special characteristics of ruthenium-based drugs, such as slow ligand exchange rates, a variety of oxidation states (Ru(II), Ru(III), and Ru(IV)), and favourable water solubility compared to those of conventional platinum drugs.

[52] **Rafael A. Adrian et.al (2020)** have reported that the presence of offset interactions between the terpyridine rings in various layers is the primary characteristic of the title complex packing. This complex is the first instance of a zinc(II) 4-chloroterpyridine complex with coordinating nitrate ions that is known to exist. Since they can produce supramolecular frameworks and exhibit photosensitive features, metal-organic complexes of 4-chloro-2,2':6,2'-terpyridine have been studied. Here, we disclose the synthesis and structure of the mentioned zinc(II) complex as part of our research on the coordination chemistry of metal ions with bipyridine and terpyridine ligands

[53] **Max Mennicken et.al (2020)** reported the strong conductivity and inherent switching capability of transition metal complexes, which involves a metal-to-ligand charge transfer, make them electro functional molecules. Here, a method is given for electrically maintaining the functionality of a few to one redox-active Ru-terpyridine complex while reliably contacting them in compatible nano device. The hysteretic current versus voltage curves in two well-separated conductance ranges are displayed by the Ru-complex gold nanoparticle devices in both symmetric and asymmetric forms. Using theoretical approximations built on the single-channel Landauer model, the charge transport via the created double-barrier tunnel junction is carefully examined, and its sensitivity to the molecule/metal contact is made clear. It can be confirmed that decoherent hopping transport only plays a minimal role, with tunnelling transport through the HOMO serving as the primary transport mechanism.

[54] **Johannes Karges et.al (2019)** have reported New classes of chemicals must be developed immediately due to acquired resistance or limits of the existing approved cancer treatments. The usage of Ru(II) polypyridyl complexes is among the topics receiving more and more attention. The majority of investigations in the literature focused on complexes based on the coordination of N-donating bidentate ligands to the ruthenium core, while studies on 2,2':6',2''-terpyridine (terpy) coordinating ligands are rather rare. However numerous investigations have revealed that  $[\text{Ru}(\text{terpy})_2]^{2+}$  derivatives can bind to DNA through a variety of binding mechanisms, making these substances potentially acceptable as chemotherapeutic agents. These substances may be used as photosensitizers (PSs) for photodynamic therapy as it was demonstrated that light irradiation of the compounds enabled DNA cleavage .

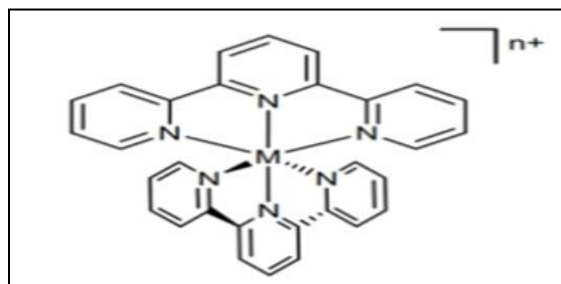
[55] **Mira Rupp et.al (2019)** have synthesized a new terpyridine ligand, 4'-(4-bromophenyl)-4,4''':4'',4''''-dipyridinyl- 2,2':6',2''-terpyridine (Bipytpy) and used it to prepare the heteroleptic complex  $[\text{Ru}(\text{Tolytpy})(\text{Bipytpy})](\text{PF}_6)_2$  (1; Tolytpy = 4'- Istolyl-2,2':6',2''-terpyridine). Comparing the quantum yield and excited-state lifetime of Complex to those of  $[\text{Ru}(\text{Tolytpy})_2](\text{PF}_6)_2$  (3  $10^{-5}$  and 0.74 ns, respectively), Complex shows improved photo physical attributes (7.4  $10^{-4}$  and 3.8 ns, respectively). We used the complex for hydrogen evolution that was triggered by visible light because of its improved photo physical properties and the potential for PS-catalyst contact through the peripheral pyridines.

[56] **John Kargeseth, et al (2019)** reported a there is a pressing need for the creation of new classes of chemicals due to acquired resistance or limits of the cancer treatments that are already licenced. Among other things, Ru(II) polypyridyl complexes are receiving more and more attention. Studies on 2,2':6', 2''-terpyridine (trpy) coordinating ligands are comparatively rare, with the majority of investigations in the literature being made on complexes based on the coordination of N-donating bidentate ligands to the ruthenium core. The ability of  $[\text{Ru}(\text{terpy})_2]^{2+}$  derivatives to bind to DNA through a variety of binding mechanisms, however, has been demonstrated in numerous investigations, making these substances potentially useful as chemotherapeutic agents. Also, it was demonstrated that these substances can be used as photosensitizers for photodynamic treatment after being exposed to light .

[57] In their article from **2019**, **Ana Rilak Simovic et.al** outlined the work over the previous few years on the production of Ru complexes with potential anticancer activity. We designed, synthesized, and extensively studied a number of Ru(II) complexes in order to

establish the structure-activity relationship for Ru(II) compounds. These complexes were divided into three major categories: Ru(II) half-sandwich coordination complexes containing neutral face-capping macrocyclic ligands, such as 1,4,7-trithiacyclononane and 1,4,7-triazacyclononane Ru(II)-arene complexes; and iii) Ru(II)-polypyridyl complexes. Our most recent research focused on the chemistry, production, and reactivity of the heteronuclear ruthenium(II) ferrocene complexes

[58] Using a variety of bidentate ligands (1,10-phenanthroline-5,6-dione, 6,6'-dimethylbipyridyl, 1,10-phenanthroline-pyrazine), **Rose Kumari and M.N. Sivakumar (2018)** have synthesized a chloride ligand, a binuclear ruthenium complex with 1,10-phenanthrene fused planar ligands (L1), and (L2) and 4'-thiophene-2-yl fused 2,2':6'2''-terpyridine. Using a modified literature technique, ligands have been synthesized with a good yield. A total of eight complexes were drawn from an aqueous solution and precipitated as hexafluorophosphate salt. These complexes have total solubility in weakly solubly in water and acetonitrile.



**Figure 2.1(c) 2,2':6'2''-Terpyridine[M(tpy)<sub>2</sub>]**

[59] **Tamilarasu Ezhilarasu and Sengottuvelan Balasubramanian (2018)** have synthesized Ru complexes was carried out, and their characteristics were investigated using UV/Vis, Fluorescence, FTIR, <sup>1</sup>H & <sup>13</sup>CNMR, ESI-mass spectral investigations, and electrochemical tests. By using single crystal X-ray diffraction, the crystal structure of the HOTpy ligand was identified. A quasi-reversible oxidation peak corresponding to the RuII/RuIII process may be seen in the cyclic voltammograms of Ru(II) complexes. When the scan rate is increased, the peak currents also rise. When four human diseases and the fungus *Candida albicans* were used as test subjects for the Ru(II) complexes, they demonstrated good antibacterial and antifungal activity. UV/Vis spectroscopy was used to analyse the binding of Ru(II) complexes to the DNA of the calf thymus. Ruthenium(II) complexes can cleave DNA

more effectively than controls, according to research on their cleavage activity using gel electrophoresis.

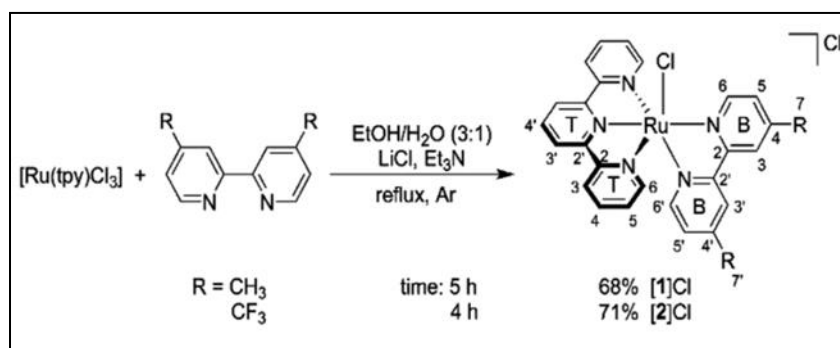
[60] According to **Milan M. Milutinovic et.al (2018)**, the synthesis and reactivity of a novel ruthenium(II) terpyridine complex with a bidentate enantiopure camphor-based diamine ligand is disclosed. Guanosine-50-monophosphate, used as a model for DNA bases, was found to have a high affinity for the Ru(II) complex in reactivity studies. Moreover, it was discovered that DNA binding ability and the Ru(II) complex interact. This points to the highly promising anticancer properties of the recently synthesised ruthenium compound. NMR spectroscopy, Mass spectrometry, and UV-Vis spectrophotometry were used to completely characterize the resulting novel ruthenium(II) terpyridine complex . UV-Vis spectroscopy was used to examine the novel complex's chemical behaviour in aqueous solution and its binding characteristics to biomolecules serving as model DNA bases.

[61] **Ganesh Koya et.al (2018)** have reported By adhering MC113-MC117 ruthenium complexes on TiO<sub>2</sub>-Pt composites, five new photo catalysts have been created in an effort to increase the photo responsiveness up to the visible range. We tested these ruthenium complexes for photo catalytic activity because of their ability to capture highlights. The fabricated photo catalysts' absorption curves went all the way to 750 nm. Using powder X-ray crystallography and Scanning electron microscope morphological investigations of photo catalysts have been conducted. The photo catalytic activity of MC113PC, which was the highest of all photo catalysts with 9474 TONs, was quite high. The catalysts efficiency at introducing electrons and their fluorescence quenching investigations indicated how well they capture light. In order to get the best photo catalytic performance, the photo catalytic activity of photo catalysts was carefully tested at various pHs and using various sacrificial electron donors.

[62] **Sara S. M. Fernandes and others (2017)** havereported To examine the changes brought about in their optical and electrical properties by coupling various (hetero)aromatic electron donor moieties at 4'-position, push-pull terpyridine derivatives 3 were created and described. The location of the terpyridine moiety that is electron-deficient. The complete donor-acceptor systems 3a-g have been created .By combining the precursor aldehydes 1, with 2-acetylpyridine 2, the Krohnke condensation produced fair to good yields. Hyper-A fundamental wavelength of 1064 nm was used to study Rayleigh scattering in dioxane solutions,their optical features of second order nonlinearity. functionalized with the 9-ethyl-9H-terpyridine derivative .

[63] **Raja Lakshmanan et al (2017)** have prepared Ruthenium (III) complexes with the formulas  $[\text{Ru}(4\text{-Mephtpy})_2]\text{Cl}_3(1)$ ,  $[\text{Ru}(3,4,5\text{-tmphtpy})_2]\text{Cl}_3(2)$ , and  $[\text{Ru}(4\text{-thtpy})_2]\text{Cl}_3(3)$ , (where  $\text{L}=\text{terpy}=2,2':6'2''$  terpyridine ligands), Spectroscopic, electrochemical, and elemental investigations were used to characterize the complexes. The geometric optimization and electronic charge transfer of these complexes are described by the density functional theory (DFT). The photo physical behaviour is dependent on the Metal to ligand transition process because of the heavy metal action of Ru (III) ions. The three  $\text{Ru}(\text{L}1\text{-L}3)$  complexes are all falling orange emission

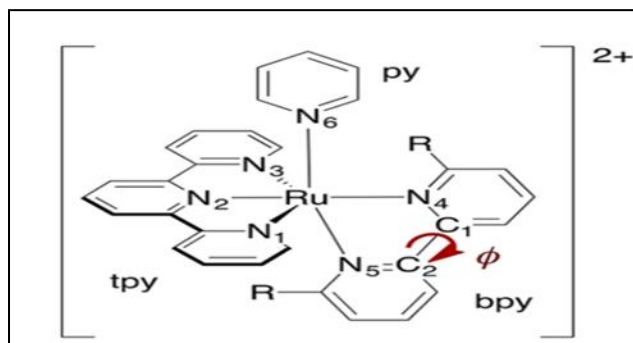
[64] **Hyo Jin Jang et al. (2017)** have synthesized  $\text{Ru}(\text{tpy})(\text{R}_2\text{bpy})(\text{L})](\text{X})_n$  complexes and their characterisation is presented. In order to study the effects of electron-donating and electron-withdrawing ligands on the frontier orbital energetics and the photoreactivity of these ruthenium polypyridyl complexes for five phototypical monodentate ligands, bidentate ligands are used. All of the complexes in acetone's  $^1\text{H}$  NMR spectroscopy showed a pattern in the alpha proton's chemical changes on the bipyridine ligand.



**Figure 2.1(d) synthesis and atom numbering for  $[\text{Ru}(\text{tpy})(\text{R}_2\text{bpy})(\text{Cl})](\text{Cl})$**

[65] **Marta Chrzanowska et.al (2017)** have reported The crystal structures of  $[\text{RuII}(\text{terpy})(\text{bipy})\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}$  and  $[\text{RuII}(\text{terpy})(\text{en})\text{Cl}]\text{Cl} \cdot 3\text{H}_2\text{O}$ , where  $\text{terpy} = 2,2':6',2''$ -terpyridine,  $\text{bipy} = 2,2'$ -bipyridine and  $\text{en} = \text{ethylenediamine}$ , were determined and compared to the structure of the complexes in solution obtained by multi-nuclear NMR spectroscopy in DMSO as a solvent. As was discovered in the current study, hydrogen bonding networks are critical in proton-coupled electron-transfer reactions and can have an impact on a species lability. An ongoing investigation into a systematic variation is being conducted in our laboratories.

[66] **Khalin Nisbet et.al(2017)** have reported photo activatable Ru(II)-centered are typically made up of tridentate or bidentate ligands as ancillary compounds, such as 2,2':6',2''-terpyridine (tpy), 2,2'-bipyridine (bpy), and 1,10-phenanthroline (phen), and one or more monodentate ligands as the active species for release. As an alternative, the photo dissociation can be utilized to liberate reactive species and molecules while the ruthenium fragment left over is nonpoisonous, which is a highly desirable quality for chemical instrument.



