ELECTROCHEMICAL STUDIES OF METAL COMPLEXES

Submitted in partial fulfillment of the requirements for the award of
Master of Science in CHEMISTRY

by

MUKKAPATI ANIL

Register No:38910017

DEPARTMENT OF CHEMISTRY
SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited with Grade “A” by NAAC
JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119

APRIL – 2021

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited with “A” grade by NAAC
Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600 119
www.sathyabama.ac.in

DEPARTMENT OF CHEMISTRY

BONAFIDE CERTIFICATE

ThisistocertifythatthisProjectReportisthebonafideworkof**MUKKAPATI ANIL(39910013)**whocarriedouttheprojectentitled“**ELECTRO CHEMICAL STUDIES OF METAL COMPLEXES”** under our supervision from November 2019 to April2020.

Internal Guide

(Dr. S. SUPRIYA)

Head of the Department
(Name in Capital letters with Seal & Signature)

Submitted for Viva voce Examination held on______________________

Internal examiner External Examiner

DECLARATION

I,**MUKKAPATI ANIL (39910013)** hereby declare that the Project Report entitled **“ELECTROCHEMICAL STUDIES OF METAL COMPLEXES”** done by me under the guidance of **Dr. S. SUPRIYA M.Sc., M.Phil., Ph.D.** Assistant Professor, Department of Chemistry, **Sathyabama Institute of Science and Technology**, Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600119 is submitted in partial fulfillment of the requirements for the award of Master of Science degree in Chemistry.

DATE:
PLACE: **SIGNATURE OF THE CANDIDATE**

ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

I convey my thanks to **Dr. S.SUPRIYA, School of Science and Humanities** and **Dr. J KARTHIKEYAN, Head of the Department, Dept. of Chemistry** for providing me necessary support and details at the right time during the progressive reviews.

I would like to express my sincere and deep sense of gratitude to my Project Guide's **Dr. S SUPRIYA M.Sc., M.Phil., Ph.D.** for their valuable guidance, suggestions and constant encouragement paved way for the successful completion of my project work.

I wish to thank my parents and friends for their constant help and support throughout the course of the project.

I wish to express my thanks to all Teaching and Non-teaching staff members of the Department of Chemistry who were helpful in many ways for the completion of the project.

M. ANIL

ABSTRACT

The electrochemical behavior of the designed complexes is also studied using cyclic voltammetry. Voltammetry. Stochiometry form with the ligands in characterized by elemental analysis. EPR IR UV-VIS spectroscopic and other analytical techniques. Cyclic voltammetry measurement of the complexes. The electrochemical properties of these species have been carried out by using cyclic voltammetry studies to see the differences in the potential activity during and after the electron transfer process. Spectroscopic studies is shows that ligand coordinate to the metal center through the some complexes. The measurement show that these compounds are molecular in solution. In the singal crystal structure of copper,and nickel complexes exhibits slightly distorted square planer geomentry.In this ligand exhibited an irreversible one electrorn transfer and redox diffusion and controlled. All complexes had deviation of current and potential to more anodic values when the cyclic sweep was applied at different scan rates.

TABLE OF CONTENTS

CHAPTER 1 - INTRODUTION

CHAPTER 2 – LITERATURE SURVEY

CHAPTER 3 -AIM AND SCOPE

CHAPTER 4 – RESULTS AND DISCUSSION

CHAPTER – 5

1.1 ELECTROCHEMICAL ANALYSIS

Electrochemical analysis is a collection of techniques that use electrical stimulation to analyze the chemical reactivity of a sample surface or a solution oxidation and reduction reaction rates are controlled and measured by a potentiostart connected to electrodes submerged in an electrolyte. Electrochemical analysis is used for degradation of a material due to reaction with its environment. The conditions can be varied to gain insight in the corrosion mechanism in specific environments. Electrochemical analysis is useful for materials selection during the design phase phase or prediction of failure mechanisms and life time during operation.In electrochemical corrosion studies the working electrode is the material under investigation. which is oxidized in a controlled way. The complementary reactions to maintain charge balance takes place at usually inert counter electrode. A reference electrode is used to control the potential close to the working electrode surface. Various techniques are used to measure corrosion resistance.