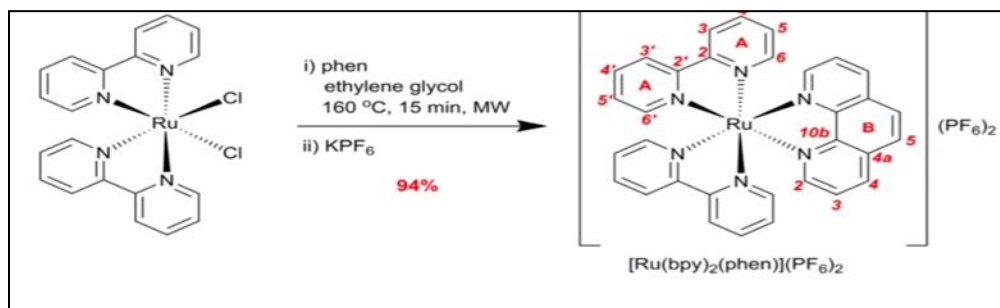
**Figure 2.1(e) structure of  $[\text{Ru}(\text{Tpy})(\text{Bpy})(\text{py})]^{2+}$**

[67] **A. David et.al (2016)** have synthesized complexes of the form  $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-R-py})]$ . In order to study how the pyridine substitution affected the ground and excited state characteristics, were synthesized. Researchers working to improve ligand exchange quantum yields for applications in drug delivery and caged active molecules, as well as those who must stop the ligand dissociation pathway, such as for the stable complexes required in dye-sensitized solar cells and in sensors, may find these findings interesting. Theoretical simulations demonstrate that the electron-donating groups raise and the electron-withdrawing groups decrease the energy difference between the ligand field state (LF) and MLCT, respectively, leading to different excited state features. These results show how a succession of compounds can be tuned synthetically, allowing for different photochemistry.

[68] **Davide Saccone et.al (2016)** have prepared Complexes based on terpyridine and quaterpyridine enable broad light harvesting of the solar spectrum. In comparison to bipyridines, terpyridines enable the construction of metal-complexes with reduced band gaps in the metal-to-ligand transition (MLCT), leading in improved absorption at lower energy wavelengths and an improvement in the capacity to absorb solar light. To create cyclo metalated or heteroleptic compounds, quaterpyridines have been employed in place of terpyridines, other metals have been used in place of ruthenium, and various pinchers have been used in place of thiocyanates. The

review summarises design principles, common synthetic pathways, optical and photovoltaic characteristics of terpyridine and quaterpyridine ligands applied to photovoltaic, with a particular emphasis on n-type DSCs.

[69] **Ena T. Luis et.al (2016)** have reported was optimised for the very efficient synthesis of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{bpy})_2(\text{phen})](\text{PF}_6)_2$ , and  $[\text{Ru}(\text{phen})_2(\text{bpy})](\text{PF}_6)_2$ . The entire  $^1\text{H}$  NMR assignments for  $[\text{Ru}(\text{bpy})_2(\text{phen})]^{2+}$  and  $[\text{Ru}(\text{phen})_2(\text{bpy})]^{2+}$  were found using 1D and 2D NMR techniques, and they unmistakably validate the spatial positioning of the ligands with regard to one another in the two species. The straightforward synthesis of larger compounds based on these tiny complexes will be made possible by proven techniques for their creation, and these assignments serve as a useful manual for larger assemblies more complex NMR spectra.



**Figure 2.1(f) synthesis of  $[\text{Ru}(\text{bpy})_2(\text{phen})](\text{PF}_6)_2$**

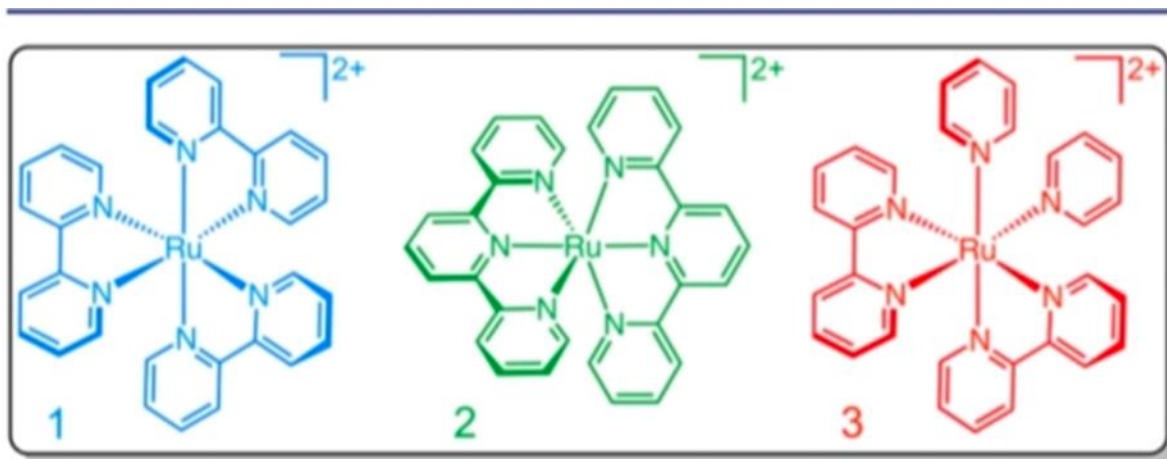
[70] In **2016, Dharmasivam Mahendirana et.al** have synthesizing and characterising homoleptic bis(terpyridine)copper(II) complexes of the type. The single crystal XRD analysis validated the molecular structure of the complex, and the geometry of the complexes is best described as deformed octahedral. The structural parameters determined by the crystallographic and DFT analyses match well with one another. The tiny HOMO-LUMO energy gap contributes to the complexes' bioefficacy

[71] In **2016, Binitendra Naath Mongal et.al** have synthesized new ruthenium photosensitizer complexes and studied them using IR, UV-Vis, NMR, and mass spectroscopy. At 511 nm, the molecule exhibits an Metal to ligand charge transfer band of moderate intensity. The molecule also exhibits multiple high energy Metal to ligand charge transfer bands, which have been nicely represented by the calculation, along with the intra ligand transitions in the UV region. The Density function theory-optimized structure reveals deformed octahedral geometry

around the central ruthenium atom, with the terpyridine moiety's phenyl ring torsioning at a 34.09 degree angle with the central pyridine ring. By examining the Metal to ligand charge transfer band position's fluctuation with pH and using spectrophotometry, the pKa of the -COOH functionalities was reported to be 3.98. measurements of the dye's photovoltaic efficiency in a standard DSSC setup.

[72] Three new ruthenium(II) compounds are described by **Binitendra N. Mongal et.al in (2016)**. Common spectroscopy methods, such as FTIR, UV-Vis, mass, and NMR, were used to characterise all the complexes. To ascertain the pka of carboxyl and aqua moiety coordinated to ruthenium centre, a thorough pH-based spectroscopic and electrochemical investigation of the complexes was conducted. Complex 2's ( $pK_{\text{COOH}}=3.13$ ) and Complex 3's ( $pK_{\text{COOH}}=3.98$ ) COOH groups are both somewhat more acidic. Nonetheless, as would be predicted, the  $pK_{\text{H}_2\text{O}}$  values for complexes 1 (12.33) and 3 (12.27) are similar. The aqua complex contains a Pourbaix diagram, according to reports. To explain the diverse experimental results, a comprehensive Time dependent density function theory (TD-DFT) study of all three synthesized complexes and in-situ produced hydro complex in the aqueous medium at increasing pH has been performed.

[73] **Claudio Garino et.al (2016)** have reported DFT and TD-DFT are two computer techniques that are frequently used in research to characterise, among other things, the optical characteristics of transition metal complexes. Undergraduate inorganic/physical chemistry courses cover these techniques, but frequently just from a theoretical standpoint. Students are led step-by-step through the computational investigation of the photophysics and photochemistry of polypyridyl Ru(II)  $d^6$ -metal complexes in the calculation exercise herein presented. They are specifically asked to look at and interpret a set of experimental data that describes the absorption, emission, and photochemical behaviour of three structurally related ruthenium complexes, namely  $[\text{Ru}(\text{bpy})_3]^{2+}$  (1),  $[\text{Ru}(\text{tpy})_2]^{2+}$  (2), and  $[\text{Ru}(\text{bpy})_2(\text{py})_2]$  using DFT and TD-DFT calculations . Due to their exhibits, these complexes are especially ideal for educational purposes.



**Figure 2.1(g) structure of (1)  $[\text{Ru}(\text{bpy})_3]^{2+}$ , (2)  $[\text{Ru}(\text{tpy})_2]^{2+}$ , (3)  $[\text{Ru}(\text{bpy})_2(\text{py})]^{2+}$**

[74] **Hasti Iranmanesh et al. (2016)** have synthesized a series of enantiopure ruthenium (II) polypyridyl complexes with pendant pyridyl groups ideal for creating more substantial self-assembled structures. NMR spectroscopy, cyclic voltammetry, photophysical techniques, as well as single-crystal X-ray crystallography, are used to thoroughly characterize the complexes both in solution and in the solid state. When the pendant pyridyl groups are protonated, the complexes lengthily excited-state lifetimes, which are luminous, are quenched. A mixed-metal one-dimensional coordination polymer that was identified by single-crystal X-ray crystallography is produced by reaction with cadmium (II) ions.

[75] **Ganesh Koyada and other (2015)** have reported a sensitizers for dye-sensitive solar cells, three novel ruthenium complexes based on terpyridine, designated MC124, MC125, and MC127, were created. Using experimental methods and then theoretical calculations, the MC dyes were characterized. Our decision to use these dyes in functional devices was motivated by their promising optical features, which included higher molar extinction coefficients than the prototype N749 dye and acceptable energy level location. The MC dyes have demonstrated just average performance when combined with liquid redox electrolyte; the highest Photon to collected electron efficiency was achieved with MC124 used as a co-adsorbent, at 2.3%.

[76] **Vadde Ramu et.al (2015)** have synthesized a novel binuclear RuII-PtII combination,  $\text{Ru}(\text{tpy})(\text{tpypma})\text{Pt}(\text{Cl})(\text{DMSO})$ , is synthesised and characterised in this article. 2,2':6',2''-terpyridine and 4,([2,2':6',2''-terpyridine]-terpyridine-4'-yl)-N-(pyridin-2-ylmethyl)aniline), VR54, which links the two metal centres using an extended terpyridine tpy

pma ligand. VR54 does not irreversibly bind guanosine and binds DNA in vitro by non-intercalative reversible processes ( $K_b = 1.3 \times 10^5 \text{ M}^{-1}$ ). According to cell research, VR54 inhibits the growth of cisplatin - resistant A2780 ovarian cancer cells without causing any cross-resistance. We discover that both metal centres are necessary for this anti-proliferative effect by creating mononuclear RuII and PtII structural derivatives.

[77] **F.Richard Keene and Nicholas C. Fletcher (2014)** have reported that the carbonyl ligand is swapped out for a suitable monodentate molecule, complexes of the type) can serve as flexible precursors for the synthesis of complexes with vastly different redox and photophysical properties. The decarbonylation process appears to be rather universal and moves forward while maintaining the metal center's stereochemistry. In comparison to the dicarbonyl species, the monocarbonyl compounds  $[\text{Ru}(\text{terpy})(\text{pp})(\text{CO})][\text{PF}_6]_2$  have much simpler  $^1\text{H}$  NMR spectra.

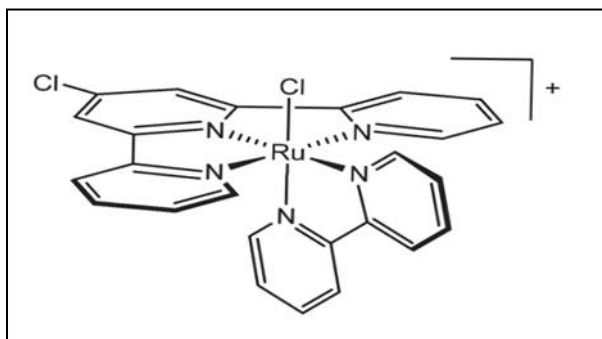
[78] **Song et.al (2014)** have reported a variety of metal ions were used to prepare terpyridine-functionalized graphene oxides for self-assembly into 3D architectures (e.g., Fe, Ru). The final electrode materials demonstrated dramatically enhanced electro activities for effective energy storage and conversion. They shown potential for use in super capacitance, photocurrent production, and the oxygen reduction reaction.

[79] **Nicholas C. Thomas an et.al (2014)** have prepared and showing that the  $\text{CF}_3\text{SO}_3$  groups are easily replaced by bidentate ligands indicating that is an useful reagent for the production of additional ruthenium complexes containing nitrogen donor ligands. The octahedral  $[\text{Ru}(\text{CO})_2(\text{bidentate})(\text{tpy})]^{2+}$  cationic complexes contain a novel bidentate terpyridyl ligand and are produced by the reaction of with 2,2':6',2''-terpyridyl (tpy), which has now been explored. A colourless acetone solution of (bidentate = bpy), when exposed to UV-visible radiation, changes colour and undergoes considerable changes in the  $\nu(\text{C}=\text{O})$  area of the solution IR spectrum. As the irradiation process continues, a new band at  $1995 \text{ cm}^{-1}$  emerges and the two bands at  $2040$  and  $2078 \text{ cm}^{-1}$  lose intensity.

[80] **Jessica D. Knoll et.al (2014)** have Synthesized Ru(II) complexes by significant applications in solar energy conversion, molecular electronics and switches, and photo chemotherapy (PCT). Due to their frequent use in these schemes, Ru(II) polypyridyl complexes exhibit relatively significant absorbance in the visible and ultraviolet spectrums, chemical stability in solution, long lifetimes in the excited state, and reactivity that is unavailable in the ground state. The photolysis of 13 in  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  is analyzed from a spectroscopic

perspective, and theoretical calculations and quantum yields of pyridine exchange are used to demonstrate how distortion brought on by sterically demanding bidentate ligands affects the quantum yields of pyridine exchange.

[81] **Dejan Lazic et.al (2014)** have synthesized ruthenium(II) terpyridine complexes, were chosen and a detailed study of the kinetic parameters of their reactivity towards L-histidine, using the UV-Vis and <sup>1</sup>H NMR techniques, was developed the results on in vitro anticancer activity confirmed that only compounds that hydrolyze the monodentate ligand at a reasonable rate show moderate activity, provided that the chelate ligand is a hydrogen bond donor. The capacity of the complexes to attach to Calf thymus DNA covalently through N7 of guanine residues and non-covalently by intercalation was demonstrated by UV-Vis spectroscopy experiments, DNA viscosity measurements, and competitive binding studies. By using the MTT assay, the cytotoxicities of the five ruthenium(II) polypyridyl complexes were evaluated against the tumour cell lines.



**Figure 2.1(h) structure of [Ru(1-cl-trpy)(Bpy)]<sup>+</sup>**

[82] **Chiyu Weib et.al (2014)** have reported on current advancements pertaining to transition metal-terpyridine complexes with a focus on their uses in catalysis and supramolecular structure building. Terpyridine derivatives can be easily produced, as well. The terpyridine ligand and its uses in coordination chemistry are the subject of this article, and we hope it can assist to provide some general viewpoints on them. This linear linker has been used in conjunction with other stiff organic frameworks to create a number of lovely supramolecular structures. Yet, there are still issues that need to be resolved, such as the overall synthesis yield being unsatisfactory and the terpyridine ligand's poor solubility.

[83] **Chih-Pei Lin et.al (2014)** have reported From 4-substituted picolines, a number of 4,4-disubstituted terpyridines with a 4-thioethanamine linker, as well as their regio isomers, have been synthesized. In order to create functionalized solid supports for the fragmentation of proteins, including antibodies, by mixed mode affinity chromatography, the substituted terpyridines were immobilised onto epoxy-activated Sepharose FF gel. The immobilised ligand's metal chelating abilities make the stationary phase suitable for use in immobilised metal-ion affinity chromatography (IMAC), as shown by the purification of appropriately tagged green fluorescent protein.

[84] **Sandip Bhowmik et.al (2014)** have reported In-depth research was done on the self-assembly behaviour of two straight forward amino-terpyridine ligands, L1 and L2, in divalent metal complexes. It was discovered that hydrogelation was significantly influenced by metal ions as well as by slight modifications to the ligand structure. Both ligand-complexes crystal packing revealed distinct variances that may have contributed to the morphological changes in the matching gel structures. It was interesting to observe how the metal ion controlled the size of these aggregated formations. Since terpyridine-based gelators have only recently been studied, this research could offer insightful information about the dynamics of such systems and aid in the development of new classes of metal ion responsive materials.

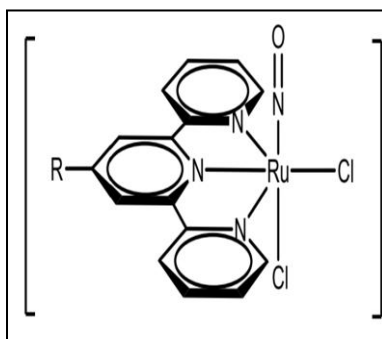
[85] According to **Christina D.M. Trang et.al (2014)**, we developed an entirely novel class of  $[M(\text{tpySSMe})_2](\text{PF}_6)_2$  ( $M = \text{Fe}, \text{Co}, \text{Zn}$ ) metal bis(terpyridine) complexes and studied their single- and multi-component SAMs on gold surfaces. In contrast to their thiol-functionalized analogues,  $[M(\text{tpySH})_2](\text{PF}_6)_2$  (MSH,  $M = \text{Fe}, \text{Co}$ ), which dissolve in 1 d, we discover that these complexes are air-stable in solution for  $>7$  d. CoSH has been reported before, however this is the first time we fully describe its synthesis and characterization. The ability of these complexes to produce SAMs with compositions similar to those of their assembly solutions, a need for flawless mixing at the molecular scale, is demonstrated by solution and surface voltammetry tests.

[86] **Yu Chen et.al (2013)** have synthesized ruthenium complexes as anticancer medications. These complexes appeared to exhibit anticancer efficacy against different cancer cells, according to in vitro cytotoxicity studies. These complexes caused apoptosis via the mitochondrial pathway, as seen by the loss of mitochondrial membrane potential and the release of cytochrome c, according to flow cytometry and signalling pathways analyses.400

spectrometer data of  $^1\text{H}$  NMR spectra were collected (400 MHz). About tetramethylsilane, all chemical changes are provided (TMS). The UV-visible spectra were captured using a Varian Cary 300 spectrophotometer.

[87] **Amlan K. Pal et.al (2013)** have Synthesized  $[\text{RuII}(\text{bpy})_2(\text{N-N})](\text{PF}_6)_2$  complexes, wherein N-N = pyridine/pyrimidine/pyrazine functionalized in various places with the electron-donating bicyclic hexahydropyrimidopyrimidine (hpp) unit, has been synthesized and characterized. Good to excellent yields (55–96%) were achieved in the synthesis of a group of bidentate ligands. Complexes were produced in modest to good yields (23–76%) in a combination of n-butanol and water, while the analogous complexes were produced in n-butanol. A number of methods, including X-ray crystallography, were used to completely characterise the ligand and complex structures. All of the complexes show a RuIII/II couple in cyclic voltammetric experiments, but it is about 500 mV less positive than the RuIII/II couple in  $\text{Ru}(\text{bpy})_3^{2+}$ .

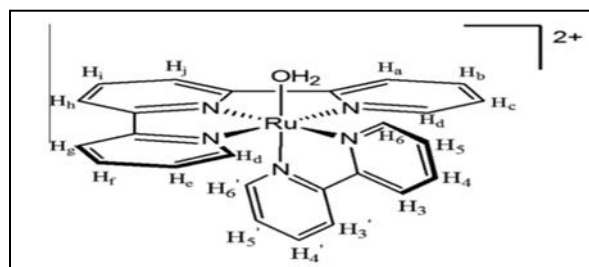
[88] According to **Pablo Labra-Vázquez et.al(2013)**, a variety of  $\text{cis}(\text{Cl},\text{Cl})\text{-}[\text{R-tpyRuCl}_2(\text{NO})](\text{PF}_6)$  and  $\text{trans}(\text{Cl},\text{Cl})\text{-}[\text{R-tpyRuCl}_2(\text{NO})]$  It is explained as  $(\text{PF}_6)$  (R = fluorenyl, phenyl, and thiophenyl; tpy = 2,2':6',2''-terpyridine). Notwithstanding the nature of the initial  $\text{cis}/\text{trans}(\text{Cl},\text{Cl})$  complexes, one chlorido ligand is replaced by a hydroxo ligand, and the final species appear as a single  $\text{trans}(\text{NO},\text{OH})$  isomer. The compounds' six X-ray crystal structures are illustrated. After Cl, OH substitution, the various  $\text{cis}/\text{trans}(\text{Cl},\text{Cl})$  complexes show an intense low-lying transition in the = 330–390 nm range that is slightly blue-shifted. In water, both of the  $\text{cis}/\text{trans}(\text{Cl},\text{Cl})$  isomers transform into a single  $\text{trans}(\text{NO},\text{OH})$  isomer in which one chlorido- and one hydroxo-ligand are swapped out, avoiding the laborious separation process.



**Figure 2.1(i) structure of  $\text{cis}(\text{Cl},\text{Cl})\text{-}[\text{R-tpyRuCl}_2(\text{NO})]$**

[89] **G. Ragazzon et.al (2013)** have reported To better comprehend and take advantage of their visual absorption, redox, and photochemical processes, transition metal polypyridine complexes in general, and ruthenium complexes and dyads in particular have been extensively researched. This usually has an application in the broad fields of photosensitizers, dyes, sensors, LEDs, catalysts, and nanotechnology. Several of the important complex's excited-state characteristics, including efficiency and luminescence decay rates, are greatly influenced by ligand alteration. Bidentate or tridentate interactions are the most common binding modes for polypyridine ligands, which result in complexes with various coordination geometries and characteristics. Tridentate ligands can provide access to complexes with 1D-linear geometries, in fact.

[90] **Aleksandar Mijatovic et.al (2012)** have synthesized Complexes containing ruthenium, primarily in its lower oxidation state, have also been prepared and tested for antitumor activity. These complexes are metal-based drugs that were synthesized and have complementary activities to cisplatin. In addition to good performance in screening experiments, a number of ruthenium compounds containing nitrogen ligands have been developed. For  $^1\text{H}$  NMR, the substitution process involving the  $[\text{Ru}(\text{terpy})(\text{bipy})(\text{H}_2\text{O})]^{2+}$  complex and thiourea was too quick. Yet coordination to the complex was revealed by the  $^1\text{H}$  NMR signals for free, at 9.56 ppm, and for substituted complex, at 10.13 ppm, as well as by the  $^{13}\text{C}$  NMR spectra, which showed an upfield shift of 6 ppm for the carbon resonance.



**Figure 2.1(j) structure of the  $[\text{Ru}(\text{trpy})(\text{Bpy})(\text{H}_2\text{O})]^{2+}$**

[91] **Derek J. Wasylenko et.al (2010)** have prepared mononuclear coordination complexes are demonstrated to be effective catalysts in the Ce(IV)-driven oxidation of water in acidic conditions. The systematic placement of electron-withdrawing and electron-donating groups at various locations around the polypyridyl framework's periphery provides information regarding how electronic parameters affect the characteristics of water oxidation catalysts.

Further effective catalysts are Ru compounds. Because mononuclear systems are typically simpler to investigate and synthesis than systems with larger nuclearities, this result has significant significance for the development of homogenous water oxidation catalysts.

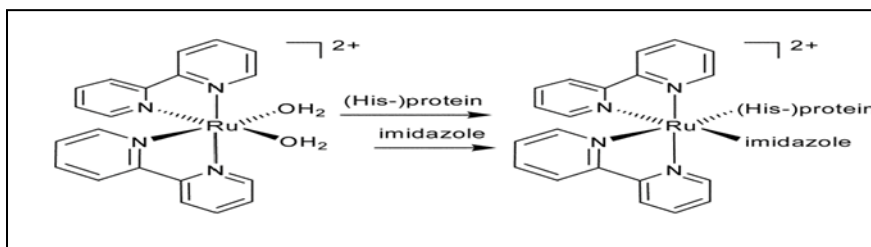
[92] **Rita Annunziata et.al (2008)** noted that 6,6-Disubstituted 2,2':6,2'-terpyridines caught their attention as a scaffold that can adopt distinct conformations for a number of reasons, including the fact that it has been shown that bis(protonation) and metal complexation result in adducts with a very similar electronic structure as determined by their UV spectra. Future research will concentrate on creating a terpyridine-based folding inducer that is water soluble and attaching peptide residues to it that are more likely than AlaGly/GlyAla to establish interchain hydrogen bonds when the scaffold is in its folded shape.

[93] **Ramasamy Indumathy et.al (2006)** have synthesized and characterization of two novel cobalt complexes,  $[\text{Co}(\text{pytpy})_2](\text{ClO}_4)_2$ , 1, and  $[\text{Co}(\text{pytpy})_2](\text{ClO}_4)_3$ , 2, have been completed. Both complexes' single-crystal X-ray structures have been determined. The complexes are monomeric cobalt (II) and cobalt (III) species, and the structure reveals that two pytpy ligands are coupled to the metal ion to create a six coordinate complex. The crystallisation of cobalt (II) and cobalt (III) complexes is meridional. Using absorption, emission, electrochemical, and viscosity tests, researchers have investigated how these complexes interact with the DNA of the calf thymus.

[94] **Christine Goze et.al(2007)** have reported From compounds with reactive bromo functionalities, a number of heteroleptic and homoleptic ruthenium-terpyridine complexes with two and four ethynylpyrenyl residues have been created. It has been effectively employed to prepare the target complexes through cross-coupling facilitated by low-valent palladium) on these premade complexes. Single-crystal X-ray diffraction was used to establish the structure of a bis-terpyridine complex containing four ethynylpyrenyl subunits. This structure displays deformed octahedral geometry around the metal centre, with the ethynylpyrenyl fragment tilted (by roughly  $5^\circ$ ) from the terpyridine plane.

[95] **Yang Xiao-Juan et al (2005)** have reported  $[\text{RuII}(\text{bipy})(\text{terpy})\text{L}]$  compounds ( $\text{PF}_6$ ) Imidazoles (imi), 4-methylimidazole, 2-methylimidazole, benzimidazole, 4,5-diphenylimidazole, indazole, pyrazole, and 3-methylpyrazole have been created and characterised by  $^1\text{H}$  NMR, ESI-MS, and UV/V using digestion of the Ru-coupled protein by trypsin and analysis of the tryptic

peptides by HPLC-high resolution MS. Starting from the Ru-aqua complex, the  $[\text{Ru}(\text{bipy})(\text{terpy})]^{2+}$  fragment was successfully coupled to cytochrome c at 35 °C and pH 7.0 after 5 days of argon-free darkness. By using UV/Vis, emission, and mass spectrometry, the  $[\text{Ru}(\text{bipy})(\text{terpy})(\text{cyt c})]$ -product was identified. Trypsin digestion of the Ru-coupled protein and HPLC-high resolution MS analysis of the tryptic peptides allowed the position of the  $[\text{Ru}(\text{bipy})(\text{terpy})]$  complex's coupling to the protein to be identified as Histidine44.



**Figure 2.1(k) scheme of  $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]$  to form of  $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})(\text{protein})]$**

[96] **Raymond Ziese et.al (2004)** have reported the reactivities of  $\text{RuII}(\text{terpy})(\text{DMSO})\text{Cl}_2$  complexes with CO and substituted 2,2':6',2''-terpyridine (terpy) moieties have been studied. By using spectroscopy and X-ray diffraction, the structure of a trans isomer and its CO adduct has been clearly determined. The cis- $[\text{Ru}(\text{terpy})(\text{terpy}-\text{Br})]^{2+}$  complex, which is shown to be a helpful building block in cross-coupling reactions with ethynylated but metal free bipyridine, phenanthroline, and bipyrimidine fragments, is also accessible using this approach.

[97] **Harald Hofmeiera and Ulrich S. Schuber (2004)** have reported new advances in the study of terpyridine-metal complexes supramolecular chemistry. It is addressed how single as well as many homo- and heterometallic complexes are made, as well as their properties. Moreover, extended aggregates of various designs, rings, fullerene complexes, and biological building elements are also given. Particular focus is given to the characteristics of functioning systems. It is addressed how these technologies might be used in solar cells, molecular switches, and optical nano-devices.

[98] **Etienne Baranoff and others (2004)** have reported these transition metal complexes,  $\text{M}(\text{tpy})_2$ , which have an acceptor group on one side and a donor group on the other, show the many systems examined as well as the factors that lead to the creation of new systems with enhanced performances. Systems based on  $\text{M}(\text{tpy})_2$  are intriguing representations of the

Reaction centre. Although  $M(\text{tpy})_2$  complexes don't glow as brightly as  $M(\text{bpy})_3$  complexes, systems based on the former exhibit unambiguous control over shape and may allow the creation of multinuclear compounds. Other compounds using  $\text{Ru}(\text{tpy})_2$  as PAC,  $\text{Ir}(\text{tpy})_2$  as a luminous label for proteins, or anions sensor based on  $M(\text{tpy})_2$  compounds should also be highlighted recently.