In potentiostatic measurements. The potential of the constant and the current is monitored as a function of time. In potentiodynamic measurements the potential is usually ramped up slowly and the current as a function of voltage is measured. The current voltage curve around the corrosion potential can be fitted giving the corrosion rate in equilibrium. Scans to higher voltage can be used to determine passivation and passivation breakdown. Cyclic voltammetry is a special form of potentiodynamic analysis. Where the voltage is swung up and down repeatedly. In chemical impedance spectroscopy an alter native voltage around zero offset is applied over usually a large frequency range provides information on time dependent phenomena like ion conduction in dielectric films solid state chemical reaction dipole relaxation and so on.

The measurement uses a device known as a potentiostat, which is an electronic component that can run a three electrode cell. The potentiostat maintains the potential of the working electrode at a constant level with respect to the reference electrode. In some cases it will be important that there be no current running through the reference electrode which is achieved by having the system at a high impedance.While a Ag/AgCl electrode is commonly used as a reference so that potentials are measured relative to it for the purposes of the methods discussed herein we will use the standard hydrogen electrode as the reference electrode. Since the potential of the is this will allow us to use the numbers directly from a table of standard electrode potentials without having to correct for the potential of the reference electrode.

*1.2*ELECTRO CHEMICAL STUDIES

The electrochemical study indicates that the pyrrole ring stabilizes the metal ion makes the complex more positivity charged and causes it to be more easily reduced. The bio efficacy of the ligand and their complexes has been examined against the growth of bacteria in vitro to evaluate their antimicrobial potential.

A platinum based anticancer metallodrug research on metal based compounds and complexes as potential anticancer agents has gained importance in modern medical and chemical sciences. electrochemical techniques provide useful complements to other analytical methods of analysis such as UV-visible and fluorescence spectroscopy. Since the redox active metal complexes are not to spectroscopic techniques either due to weak absorption bands or overlap of electronic transitions with those of DNA they can potentially be studied via electrochemical techniques and cyclic voltammetry The electrochemical properties of the complexes depend in a number of factors such as chelate ring size axial ligation degree distribution of unsaturation pattern in the chelating ring. Charge type and coordination number. The redox behaviors of thiosemicarbazone and its complexes have been investigated by cyclic voltammetry in the range. The cyclic voltammetry of the complexes show metal cantered processed and waves corresponding to the ligand. Repeated scans as well as different scan rates showed that dissociation does not take place in these complexes. The electrochemical data of the complexes. The cyclic voltammogram of the ligand in shows an irreversible of the anodic waves in the positive range and irreversible cathodic wave in the negative range.