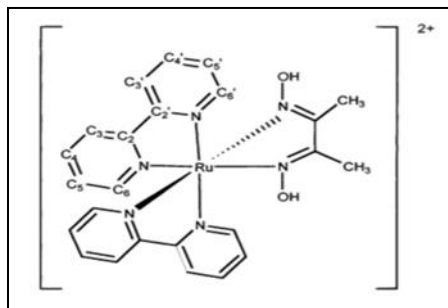
[99] **Anjan Kumar Das et.al (2000)** have noted that ruthenium chemistry of diimine ligands is a topic of intense present research, particularly in light of the complexes photo physical and photochemical characteristics. Due to the significance of the bis-dioximate complexes of transition metal ions as potential models for vitamin B<sub>12</sub>, the chemistry of these complexes has been receiving constant research NMR spectra for <sup>1</sup>H and <sup>13</sup>C were recorded. Using samples made into KBr pellets, IR spectra were acquired using a 783 spectrometer. On the UV 240 spectrophotometer, electronic spectra were captured.

[100] **Biplab Mondal et.al (2000)** have reported Complexes with ruthenium terpyridine. In this article, we describe the synthetic features, specific spectro electrochemical characteristics of the complexes, and the crystal structures of two series members (chloro- and aqua-species). Strong MLCT bands near 500 nm and ligand-based transitions in the UV region can be seen in the complexes 1 through 5 emit emissions that are moderately strong at 77 K at 600 nm. The ruthenium (II)-ruthenium (III) couples and three to four sequential one-electron ligand based reductions are visible in the chloro and hydro complexes. The  $[\text{Ru}^{\text{II}}(\text{trpy})(\text{L})(\text{H}_2\text{O})]^{2+}$ - $[\text{Ru}^{\text{IV}}(\text{trpy})(\text{L})(\text{O})]^{2+}$  reversible 2e/2H single-step oxidation process is demonstrated by the aqua-complexes in the pH range of 1-5.5. 2 pair, and the potential falls off linearly as pH rises. Moreover,  $[\text{Ru}^{\text{IV}}(\text{trpy})(\text{L})(\text{O})]^{2+}$  is produced when an excess of  $\text{Ce}^{\text{IV}}$  in 0.5 M  $\text{H}_2\text{SO}_4$  chemically oxidises the compounds.

[101] **Rezarta Llanguri et.al.(2000)** A variety of  $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{oxime})]^{2+}$  complexes (where  $\text{bpy}$ =2,2'-bipyridine and  $\text{oxime}$ =cyclohexanedione dioxime (cyclo $\text{dioxH}_2$ ), diphenylglyoxime (dpg $\text{H}_2$ ), difurilglyoxime (dfg $\text{H}_2$ ), and 2-acetylpyridine oxime (acetoxH)) have been synthesized and characterised. The compounds' cis-configuration is shown by the <sup>1</sup>H and <sup>13</sup>C NMR spectra. Cyclic and differential pulse voltammetry have shown that the vicinal dioxime complexes exhibit solvent and pH-dependent electronic spectra as well as proton-coupled electron transport. The ruthenium complexes' pK<sub>a</sub> values were calculated, and the

results were compared to electrochemical, electronic, and NMR spectroscopic data. The energy of the MLCT band in the visible range correlates with the Ru center's redox potential.

[102] **Elisabeth T et.al (1999)** have synthesized the compound cis-[Ru(II)(bpy)<sub>2</sub>(dmgH<sub>2</sub>)<sup>2+</sup>]. The complex's oxime ligand contributes two donate able protons while still retaining strong s and p donor properties that can stabilize the higher oxidation state ruthenium complexes. The oxime ligand in the ruthenium complex is doubly protonated when it is isolated, which allows the complex to transmit up to two protons along with two electrons. In methanol, <sup>1</sup>H and <sup>13</sup>C NMR spectra were captured using a Varian 300 MHz Fourier transform spectrometer. Tetramethyl silane was used as a reference in the <sup>1</sup>H NMR spectra, which were recorded at 299.9 MHz.



**Figure 2.1(i) structure of [Ru(II)(bpy)<sub>2</sub>(dmgH<sub>2</sub>)<sup>2+</sup>]**

[103] **Chiyu Wei et.al (1997)** have reported the 2,2':6',2''-terpyridine, a bidentate ligand, is a key component in coordination chemistry. Terpyridine and its derivatives are one of the usual Pincer ligands and/or non-innocent ligands in transition metal catalysis because they have three coordination sites and a low LUMO. These tpy-metal complexes have interesting catalytic reactivities that target several difficult reactions, like C-C bond synthesis and hydro functionalization. The development of transition metal-terpyridine compounds recently is summarised in this study, with an emphasis on their uses in catalysis and supramolecular structure building. Terpyridine derivatives' simple synthesis is also detailed.

[104] **Seth C. Rasmussen et.al (1995)** have synthesized a series of polypyridyl ruthenium(II) complexes that contained monodentate pyridyl and cyano-substituted acetylenes. These complexes could be precursors to metal-coordinated polyacetylene due to the inclusion of the functionalized acetylene groups. The acetylenic compounds can now be employed as

monomeric starting materials to create polyacetylene complexes with substituted metals. The ruthenium center's properties are not altered by the acetylenic functionality, which predicts that the polymer will contain ruthenium (II) centres with their typical excited-state characteristics near to the polymeric backbone.

[105] **Clark R. Hecker et.al (1990)** have reported Due to the wide range of excited-state phenomena that have been observed, including photoluminescence, chemiluminescence, photo redox chemistry, and photo substitution processes, complexes of ruthenium with polypyridyl ligands have been extensively explored. To further reduce the difficulties brought on by the production of a solvent adduct during the substitution reaction, the photochemistry has been implemented in acetonitrile

[106] **Kenneth J. Takeuch et.al (1983)** have reported Using electrochemical method, the complexes  $[(\text{trpy})(\text{bpy})\text{M}-\text{H}_2]^{2+}$  have been synthesized and their redox characteristics in aqueous solution have been examined. Data comparisons between analogous Osmium and Ru complexes also shed light on variations in  $pK_a$ , values in the pH domains of oxidation-state stability, and the likely contribution of the Metal oxygen bond interaction to the redox characteristics of both systems.

[107] **B.Patrick Sullivan et.al (1980)** Although the prevalence of cis-trans isomerism in octahedral metal complexes, there have been comparatively few investigations into the divergent chemical and physical characteristics of a cis trans pair, particularly for the second and third row transition metals. The complexes of the type  $(\text{trpy})\text{Ru}(\text{L})\text{Cl}$  ( $\text{L}=\text{PPh}_3, \text{P}(\text{P}-\text{C}_6\text{H}_4\text{Me})_3, \text{pyridine}$ ) that are generated from the planar, tridentate ligands 2,2',6'2'' terpyridine are described here. The synthetic process are based on the terpyridine ruthenium chloride complex a valuable precursor complex. It is also claimed that cis and trans isomer of the phosphine derivative exhibit some quite remarkable changes in their characteristics.

# ***Materials and methods***

### 3. Materials and methods

#### 3.1 Preparation of Ruthenium based complexes

Ruthenium trichloride was purchased from Sigma Aldrich, 2,2':6'',2''-Terpyridine from TCI, Dimethyl glyoxime from Lobal chemie, Diphenyl glyoxime from suvidhinath laboratories, 1,10 phenanthroline from SDFCL chemical, 2,2 Bipyridine from SRL chemical were purchased in 99% purity.

#### Solvent used

- ❖ Ethanol
- ❖ Triethyl amine
- ❖ Diethyl ether
- ❖ Ethylenediamine

#### 3.2 Methods of synthesis

Preparation of Ruthenium complexes

##### Preparation of [Ru(trpy)Cl<sub>3</sub>]

To 125 mL of absolute ethanol in a 200-mL Iodine flask flask was added 262 mg of “RuCl<sub>3</sub>·3H<sub>2</sub>O and 233 mg of 2,2':6'',2''-terpyridine .The mixture was heated at reflux for 3 h while vigorous magnetic stirring was maintained. After this time the reaction was cooled to room temperature, and the fine brown powder which had appeared was filtered from the reddish yellow solution. The product was washed with 3 X 30-mL portions of absolute ethanol followed by 3 X 30-mL portions of diethyl ether and air-dried; yield 440 mg [107].

#### Reactions of Ru(trpy)Cl<sub>3</sub> with Ligands (L)

##### 1. Preparation of [Ru(trpy)(dmg)Cl]

A weighed amount of [Ru(trpy)Cl<sub>3</sub>] (0.2 mmol) was suspended in an ethanol/water (3:1) in 100 ml iodine flask and mixture containing (1.5 mmol) of LiCl and (0.4 mmol) of triethylamine (Et<sub>3</sub>N) as a reductant. The chelating ligand dimethylglyoxime (0.2 mmol) was then added, and the mixture was refluxed for 3 hr under vigorous stirring with water condensor. The violet-to-purple solution was filtered while hot to remove any undissolved material. Rotary

concentration under reduced pressure to ca. 1/4 of the initial volume and storage at 4.0 °C for 24 h induced formation of the product as a dark solid. It was collected by filtration, washed with ice-cold water, cold acetone, and diethyl ether, and vacuum-dried [107].

## **2. Preparation of [Ru(trpy)(dpg)Cl]**

A weighed amount of [Ru(trpy)Cl<sub>3</sub>] (0.2 mmol) was suspended in an ethanol/water (3:1) in 100 ml iodine flask and mixture containing (1.5 mmol) of LiCl and (0.4 mmol) of triethylamine (Et<sub>3</sub>N) as a reductant. The chelating ligand diphenyl glyoxime (0.2 mmol) was then added, and the mixture was refluxed for 3 hr under vigorous stirring with water condenser. The violet-to-purple solution was filtered while hot to remove any undissolved material. Rotary concentration under reduced pressure to ca. 1/4 of the initial volume and storage at 4.0 °C for 24 h induced formation of the product as a dark solid. It was collected by filtration, washed with ice-cold water, cold acetone, and diethyl ether, and vacuum-dried.

## **3. Preparation of [Ru(trpy)(bpy)Cl]**

A weighed amount of [Ru(trpy)Cl<sub>3</sub>] (0.2 mmol) was suspended in an ethanol/water (3:1) in 100 ml iodine flask and mixture containing (1.5 mmol) of LiCl and (0.4 mmol) of triethylamine (Et<sub>3</sub>N) as a reductant. The chelating ligand Bpyidine (0.2 mmol) was then added, and the mixture was refluxed for 3 hr under vigorous stirring with water condenser. The violet-to-purple solution was filtered while hot to remove any undissolved material. Rotary concentration under reduced pressure to ca. 1/4 of the initial volume and storage at 4.0 °C for 24 h induced formation of the product as a dark solid. It was collected by filtration, washed with ice-cold water, cold acetone, and diethyl ether, and vacuum-dried.

## **4. Preparation of [Ru(trpy)(phen)Cl]**

A weighed amount of [Ru(trpy)Cl<sub>3</sub>] (0.2 mmol) was suspended in an ethanol/water (3:1) in 100 ml iodine flask and mixture containing (1.5 mmol) of LiCl and (0.4 mmol) of triethylamine (Et<sub>3</sub>N) as a reductant. The chelating ligand 1,10 phenanthroline (0.2 mmol) was then added, and the mixture was refluxed for 3 hr under vigorous stirring with water condenser. The violet-to-purple solution was filtered while hot to remove any undissolved material. Rotary concentration under reduced pressure to ca. 1/4 of the initial volume and storage at 4.0 °C for 24

h induced formation of the product as a dark solid. It was collected by filtration, washed with ice-cold water, cold acetone, and diethyl ether, and vacuum-dried.

### **5. Preparation of [Ru(dpg)<sub>2</sub>bpy]**

The ruthenium chloride salt was taken about 0.005 mmol in ethanol and diphenyl glyoxime of 0.010mmol was also taken and stirred about an hour with heating of about 20-40 centigrade in iodine flask fitted with water condenser in magnetic stirrer at constant rpm of 550. After an hour Bipyridine which is a co-ligand of 0.005 mmol was taken as ethanolic solution, added to the stirring core complex solution and allowed to stir for 2 hours. The brown precipitate was obtained, filtered and dried[102].

### **6. Preparation of [Ru(bpy)<sub>2</sub>dpg]**

The ruthenium chloride 0.005 mmol in ethanol and Bipyridine of 0.010mmol was also taken and stirred about an hour with heating of about 20-40 centigrade in iodine flask fitted with water condenser in magnetic stirrer at constant rpm of 550. After an hour Diphenyl glyoxime which is a co-ligand of 0.005 mmol was taken as ethanolic solution, added to the stirring core complex solution and allowed to stir for 2 hours. The brown precipitate was obtained, filtered and dried.

### **7. Preparation of [Ru(dpg)<sub>2</sub>en]**

The ruthenium chloride 0.005 mmol in ethanol and diphenyl glyoxime of 0.010mmol was also taken and stirred about an hour with heating of about 20-40 centigrade in iodine flask fitted with water condenser in magnetic stirrer at constant rpm of 550. After an hour Ethelenediamine which is a co-ligand of 0.005 mmol was taken as ethanolic solution, added to the stirring core complex solution and allowed to stir for 2 hours. The brown precipitate was obtained, filtered and dried.

### **8. Preparation of [Ru(bpy)<sub>2</sub>en]**

The ruthenium chloride 0.005 mmol in ethanol and Bipyridine of 0.010mmol was also taken and stirred about an hour with heating of about 20-40 centigrade in iodine flask fitted with water condenser in magnetic stirrer at constant rpm of 550. After an hour Ethelenediamine which

is a co-ligand of 0.005 mmol was taken as ethanolic solution, added to the stirring core complex solution and allowed to stir for 2 hours. The brown precipitate was obtained, filtered and dried.

### **9. Preparation of [Ru(dmgy)<sub>2</sub>bpy]**

The ruthenium chloride 0.005 mmol in ethanol and dimethyl glyoxime of 0.010mmol was also taken and stirred about an hour with heating of about 20-40 centigrade in iodine flask fitted with water condenser in magnetic stirrer at constant rpm of 550. After an hour Bipyridine which is a co-ligand of 0.005 mmol was taken as ethanolic solution, added to the stirring core complex solution and allowed to stir for 2 hours. The brown precipitate was obtained, filtered and dried.