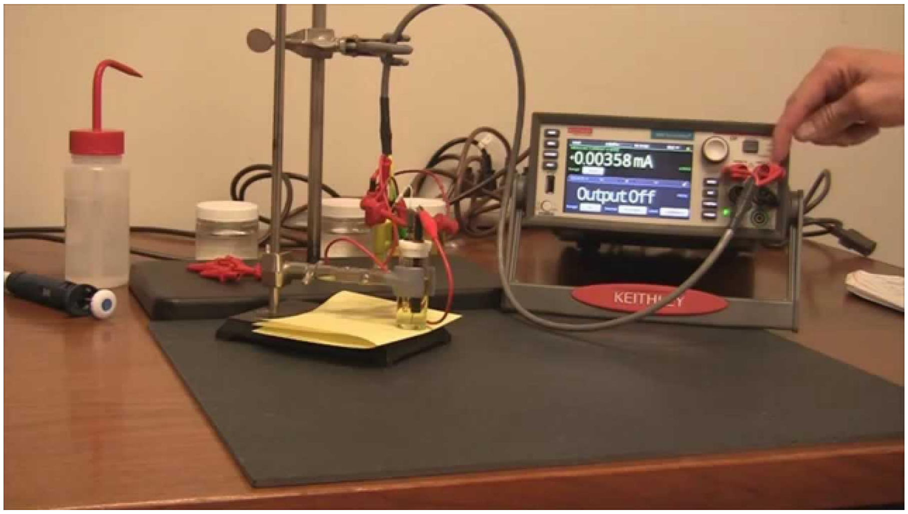
1.2.ADVANTAGES OF ELECTROCHEMICAL STUDIES

- Electrochemical techniques have their advantages because of their simplicity low cost and speed. The only condition for this method of monitoring enzyme kinetics is that direct electron transfer must be possible or able to be achieved by mediators [14–18].
- Developed to qualitatively or quantitatively analyze target molecules through measuring the electrical and electrochemical parameters

1.3 CYCLIC VOLTAMMETRY

Cyclic voltammetry is an electrochemical technique for measuring the current response of a redox active solution to a linearly cycled potential sweep between two or more set values. It is a useful method for quickly determining information about the thermodynamics of redox processes the energy levels of the analyte and the kinetics of electronic-transfer reactions. Like other voltametric methods cyclic voltammetry uses a three electrodes system consisting of a working electrode, reference electrode and counter electrode. To perform cyclic voltammetry the electrolyte solution is first added to an electrochemical cell along with a reference solution and the three electrodes. A potentiostatic is then used to linearly sweep the potential between the working and reference electrodes until it reaches a preset limit at which point it is swept back in the opposite direction.

This process is repeated multiple times during a scan and the changing current between the working and counter probes is measured by the device in real time. The result is a characteristic duck-shaped plot known as a cyclic voltammogram.An electrochemical cell is a device in which a chemical reaction generates an electrical response or conversely an electrical current is used to trigger a chemical reaction. The simplest possible electrochemical cell consists of two connected electrodes in an electrolyte solution. In cyclic voltammetry three electrodes are used.coordination complexes are particularly important in the chemistry of the transition metals some main group elements also form complexes.Although you need to be aware of capacitive currents in cyclic voltammetry, the real power of this technique lies in its ability to investigate mechanisms and potentials of electrode reactions.
Usaully we use conditions where capacitive current is small compared to current from electron transfer. This cyclic voltammetry is a method for scientific investigation and innovation due to the fact most processes involve electron transfer. Which makes them be able to be monitored by this techniques. If the electron transfer at the working electrode surface is fast and the current is limited by the of analyte species to the electrode surface then the peak will be proportional to the of the scan rate.



1.3.1 USES OF CYCLIC VOLTAMMETRY

Cyclic voltammetry is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. CVis performed by cycling the potential of a working electrode, and measuring the resulting current. Cyclic voltammetry is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species. Cyclic voltammetry is also invaluable to study electron transfer initiated chemical reactions which includes catalysis. The both quantitative and qualitative analysis. The wave position is characteristic of a particular to concentration. The wave height is proportional to concentration.

1.3.2 ADVANTAGES OF CYCLIC VOLTAMMETRY

- Cyclic voltammetry is a powerful and popular electro- chemical technique commonly employed to investigate the reduction and oxidation processes of molecular species

- CV is also invaluable to study electron transfer-initiated chemical reactions, which includes catalysis.

- Very sensitive for detection of trance metals
- Favorable signal to background ratio
- Low cost instrumentation
- There are different versions of stripping analysis depending

- On the nature of the depending and stripping steps

1.2.3 APPILICATIONS OF CYCLIC VOLTAMMETRY

- Cyclic voltammetry can be used to study qualitative information about electrochemical processes.

- under various conditions such as the presence of intermediates in oxidation reduction reactions the reversibility of a reaction.

- Cyclic voltammetry is a powerful and popular electro- chemical technique commonly employed to investigate the reduction and oxidation processes of molecular species.
-
- Cyclic voltammetry is a powerful and popular electro- chemical technique commonly employed to investigate the reduction and oxidation processes of molecular species.

- Cyclic voltammetry has become an important and widely used electroanalytical technique in many areas of chemistry.

- It is often used to study a variety of redox processes to determine the stability of reaction products the presence of intermediates

- In redox reactions electron transfer kinetic and the reversibility of a reaction.
- Cyclic voltammetry can also be used to determine the electron stoichiometry of a system the diffusion coefficient of an analyte and the formal reduction potential of an analyte which can be used as an identification tool.

- In addition because concentration is proportional to current in a reversible Nernstian the concentration of an unknown solution can be determined by generating a calibration curve of current vs concentration.

CHAPTER 2

LITRATURE SURVEY

2.*1 LITRATURE REVIEW FOR* **β***-DIKETONE AND ITS METAL COMPLEXES*

Cyclic voltammetry of the ligand and its ligand and its complexes 4=[Ni(L)2(H2O)2] and 5=[Cu(L)2(H2O)2] have been it recorded in dimethylformamide the solution containing 10-3 M and 0.1 M sodium perchlorate as this supporting electrolyte. An electrode cell it was used which was equipped with platinum working and counter electrode and then an Ag/AgCl reference electrode in the potential range +0.2 to -0.2V. All the solution were purged with N2 for about 3 minutes prior to each experiment. The electrochemical behavior of the metal complexes is very similar except some of the slight shift and to and current caused by different metal ions. The ligand and complexes showed assimilar electrochemical behavior.The electrochemical data of all the β-diketone complexes showed one well defined redox couple couple corresponding. The peaks appeared in the forward scan due to the oxidation while in the reverse scan a reduction of the oxidized. The resulted electrochemical data of the complexes. A cyclic voltammogram of the synthesized compound shows one oxidation peak corresponding to the at and reduction peak corresponding to the at respectively.

In this quasi reversible in nature is the evidence by the criteria. The increase with in increasing scan rate. Which also indicates quasi reversible redox process. The indicating that the redox process was controlled by diffusion following to the randlessevcik equation for reversible electrochemical reactions. However, in the case of coli only Cu(II) complex exhibits activity and rest of the compounds were found to be inactive.The synthesized metal complexes the increased antibacterial activity of some metal complexes compared with that of ligand is the due to chelating tends to make to metal complexes act as more influential and powerful bacteriostatic agents thus inhibiting the growth of the microorganisms. In increases the delocalization of p-electrons over the whole chelate ring and enhances the penetration of the complexes into membranes and blocking of the metal binding sites in the enzymes of microorganisms.

This complexes may also disturb the respiration process of the cell and thus block the synthesis of proteins.The restricts further growth of the organism. In general metal complexes are more active than the ligands because metal complexes serve as a vehicle for activation of ligands as the principle cytotoxic species. The difference in the activity of the β-diketone metal complexes may be ascribed due to the coordination environment and the redox properties. In general the redox properties of the complexes depend on several factors such as chelate ring size axial ligatio the degree of unsaturation in the chelate ring.In the spectra of metal β-diketone complexes the band of the longest wavelength shows an obvious bathochromic shift relative to their free ligand.

2.2 LITRATURE REVIEW FOR N–(DIMETHYALCARBAMOTGIOYL)–4-FLUROBENZENE OF METAL COMPLEXES

All experiments were conducted in CH2Cl2 with tetrabutylammonium hexafuorophosphate as the supporting electrolyte. The Electrochemical experiments were conducted in a three component cell consisting of a wire auxiliary electrode a nonaqueous reference electrode (Ag/Ag+) and a glassy carbon as working electrode in the range for Cu(II) and Ni(II) ions, respectively. Cyclic voltammogram of CuL_2 and NiL_2 in dichloromethane are complexes. The results indicate that CuL_2 undergoes one electron reversible redox waves in potential range of 400 to −400 mV. It can be seen from the this cyclic voltammogram of Cu(II) complex in at a scan rate of that a well defned redox process exists.the electrochemical behaviors of these copper(II) and nickel(II) complexes have been investigated in solvents by cyclic voltammetry.
According to the obtained results both Cu(II) and Ni(II) complexes have shown electroactive properties.which is in accordance with the reversibility of Cu(II) Cu(I) couple. A similar study reported that thiourea Cu complexes showed the reduction of Cu(II) Cu(I) redox system undergoing an irreversible process with peak separation of about metal complexes. Duan indicated that some modified thiourea derivatives undergo one electron quasi reversible and reversible redox reactions.Ni(II) complex shows a as quasi-reversible redox wave and an irreversible oxidation peak in potential range.