### **10. Preparation of [Ru(bpy)<sub>2</sub>dmgy]**

The ruthenium chloride 0.005 mmol in ethanol and Bipyridine of 0.010mmol was also taken and stirred about an hour with heating of about 20-40 centigrade in iodine flask fitted with water condenser in magnetic stirrer at constant rpm of 550. After an hour Dimethyl glyoxime which is a co-ligand of 0.005 mmol was taken as ethanolic solution, added to the stirring core complex solution and allowed to stir for 2 hours. The brown precipitate was obtained, filtered and dried.

### **3.3 Characterization of Ruthenium complexes**

The ruthenium complexes synthesized by the above procedure are subjected to various characterization methods such as

- ✓ Ultra Violet Visible spectroscopy
- ✓ Fourier Transform Infrared spectroscopy
- ✓ Nuclear magnetic resonance spectroscopy
- ✓ Thermogravimetric analysis
- ✓ Fluorescence spectroscopy
- ✓ Antibacterial activity test

Characterization of these complexes provided useful information about structure, functional groups, presence of chromophoric group and bond formation between ligand and metal ion.

### **3.3.1 ULTRA VIOLET VISIBLE SPECTROSCOPY**

The UV-visible spectra of the complexes Fig-4.1(a) to Fig-4.1(h) of suitable concentration in DMSO and Ethanol solution were obtained by **Ultra Violet Visible Double Beam Spectrometer** using quartz cell and solvent effect was eliminated by placing DMSO and Ethanol in reference cell.

### **3.3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY**

Infrared spectroscopy of complexes from Fig-4.2(a) to Fig-4.2(f) was obtained using Shimadzu IR spectrometer. The complexes were directly placed in zinc selenide sample cavity, the spectra of complexes were obtained in interferogram technique.

### **3.3.3 NUCLEAR MAGNETIC SPECTROSCOPY**

All the ligands exhibit different signals with correct intensity ratio. The spectrums are recorded in a 400 MHz instrument with Teyramethyl silane (TMS) as an internal standard. Deuterated DMSO used as solventss to record the spectrum.

### **3.3.4 THERMO GRAVIMETRIC ANALYSIS (TGA)**

Thermo Gravimetric Analysis (TGA) studies were done for samples. This gives the information about the thermal decomposition and thermal stability of complexes. Their stability was studied using TG/DTA – EXSTAR/6300 (Thermo Gravimetric Analyzer). The thermograms were obtained from continuous Nitrogen flow with the sample which is placed in an alumina pan. The plots were made for weight loss against temperature. Graphical image of thermogam was prepared using Origin Pro.

### **3.3.5 FLUORESCENCE SPECTROSCOPY**

The fluorescence spectra of the complexes with suitable concentrations in DMSO and Ethanol were obtained by Agilent Cary Eclipse fluorescence spectrometer.

### **3.3.6 ANTIBACTERIAL TEST**

(Kirby-Bauer method)

#### **Procedure**

##### **Inoculum Preparation**

##### **Growth Method**

The growth method is performed as follows

1. At least three to five well-isolated colonies of the same morphological type are selected from an agar plate culture. The top of each colony is touched with a loop, and the growth is transferred into a tube containing 4 to 5 ml of a suitable broth medium, such as Nutrient broth.

2. The broth culture is incubated at 35°C until it achieves or exceeds the turbidity (usually 2 to 6 hours)

3. The turbidity of the actively growing broth culture is adjusted with sterile saline or broth to obtain turbidity. This results in a suspension containing approximately 1 to 2 x10<sup>8</sup> CFU/ml for *Staphylococcus aureus* and *Klebsiella pneumoniae*.

##### **Inoculation of Test Plates**

1. Optimally, within 15 minutes after adjusting the turbidity of the inoculum suspension, a sterile cotton swab is dipped into the adjusted suspension. The swab should be rotated several times and pressed firmly on the inside wall of the tube above the fluid level. This will remove excess inoculum from the swab.

2. The dried surface of a Nutrient agar plate is inoculated by streaking the swab over the entire sterile agar surface. This procedure is repeated by streaking two more times, rotating the plate approximately 60° each time to ensure an even distribution of inoculum. As a final step, the rim of the agar is swabbed.

3. The lid may be left ajar for 3 to 5 minutes, but no more than 15 minutes, to allow for any excess surface moisture to be absorbed before applying the drug impregnated disks.

4. The media was punctured by making a well of 6 mm in diameter and filled with 20 µl of a sample. Further the petriplates were placed inversely for complete diffusion and inhibition zones were examined by measuring the diameter (mm) formed around the well after 24 hrs incubation at 37°C. The zones were measured by using standard (Hi-Media) scale.

# Results AND Discussion

## 4. Results and Discussion

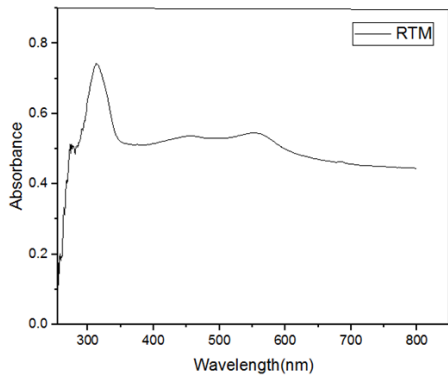
The synthesized compounds were characterized by various spectroscopic techniques

### 4.1 Ultraviolet Visible spectroscopy

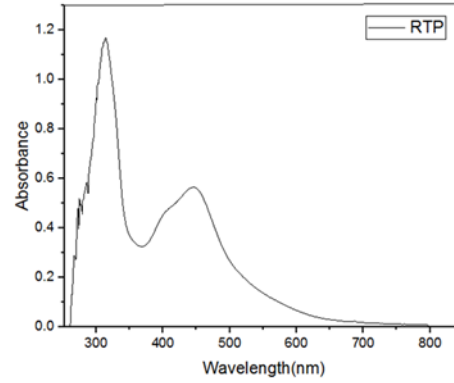
The electronic absorption spectra of the ruthenium complexes in ethanol and DMSO in the 200 to 800nm range. All the complexes show intense absorption band in the 200-350nm region which are related to ligand centered  $\Pi \rightarrow \Pi^*$  transition. The less intense and broad bands are also observed in the 400 to 600nm visible region which is sensitive to the protonation of the oxime ligand. This latter band is assigned to a metal to ligand charge transfer (MLCT) transition  $d\Pi^6(\text{Ru}) \rightarrow \Pi^*(\text{L})$  [102,108].

**Table 4.1: Absorption data of Ruthenium complexes**

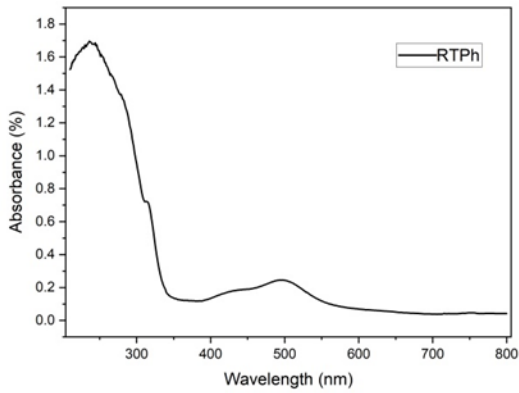
S.No	Ruthenium complexes	Absorption $\lambda_{\text{max}}$ (nm) $\Pi \rightarrow \Pi^*$	Absorption $\lambda_{\text{max}}$ (nm) MLCT
1	[Ru(trpy)(dmg)Cl]	252,284,313	459,557
2	[Ru(trpy)(dpg)Cl]	275,287,315,324	433,459
3	[Ru(trpy)(phen)Cl]	238,255,	494,497
4	[Ru(trpy)(bpy)Cl]	256,276,296,358	500,519
5	[Ru(dpg) <sub>2</sub> (bpy)]	268,270,302	487,493,502
6	[Ru(bpy) <sub>2</sub> (dpg)]	300,317,361	407,452
7	[Ru(dmg) <sub>2</sub> (bpy)]	220,240,252	404,430
8	[Ru(bpy) <sub>2</sub> (dmg)]	221,257,346	486,495,



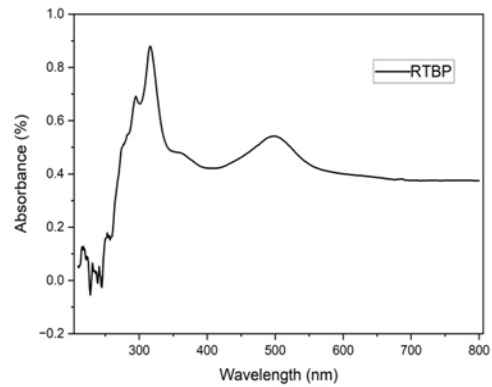
[Ru(trpy)(dmg)Cl]



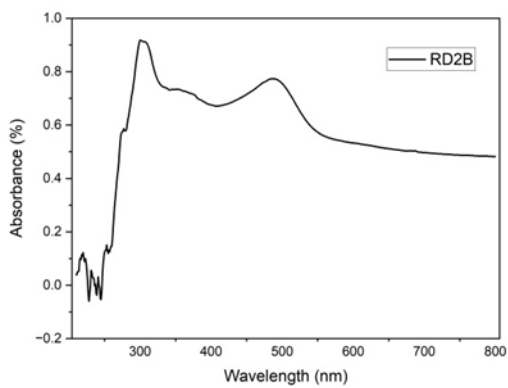
[Ru(trpy)(dpg)Cl]



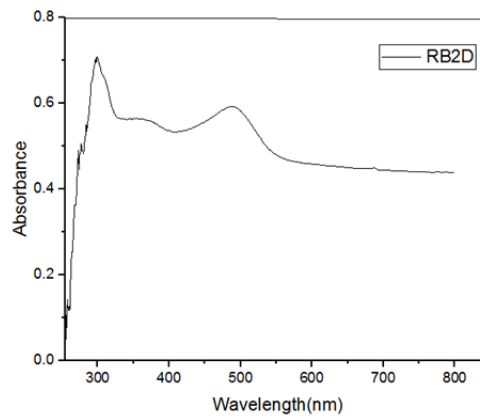
[Ru(trpy)(phen)Cl]



[Ru(trpy)(bpy)Cl]



[Ru(dpg)<sub>2</sub>(bpy)]



[Ru(bpy)<sub>2</sub>(dpg)]

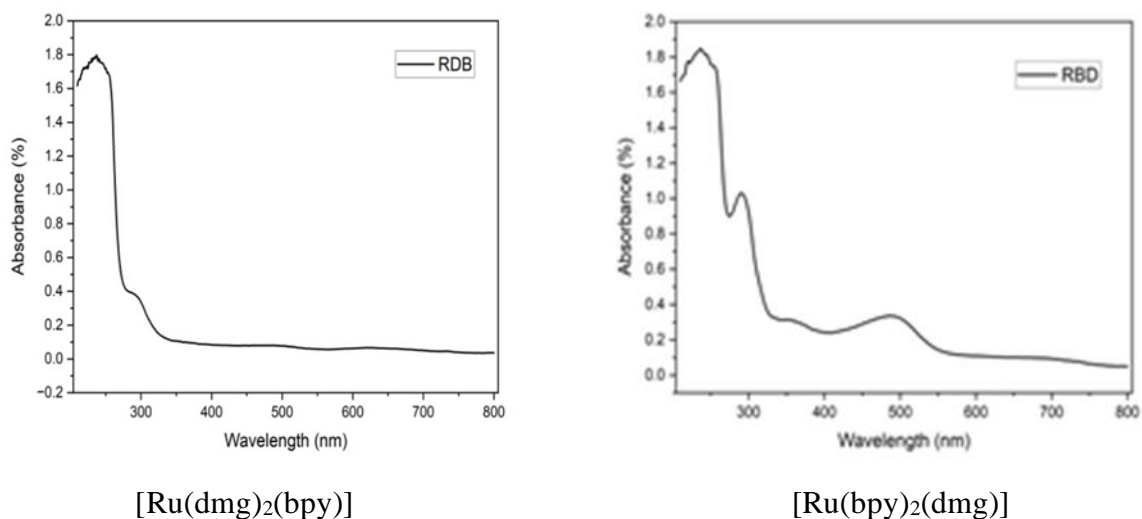


Figure 4.1 UV Spectrum of Ruthenium complexes

## 4.2 Fourier Transform Infrared Spectra:

All the prepared ruthenium complexes showed characteristic stretching frequency,  $\nu(\text{O-H})$  of  $\text{H}_2\text{O}$  around  $3400\text{ cm}^{-1}$ , which can be attributed to coordinated or lattice water molecules. For all the complexes observed stretching frequency in the range  $401$  to  $408\text{ cm}^{-1}$  can be attributed to  $\nu(\text{Ru-N})$ , which confirms the coordination of bidentate ligands to metal center. A peak at  $1440\text{ cm}^{-1}$  to  $1550\text{ cm}^{-1}$  shows the presence of  $\nu(\text{C=N})$  bond in pyridine ring.

A peak at  $530\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  in all three terpyridine complexes which indicate  $\nu(\text{Ru-N}^*)$  terpyridine ligand coordinate to metal. A peak at  $1557\text{ cm}^{-1}$  to  $1635\text{ cm}^{-1}$  shows the presence of  $\nu(\text{C=C})$  bond. A peak from the range  $980$  to  $1030\text{ cm}^{-1}$  confirms the formation of the nitrogen and oxygen bond in oxime ligand [109,110].