Cyclic voltammogram indicates that Ni(II) complex in undergoes Ni(II)/Ni(III) oxidation.Ni(II) complex also exhibits an irreversible oxidation peak at that is considered to be ligand moiety.Complex compounds were prepared according to the method described in literature. A metal acetate solution in methanol was added dropwise to the ligand in a molar ratio in methanol. Ten the pH was adjusted with for complex formation. this reaction mixture was stirred for room temperature. The colored solid complexes were and recrystallized from ethanol: dichloromethane. This N-(Dimethylcarbamothioyl)-4-fuorobenzamide compound was synthesized according to literature. A solution of 4-fuorobenzoyl chloride in dry acetone was added dropwise to a solution of potassium thiocyanate in dry acetone.

which reaction mixture was heated under reflux for and then cooled to room temperature.The white precipitated solid compound was filtered. After that crystallization of the crude product by using a mixture of dichloromethane. Complexes were obtained with good yield by stirring the appropriate metal acetate with two equivalents of N-(dimethylcarbamothioyl)-4-fuorobenzamide for to hours in methanol reaction of complex is illustrated in Ligand and its copper and these nickel complex were characterized by diferent spectroscopic techniques including elemental analysis, IR, 1 H NMR spectroscopy, and single crystal X-ray difractionstudy.Besides these, the crystal and molecular structure of synthesized complexes were analyzed by X-ray single crystal difraction method. Te comparative analysis was performed with literature data. Te structure of these compounds is consistent with the structure of other benzoylthiourea derivatives. Te bond lengths and angles also agree well with other thiourea derivatives. Te electrochemical behaviors of copper(II) and nickel(II) complexes have been investigated in aprotic solvents by cyclic voltammetry.

2.3 LITRATURE REVIEW FOR CHLORO-SALICYLIDEN ANLINE AND SOME OF ITS COMPLEXES

The cyclic voltammeter behavior of exhibited three irreversible redox peaks of one electron transfer. which may to the formation of anions and cations species due to a reduction and oxidation process corresponding to an irreversible electron transfer. These using different scan rates the deviation in current was observed and various potential anodic values is measured which may be related to the increase of the scan rates. The linearity relationship as shown to derived from redox peaks current with the square root of scan rates illustrates that the redox is a diffusion controlled process. The electrochemical data of the ligand and prepared complexes are summarized.The cyclic voltammograms of the Schiff base ligand at different scan rates. The oxidation and reduction potential values of the ligand and its complexes at scan rate. The first peak attributed to the formation of Co(II) cation radical and the second. Another weak oxidation peak for complex was noticed clearly at with a scan rate.The electrochemical behavior of ligand and metal complexes was investigated by cyclic voltammetry for 10^{-3} M of acompound in acetonitrile containing 0.1 M of tetrabutylammonium tetrafluoroborate as a supporting electrolyte at room temperature using Ag/AgCl as a reference electrode in a potential range of -1 to +2 V and a scan rate of 0.05 to 0.5 Vs-1.

The cyclic sweep for and complexes appeared two irreversible oxidation peaks but with different values and positions as caused by one-electron transfer.May be due to the presence of the phenolic hydroxyl group of the ligand excess which acts as a proton donor.The same deviation of current and to more potential to more anodic values for ligand may be observed when the cyclic sweep was done for and the ancomplexes at the different scan rates.Two peaks are reversible redox couples the first redox peaks couple are assumed to the second is assumecd reaction to the with the onelectron transfer.The plot of peak current against square root of scan rate of and respectively. The cyclic sweep for and complexes appeared several redox peaks which related to the formation of various manganese redox reaction.The scan for gave another reduction and oxidation peaks related to the presence of an to additional phenolic hydroxyl group of the as ligand which acts as a proton donor. The complexes had a deviation of current and potential to and more anodic values when the cyclic sweep was done at different scan rates.

By comparing the potential values for prepared complexes which summarized. A positive shift was observed for and may be due to the electron donating and electron with drawing properties of phenyl substituted group. The electrochemical properties of these species have been carried out by using cyclic voltammetry studies to see the differences in the potential and activity behavior during and after the electron transfer process.The cyclic voltammetry of ligand exhibited an its irreversible one electron transfer and redox diffusion controlled process due to the linearity relationship between redox peaks current and square root of scan rates. All complexes had a deviation of current and potential to more anodic values when the cyclic sweep was applied at different scan rates.

The Schiff bases as attracting chelating ligands with various transition metal ions is widely developed in coordination chemistry for their easy synthesis moderate stability diverse oxidation-reduction conditions biological activities and other extensive applications and due to their containing of donor atoms like a nitrogen and oxygen they have been used as specific catalysts for oxidation reduction and other electronic transformations process in different organic and inorganic reactions.In the to present study chlorosalicyliden aniline Schiff base and its complexes with and have been synthesized and their structures it determined using the method these and characterized with a spectroscopic techniques.

The ligands electrochemical and their complexes are being. The differences in the number of peaks and chemical shift of the free ligand and its complexes confirm that the bonding between them occurs. The cyclic voltametric behavior of the prepared complexes was studied during and after the electron transfer process. The ligand exhibited an irreversible one electron transfer and redox diffusion controlled process and the complexes appeared two irreversible oxidation peaks but with different values and positions and complexes appeared many to its redox peaks which related to the formation of various manganese redox species.

2.4 *LITRATURE REVIEW FOR BIOLOGICALLY ACTIVE AZOMETHINE 2-HYDROXYACETOPHENONE SULFAMETHOXAZOLE*

To study the effect of solvents buffers scan rates and pH on redox behavior of compound cyclic voltammograms to these recorded in acetonitrile acetone methanol and DMF solvents using phosphate is buffer mixture of 0.2 M monobasic sodium phosphate 0.2 M dibasic sodium phosphate and 0.1 M HCl/NaOH) and buffer its mixture of 0.04 M boric acid 0.04 M phosphoric acid 0.04 M acetic acid and 0.2 M sodium hydroxide.At different pH values. For this 10 ml of 1 mM concentration solution containing 1 ml of 0.01 M stock solution of these compound in appropriate solvent and remaining 9 ml of phosphate for buffer solution of in desired pH were employed in voltammetric experiment on 50, 100, 150, 200 and 250 mV/s sweep rates +1000 mV to -1800 mV potential range and at 0.1 mA current sensitivity. Thesereductions to takes place. In this cyclic voltammetry techniques metal complexes.

The cyclic voltammetric experiments were carried out using Basic Electrochemistry System. A three electrode combination system which a consisted of a working glassy carbon electrode to an Ag/AgCl reference electrode and Pt wire auxiliary electrode was used. All cyclic voltammograms were obtained, exhibits one irreversible reduction peak in the cathodic direction and no anodic peak in reverse scan. Thus to explain irreversible electrochemical reduction.peak potential, half peak potential peak current scan rate, electrode surface area number of electrons involved in electrode process and concentration of the electrolytic solution.

Antibacterial screening and antifungal screeningrespectively.The antimicrobial/antifungal spectrum of the experimental compound were determined for the bacterial/fungal species in terms of inhibited zone size around each well. For each bacterial/fungal strain controls were maintained by pure solvents instead of the compound solution The compound is reported to have most antibacterial.The electrochemical behavior of Schiff bases have been also drawn the attention of many However insuffcientinformations are available in the literature regarding the electrochemical behavior of the Schiff bases of sulfa drugs and their transition metal complexes

The antimicrobialantifungal spectrum of the experimental compound determined for the bacterial fungal species in terms of inhibited zone size around each well. For each bacterialfungal strain controls were maintained by pure solvents instead of the compound solution. It was also found that the reduction process is dependent on the polarity of the medium. The In vitro biological screening studies show sufficient activity against tested microorganisms in the compound concentration range of 20 to 60 mg/mL