**Table 4.2(a): Functional Group analysis of synthesized Ruthenium complexes by FTIR Spectroscopy**

Ruthenium Complexes	Ru-N ( $\text{cm}^{-1}$ )	C=N ( $\text{cm}^{-1}$ )	C=C ( $\text{cm}^{-1}$ )	O-H ( $\text{cm}^{-1}$ )	N-O ( $\text{cm}^{-1}$ )	Ru-N* ( $\text{cm}^{-1}$ )
[Ru(trpy)(dpg)Cl]	401	1442	1635	2877	987	563
[Ru(trpy)(phen)Cl]	408	1442	1597	2831	–	594
[Ru(trpy)(bpy)Cl]	401	1442	1597	2970	–	532

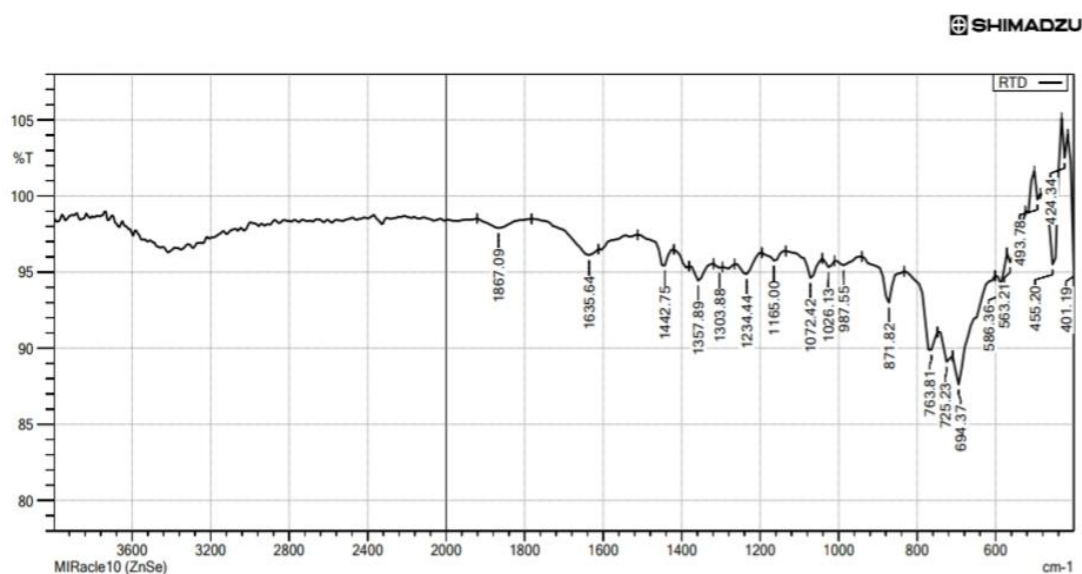
(Ru-N\*) – Indicate terpyridine ligand coordinate to metal

For all the complexes observed stretching frequency in the range 401 to 408 $\text{cm}^{-1}$  can be attributed to  $\nu(\text{Ru-N})$ , which confirms the coordination of bidentate ligands to metal center. A peak at 1440 $\text{cm}^{-1}$  to 1540  $\text{cm}^{-1}$  shows the presence of  $\nu(\text{C=N})$  bond in pyridine ring.

A peak at 440 $\text{cm}^{-1}$  to 455 $\text{cm}^{-1}$  in all three complexes which indicate  $\nu(\text{Ru-N}^*)$  another bidentate ligand coordinate to metal. A peak at 1600 $\text{cm}^{-1}$ to 1620 $\text{cm}^{-1}$  shows the presence of  $\nu(\text{C=C})$  bond. A peak from the range 980 to 1030 $\text{cm}^{-1}$  confirms the formation of the nitrogen and oxygen bond in oxime ligand [110].

**Table 4.2(b): Functional Group analysis of synthesized Ruthenium complexes by FTIR Spectroscopy**

Ruthenium complexes	Ru-N ( $\text{cm}^{-1}$ )	C=N ( $\text{cm}^{-1}$ )	C=C ( $\text{cm}^{-1}$ )	O-H ( $\text{cm}^{-1}$ )	N-O ( $\text{cm}^{-1}$ )	Ru-N* ( $\text{cm}^{-1}$ )
[Ru(dpg) <sub>2</sub> (Bpy)]	401	1442	1620	2985	987	455
[Ru(dpg) <sub>2</sub> (en)]	408	1540	1604	3309	987	455
[Ru(Bpy) <sub>2</sub> (dmg)]	401	1442	1604	3302	1026	447



**Figure 4.1(a) FTIR Spectrum of [Ru(trpy)(dmg)Cl]**

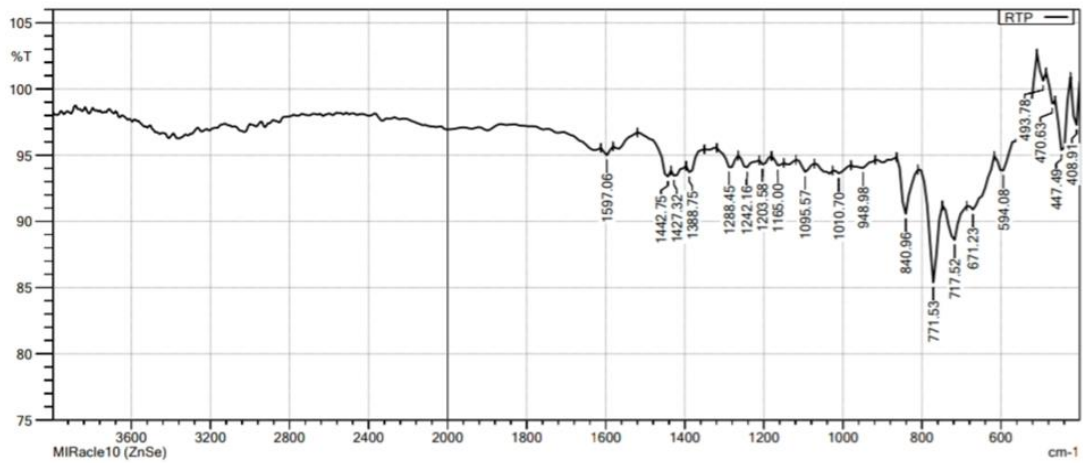


Figure 4.2(b) FTIR spectrum of [Ru(trpy)(phen)Cl]

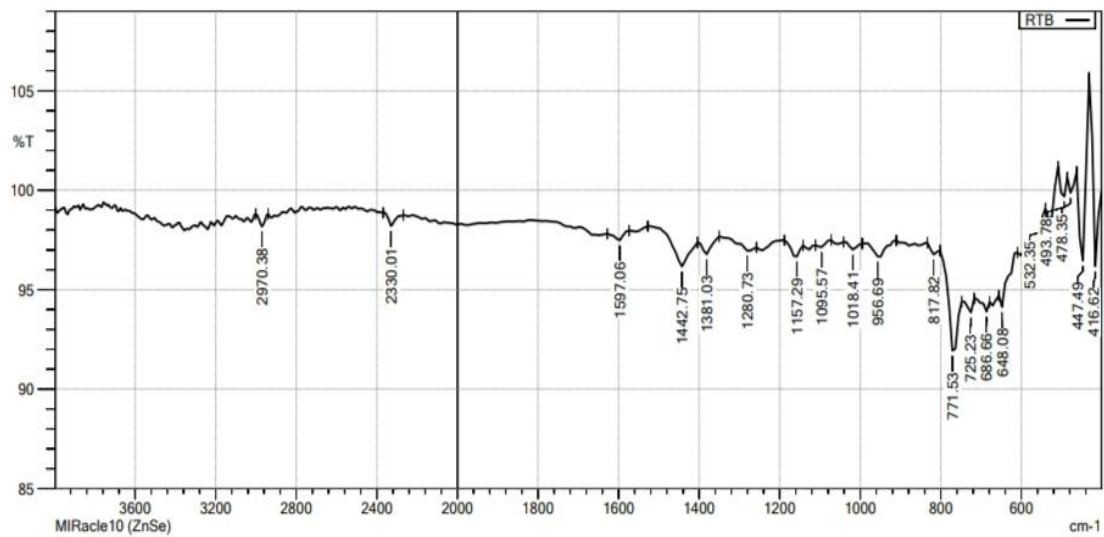


Figure 4.2(c) FTIR spectrum of [Ru(trpy)(bpy)Cl]

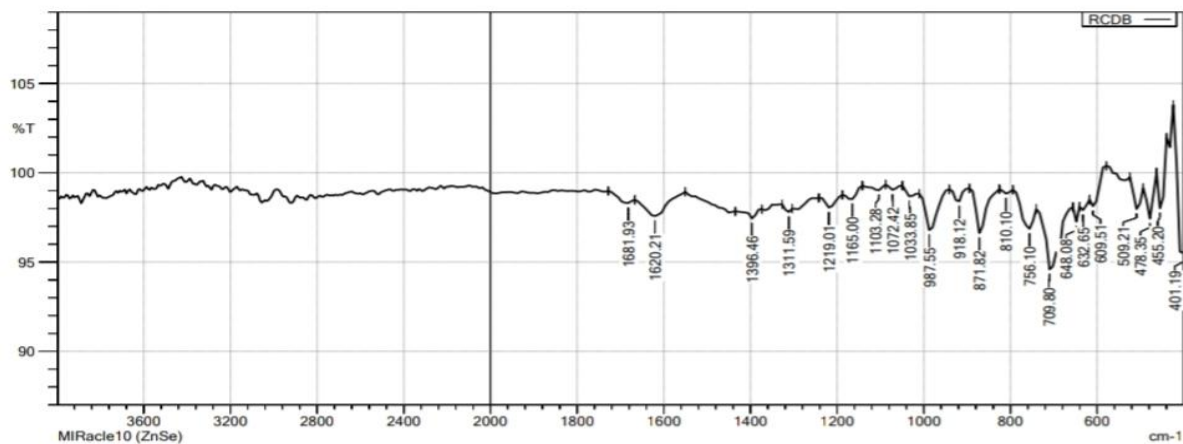


Figure 4.2(d) FTIR spectrum of [Ru(dpg)<sub>2</sub>(bpy)]

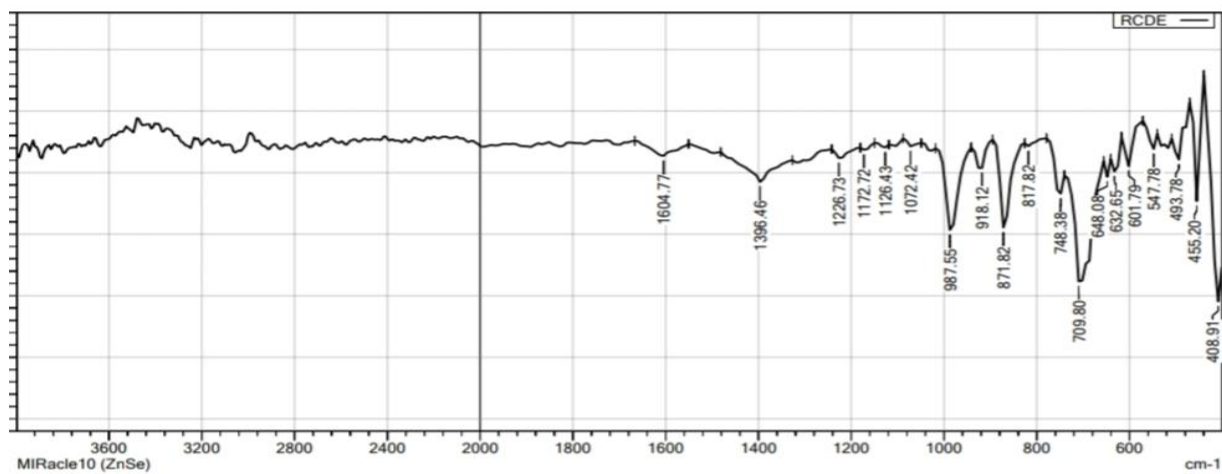


Figure 4.2(e) FTIR spectrum of [Ru(dpg)<sub>2</sub>(en)]

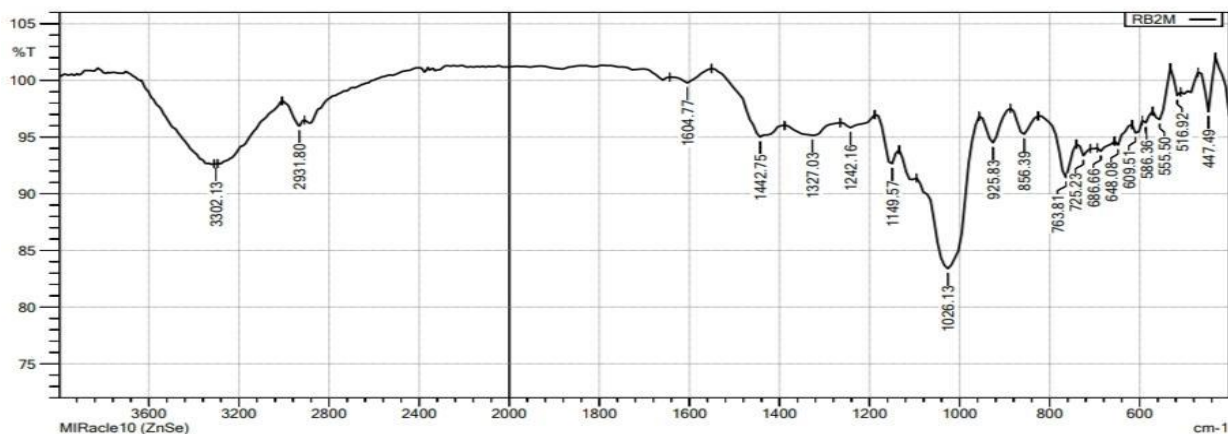


Figure 4.2(f) FTIR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{dm})]$

### 4.3 $^1\text{H}$ NMR SPECTRA

The NMR spectrum of  $[\text{Ru}(\text{trpy})(\text{phen})\text{Cl}]$  showed a doublet at  $\delta = 7.4\text{-}7.7\text{ppm}(\text{d})$  is assigned to the aromatic protons of the terpyridine ligand. A doublet in the range at  $\delta = 8.36\text{ppm}(\text{d})$  aromatic protons of the diphenyl glyoxime ligand. A singlet appeared at  $\delta = 11.39\text{ppm}(\text{s})$  corresponding to N-OH group of the diphenyl glyoxime ligand. [102,111].

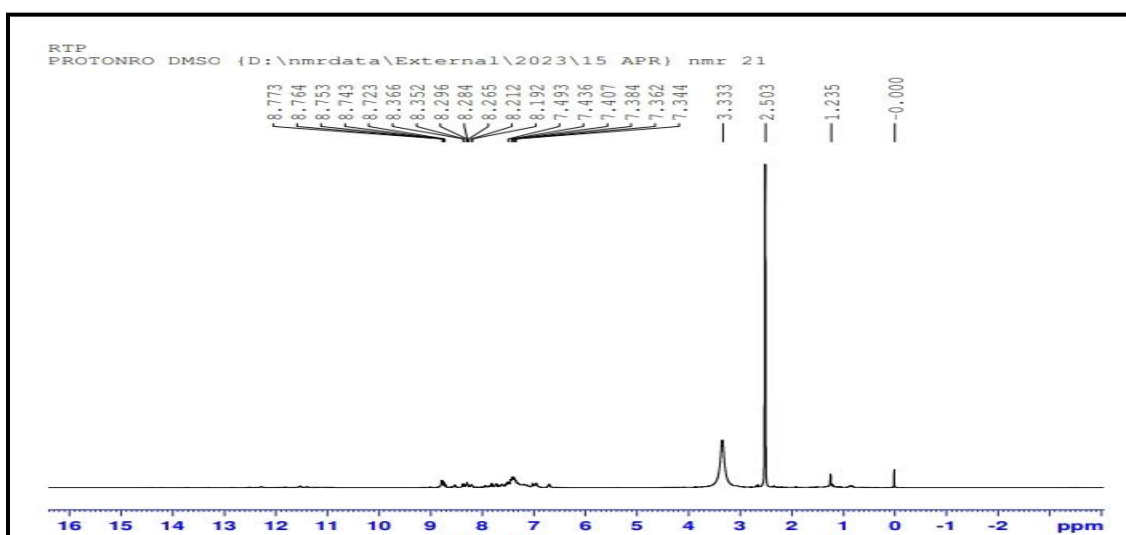
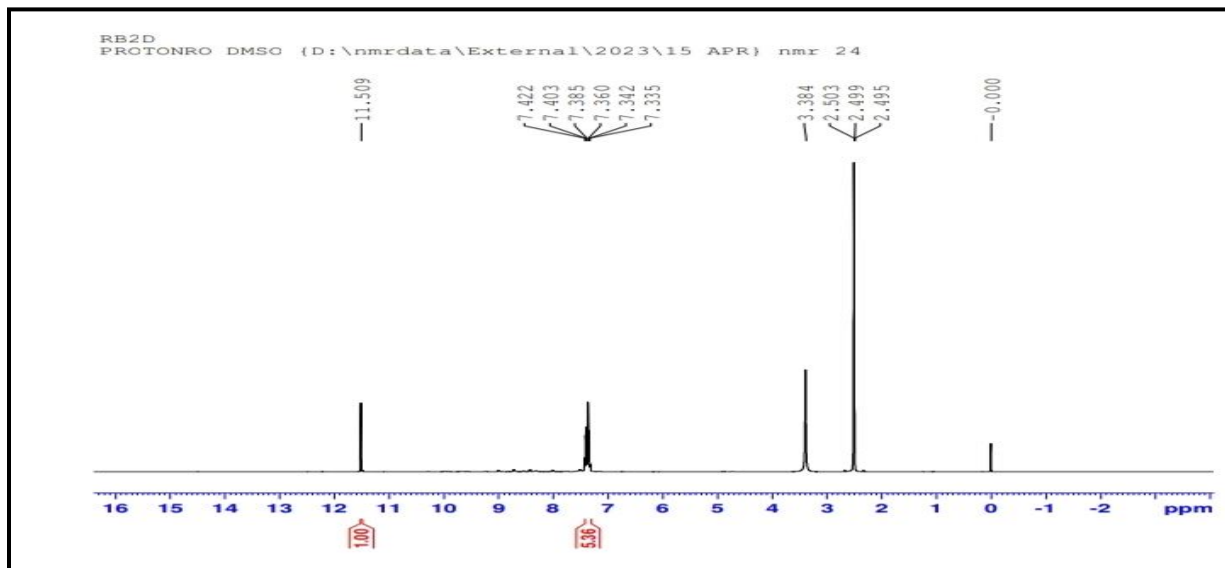


Figure 4.3(a)  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\text{trpy})(\text{dm})\text{Cl}]$

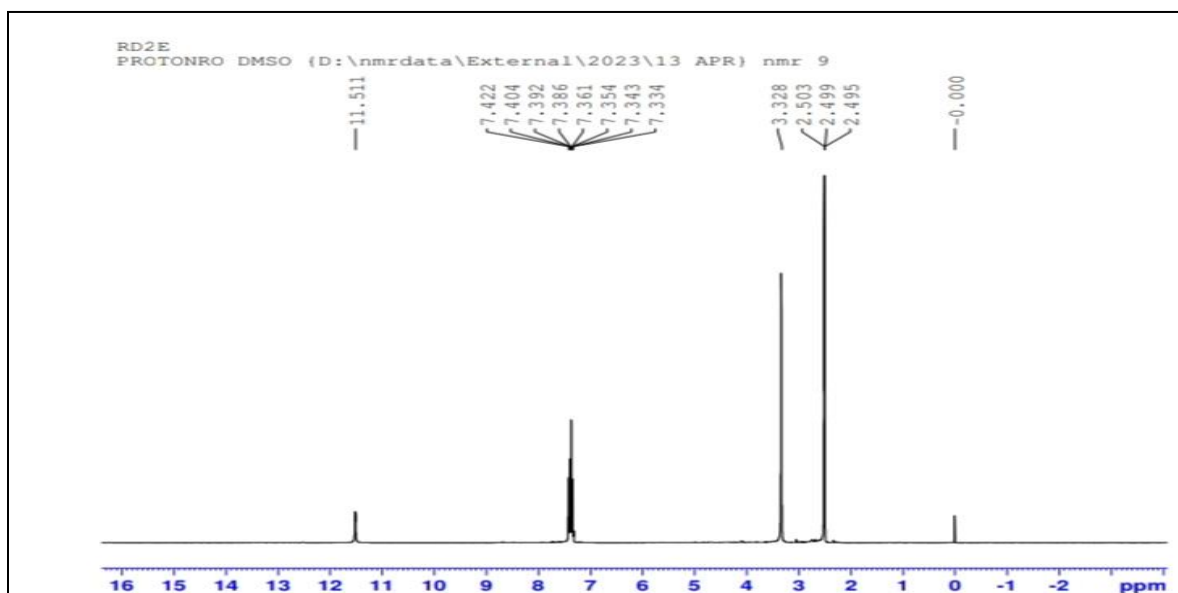
The NMR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{dpg})]$  showed a doublet peak at  $\delta = 7.3\text{-}7.4\text{ppm}(\text{d})$  was assigned to the aromatic protons on 2,2' Bipyridine ligand. A doublet in the range at  $\delta =$

8.4-8.7ppm(d) aromatic protons of the diphenyl glyoxime ligand. A singlet appeared at  $\delta = 11.50\text{ppm}(s)$  corresponding to N-OH group of the diphenyl glyoxime ligand[102].



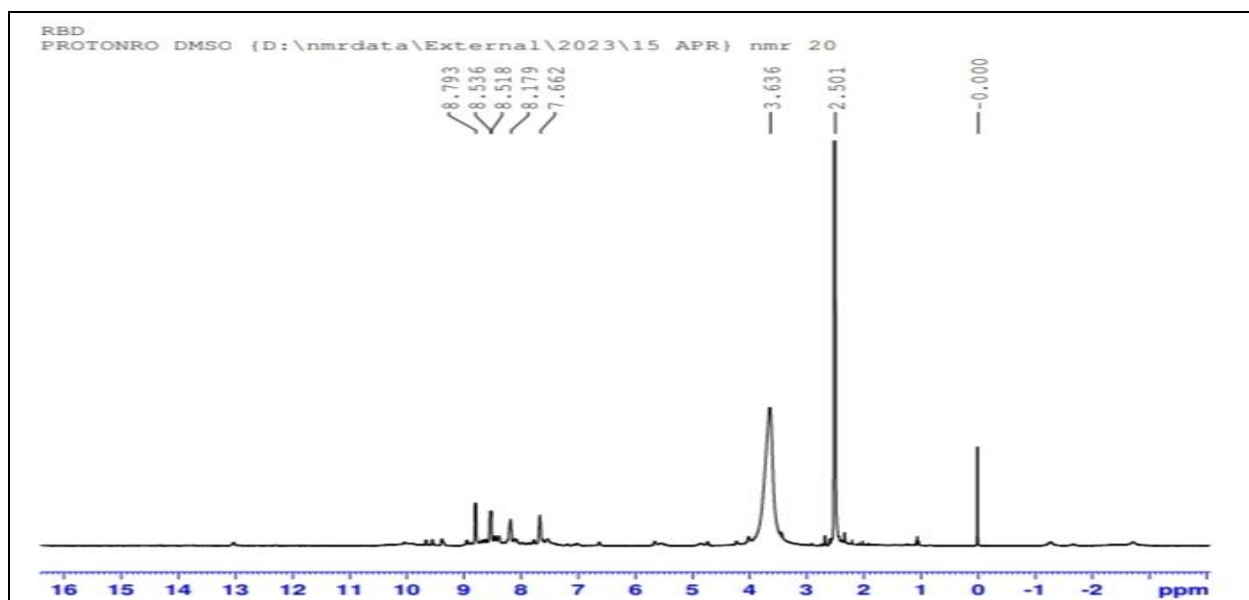
**Figure 4.3(b)  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{dpg})]$**

The NMR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{en})]$  showed a triplet at  $\delta = 2.49\text{ppm}$  was assigned to the methylene protons on ethylenediamine ligand. A doublet in the range at  $\delta = 7.72\text{ppm}(m)$  aromatic protons of the diphenyl glyoxime ligand. A singlet appeared at  $\delta = 11.5\text{ppm}(s)$  corresponding to N-OH group of the diphenyl glyoxime ligand[112].



**Figure 4.3(c)  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\text{dpg})_2(\text{en})]$**

The NMR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{dmg})]$  showed a doublet at  $\delta = 8.53$  ppm(d) was assigned to the aromatic protons on 2,2'Bipyridine ligand . A singlet at  $\delta = 2.67$ ppm(s) is assigned to the methyl group of the dimethyl glyoxime ligand. A singlet appeared at at  $\delta = 13$ ppm(s) corresponding to N-OH group of the dimethyl glyoxime ligand[102].

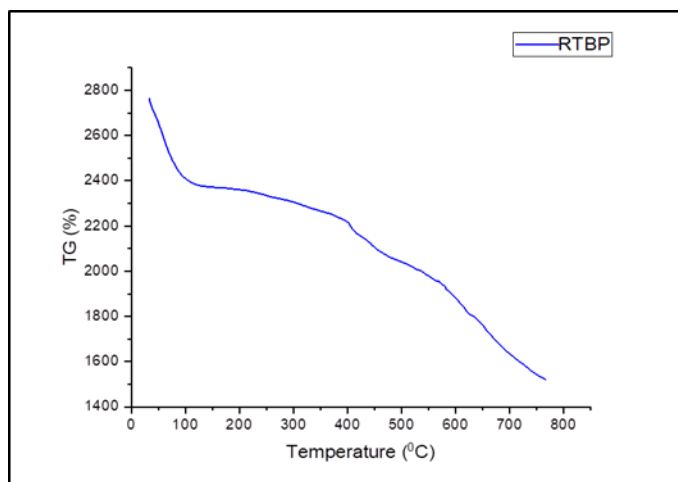


**Figure 4.3(d)  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{dmg})]$**

#### 4.4 Thermogravimetric Analysis (TGA)

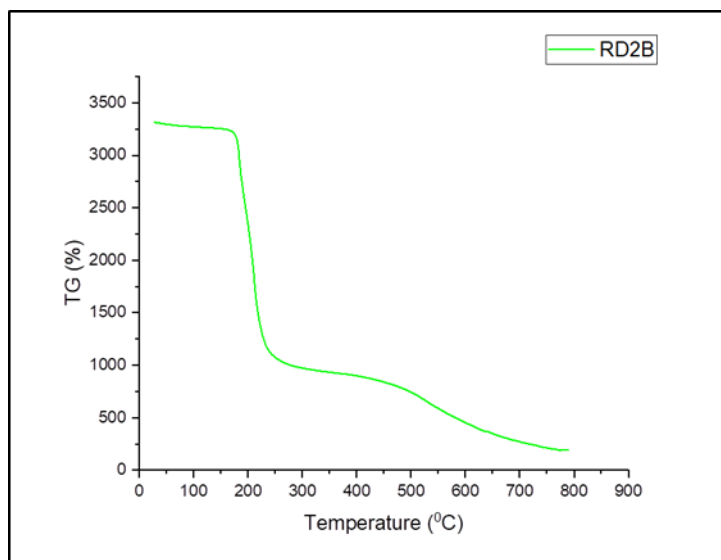
The thermal stability of three compounds was investigated on powder samples in the temperature range  $40^{\circ}\text{C}$ - $800^{\circ}\text{C}$ .

The TG graph of  $[\text{Ru}(\text{trpy})(\text{Bpy})\text{Cl}]$  compound exhibit a two step weight loss of approximately 11.6% weight loss, which is attributed to the loss of water molecule upon heating  $80^{\circ}\text{C}$ - $100^{\circ}\text{C}$ . And 27.6% of weight loss was observed because of the decomposition of bipyridine ligand molecule upon heating from  $320^{\circ}\text{C}$ - $600^{\circ}\text{C}$ . After  $600^{\circ}\text{C}$  the metal decomposes as metal oxide[113].



**Figure 4.4(a) TGA for [Ru(trpy)(Bpy)Cl]**

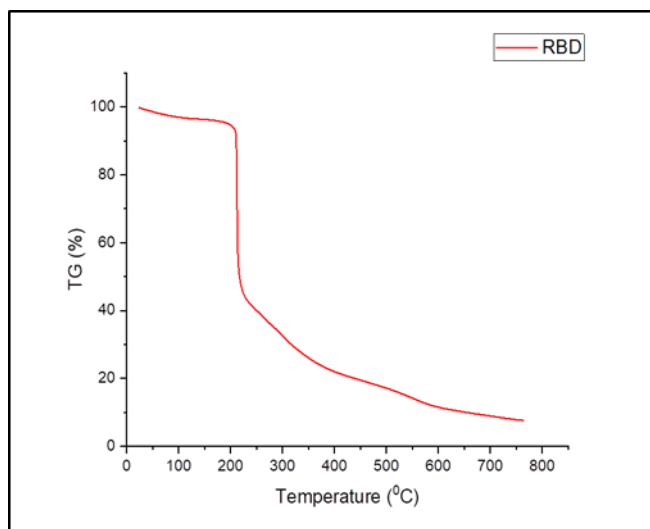
The TG graph of [Ru(dpg)<sub>2</sub>(Bpy)] compound exhibit a three step weight loss of approximately 4.5% weight loss, which is attributed to the loss of water molecule upon heating 80<sup>0</sup>-150<sup>0</sup>C. And 44.5% of weight loss was observed because of the decomposition of diphenyl glyoxime ligand molecule upon heating from 220<sup>0</sup>-300<sup>0</sup>C. And 97% of weight loss was observed decomposition of bipyridine ligand upon heating 400<sup>0</sup>-600<sup>0</sup>C. After 650<sup>0</sup>C the metal decomposes as metal oxide[114].