2.*5 LITRATURE REVIEW FOR BIOLOGICAL STUDIES OF COBALT AND CUPPER, NICKEL COMPLEXES*

Electrochemical behavior of H2L1 and its Co(II), Ni(II), and Cu(II) complexes were investigated in between −1.5 V and 1.5 V. last two waves at 0.897 and 1.105 V are attributed to the oxidation of thiophenolic and naphtholic groups respectively 41–46. For the return sweep and three cathodic waves were observed at 0.748 −0.141 and −1.075 V. First wave observed at 0.748 V corresponds to the reduced species of the oxidized thiophenolic with a naphtholic groups. The Second wave is attributed to the naphtholic reduced form at −0.141 V while the third one observed at −1.075 V is attributed to the reduction of the azomethine group. Cyclic Voltammetry Study of Ligand. cyclic voltammograms of the ligand show three anodic waves.First one observed at 0.587 V may be ascribed to the oxidation of the naphtone generated from the tautomeric equilibrium.

Cyclic Voltammetry Study of Cu(II) Complex.cyclic voltammogram of CuL1 complex (Figure 8) exhibits four oxidation peaks. First peak at0.082 V corresponds to the oxidation of Cu(I) to Cu(II) and the last three peaks at E 0.352 0.943 V, and 1.174 V are attributed to the oxidation of azomethine groupthiophenolic group and naphtholic group respectively.On the cathodic side two peaks were observed at −0.346 V and

−0.705 V which correspond to the reduction of Cu(II) to Cu(I) and the reduction of the azomethine group respectively.
When this cyclic voltammogram is compared to that of the ligand the shift in the reduction potential of the azomethine group is observed.Is confirms the involvement of the azomethine group in coordination. However the oxidation potential of the thiophenolic and naphtholic to be more positive than the value observed for the ligand which may be related to the relative stability of the coordination bonding between the oxygen and sulfur atom with copper (II) ion controlled potential electrolysis carried out shows that the peak corresponds to a oneelectron transfer process as given in Scheme.However the oxidation potential of the thiophenolic and naphtholic moieties seems to be more positive than the value observed for the ligand

Which may be related to the relative stability of the coordination bonding between the oxygen and sulfur atom with cobalt (II) ione controlled potential electrolysis carried out shows that the peak corresponds to a oneelectron transfer process. Cyclic Voltammetry Study of Co(II) Complex.Voltammograms of CoL1 complex to exhibit one oxidation peak at −0.603 V corresponding to the oxidation of Co(II) to Co(III) and a reduction peak at −0.474 V corresponding to the reduction of Co(III) to Co(II).

When this cyclic voltammogram is compare to that of the ligand a disappearance of the azomethine group reduction peak in the complex is observed. oxidation of Ni(II) to Ni(III) and a reduction peak observed at0.487 V corresponding to the reduction of Ni(III) to Ni(II). When this cyclic voltammogram is a compared to that of the ligand a disappearance of the azomethine group reduction peak in the complex is observed. This However the oxidation potential of the thiophenolic and naphtholic groups seems to be more positive than the value observed for the ligand controlled potential electrolysis carried out shows that the peak corresponds to a one-electron transfer process.Ratio of cathodic to anodic peak height.

However, the peak current increases with an increase in the square root of the scan rates. Establishes the electrode process as diffusion controlled.Ratio of cathodic to anodic peak height of redox couple Ni(III)/Ni(II) is greater. Indicates the irreversibility of the system. We can only note that the plot of the cathodic potential peak versus the logarithm of a scan rate showed a nonlinear relationshipbut the cathodic potential depends on the scan rate is indicates that the processes at the surface of the electrodes are slow.A Cyclic voltammograms of the ligand and its complexes were scanned 20 times at a scan rate of 10 mV·s −1 and superposed. Since all the peaks were observed in the same position all the cycles it can be concluded that there is a no adsorption of the compound on the glassy carbon electrode surface.