**Figure 4.4(b) TGA for [Ru(dpg)<sub>2</sub>(bpy)]**

The TG graph of [Ru(dpg)<sub>2</sub>(en)] compound exhibit a two step weight loss of approximately 10% weight loss, which is attributed to the loss of water molecule upon heating

90<sup>0</sup>-150<sup>0</sup>C. And 65% of weight loss was observed because of the decomposition of diphenyl glyoxime ligand molecule upon heating from 200<sup>0</sup>-600<sup>0</sup>C. After 600<sup>0</sup>C the metal decomposes as metal oxide[114].



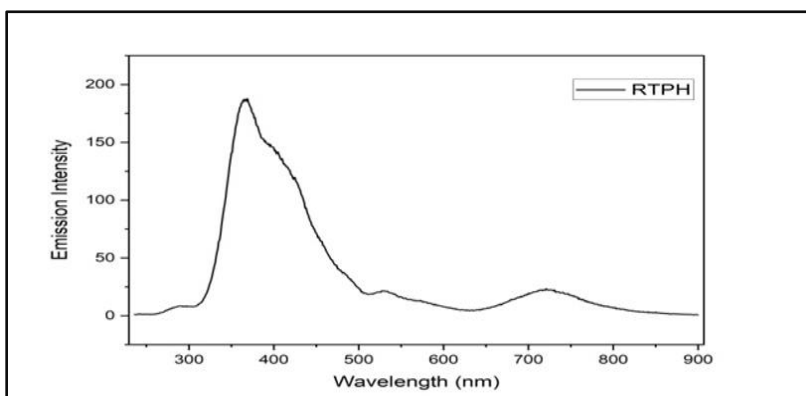
**Figure 4.4(c) TGA for [Ru(dpg)2(en)]**

#### 4.5 FLUROSENCE SPECTRA

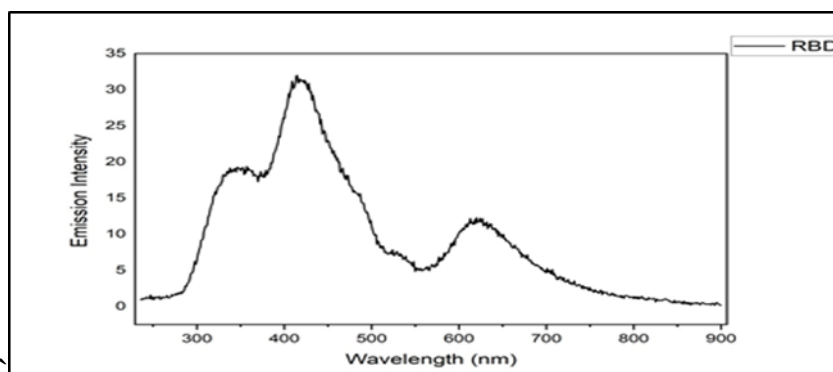
Excitation of [Ru(trpy)(phen)Cl] at 236nm gave its emission at 369nm. [Ru(Bpy)<sub>2</sub>(dmg)] when excited at 236nm, gave its emission peak at 413 nm. The fluorescence results are in good agreement with the results obtained by UV spectroscopic studies. Comparing the emissions of both the complexes [Ru(trpy)(phen)Cl] and [Ru(Bpy)<sub>2</sub>(dmg)]. Ruthenium complex of Bipyridine with DMG, provided good fluorescence activity than the terpyridine –phenanthroline complex. The emission of [Ru(trpy)(phen)Cl] is blue shifted compared to [Ru(Bpy)<sub>2</sub>(dmg)] which is due to the high field ligand terpyridine which is also a higher molecular weight moiety. Another reason is that terpyridine is a tridentate ligand. Since tridentate ligand have bad bite angle for octahedral Ru coordination. As a consequence, such complex tends to be weak emitters in comparison with analogous bipyridine complex. Therefore the complex of bipyridine showed good emission than terpyridine complex. [115,116].

**Table 4.5 : Emission spectral data of ruthenium complexes**

Ruthenium complexes	Emission $\lambda_{\text{max}}$ (nm)
[Ru(trpy)(phen)Cl]	369nm
[Ru(Bpy) <sub>2</sub> (dmg)]	413nm



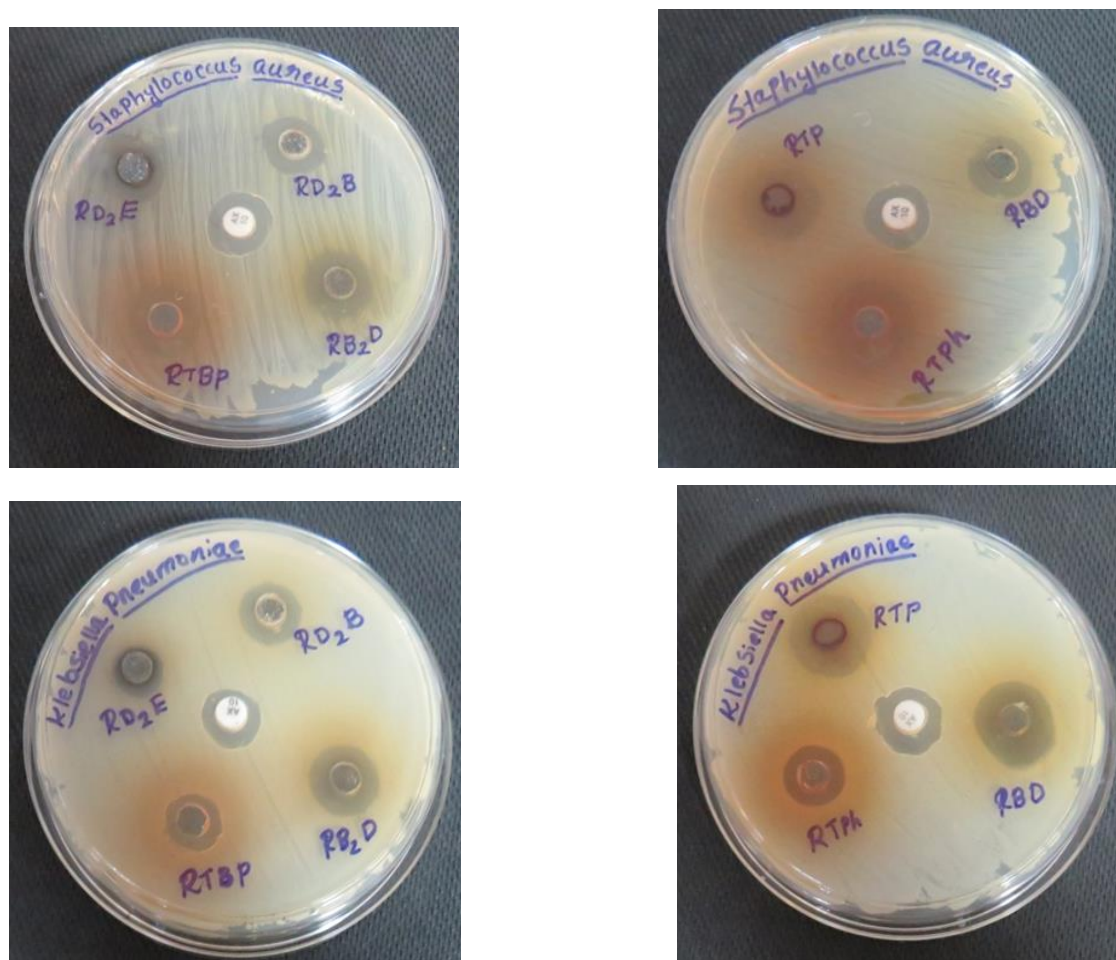
**Figure 4.5(a) Emission spectrum of [Ru(trpy)(phen)Cl]**



**Figure 4.5(b) Emission spectrum of [Ru(bpy)<sub>2</sub>(dmg)]**

#### 4.4 ANTIBACTERIAL STUDIES

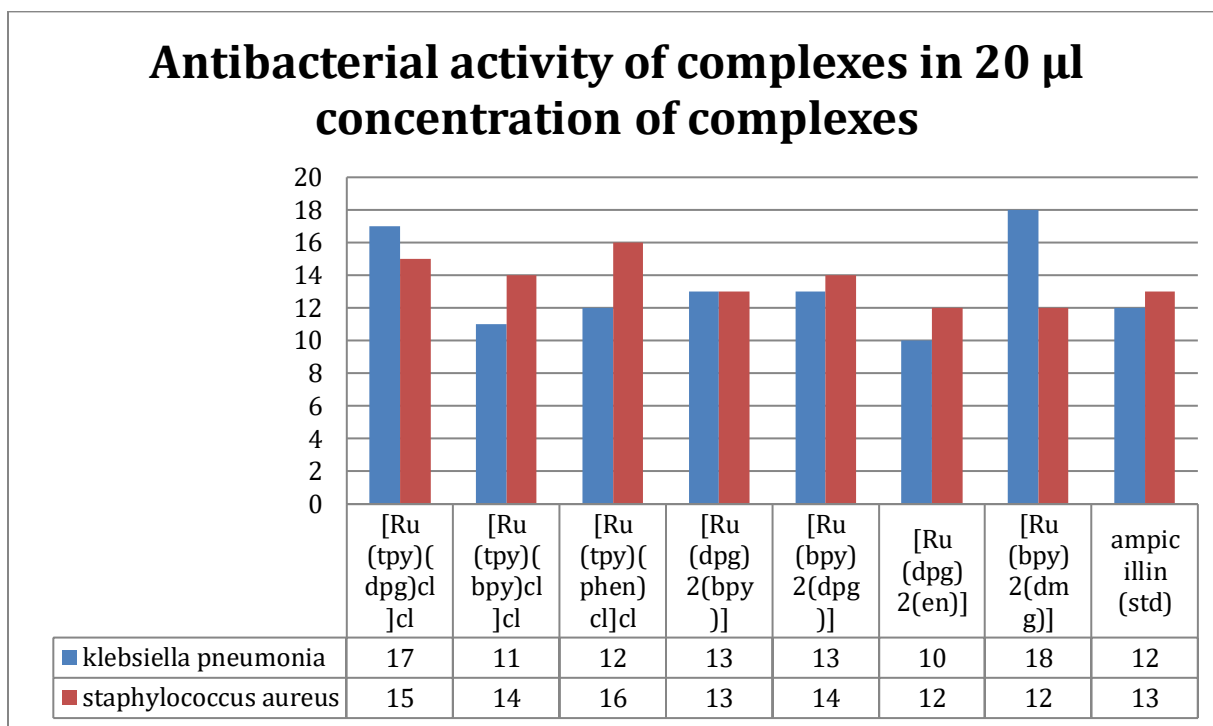
The antibacterial activity of Ru complexes tested against two human pathogens: one Gram-positive bacteria (*Staphylococcus aureus*) and one Gram-negative bacteria (*Klebsiella pneumoniae*) by the Kirby Bauer method. The Ru complexes are more effective against gram-positive bacteria (*S.aureus*) than gram-negative bacteria (*K. pneumoniae*)[117,118].



**Figure 4.6(a) Antibacterial activity of Ruthenium complexes against Ampicillin in Kirby Bauer method**

**Table 4.6: Zone of inhibition of Ruthenium complexes**

Sample	Zone of inhibition (mm)	
	Staphylococcus aureus	Klebsiella pneumoniae
Standard Ampicillin	13mm	12mm
[Ru(trpy)(dpg)Cl]	15mm	17mm
[Ru(trpy)(phen)Cl]	16mm	12mm
[Ru(trpy)(Bpy)Cl]	14mm	11mm
[Ru(dpg) <sub>2</sub> (Bpy)]	13mm	13mm
[Ru(Bpy) <sub>2</sub> (dpg)]	14mm	13mm
[Ru(dpg) <sub>2</sub> (en)]	12mm	10mm
[Ru(Bpy) <sub>2</sub> (dpg)]	12mm	18mm



**Figure 4.6(b) Antibacterial Activity of Ruthenium complexes about 20µl concentration against standard ampicillin.**

The Ruthenium complexes showed the maximum activity and the complex [Ru(trpy)(phen)Cl] and [Ru(trpy)(dpg)Cl] showed good resistant against *Staphylococcus aureus*. The Ru(bpy)<sub>2</sub>(dmg)] and [Ru(trpy)(dpg)Cl] complex showed good activity against *K. pneumonia* at the concentration 20µl. The zone of inhibition of ruthenium complexes were compared to standard drug ampicillin, the complexes were reasonably active. Also to conclude further, it can be said that the complexes of terpyridine ligand showed good bacterial resistant activity than bipyridine ligand complexes. The results of antibacterial activity of ruthenium complexes are shown in Fig [116].

# SUMMARY AND CONCLUSION

## 5. SUMMARY AND CONCLUSION

. The ruthenium complexes with different ligands were prepared and characterized by Ultraviolet visible spectroscopy, Infrared spectroscopy, Nuclear magnetic spectroscopy. Thermogravimetric analysis, Fluorescence spectroscopy and also the complexes were subjected to antibacterial studies.

The experimental results were presented in the form of tables and figures in result and discussion section. Some of the salient features of the experimental results are given below.

- From FTIR analysis a peak at the range 401 to 408 $\text{cm}^{-1}$  can be attributed to confirmation of bond between bidentate ligands and metal center. This confirms the formation of complexes
- The Ruthenium complexes were structurally confirmed by the  $^1\text{H}$  NMR analysis.
- From the fluorescence spectrum of ruthenium complexes showed good fluorescence activity with excellent emission.
- The biological effect of compound is tested by antibacterial test. The ruthenium complexes showed good resistant activity against against gram-positive bacteria ( *S.aureus*) and gram-negative bacteria ( *K. pneumoniae*).

### Future work

- ✓ This study can be further extended to anti-inflammatory, antiviral, antimalarial, antiparasitic, cytotoxicity, and fluorescence studies.

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