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

- To synthesize some metal complexes Cu,Ni……
- Characterization of the metal complexes such as Scanning electron microscope (SEM) X-Ray Diffraction (XRD). Fourier Transform Infrared Spectroscopy (FTIR) UV-Visible Spectroscopy.
- Characterization of the Ni and Cu to (Ni/Cl, Cu/Cl) such as Scanning electron microscope (SEM), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible Spectroscopy.
- The complexes undergoes the oxidation and reduction
- I want know the stebility of complexes for that region is only carrying out cyclic voltammetry. Because of the metal and ligand of it is a coordinate complexes.
- Characterization of the β-diketone product obtained such as Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible Spectroscopy, Gas Chromatography Mass Spectrometry (GC-MS), Nuclear Magnetic Resonance (NMR).
- To study the Catalytic Kinetics.
- The reduction reactions of cyclic voltammetry.

3.2 SCOPE OF THE WORK:

The scope of this project is very wide indeed. The complex is oxidation and reduction that we synthesized can be applied for any of reduction reactions and it is not just limited to primary alcohols. Generally reduction reactions can take several hours to obtain complete conversion. In industries, time is a crucial factor for economical production. Instead of additional add-on methods to contribute to powerful oxidation which can be economically exhausting, the use of such catalysts is a good solution to such industrial problems.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 β-DIKETONE

4.1.1 ABSORPTION SPECTROSCOPY FOR β-DIKETONE

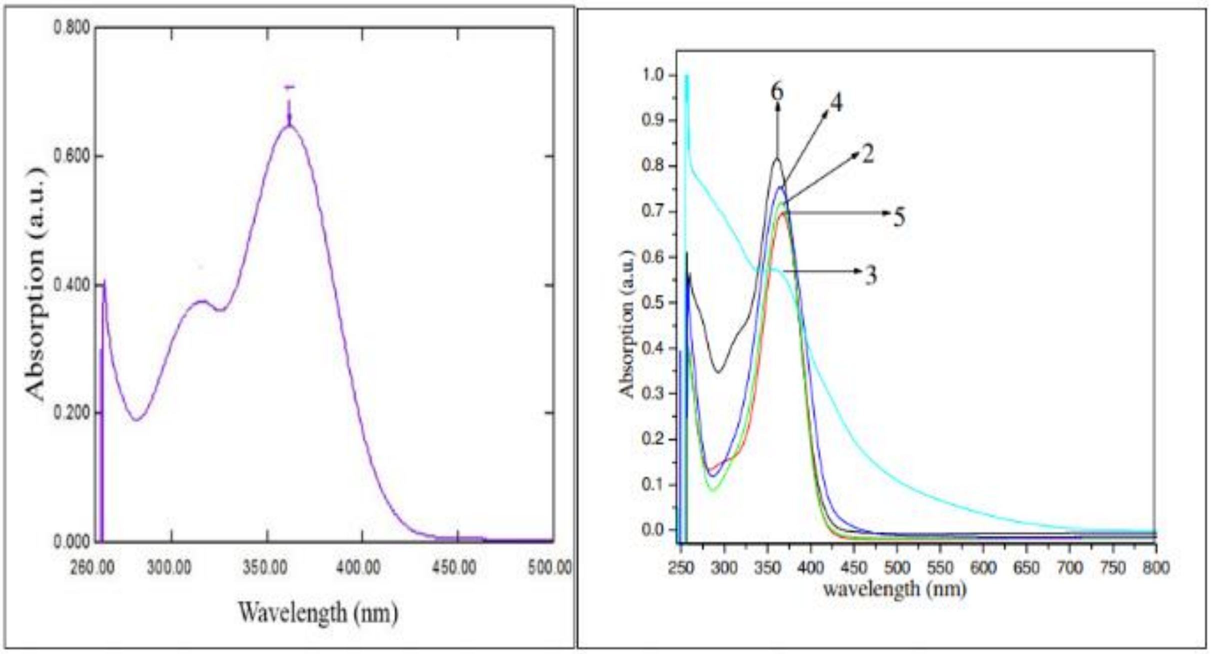
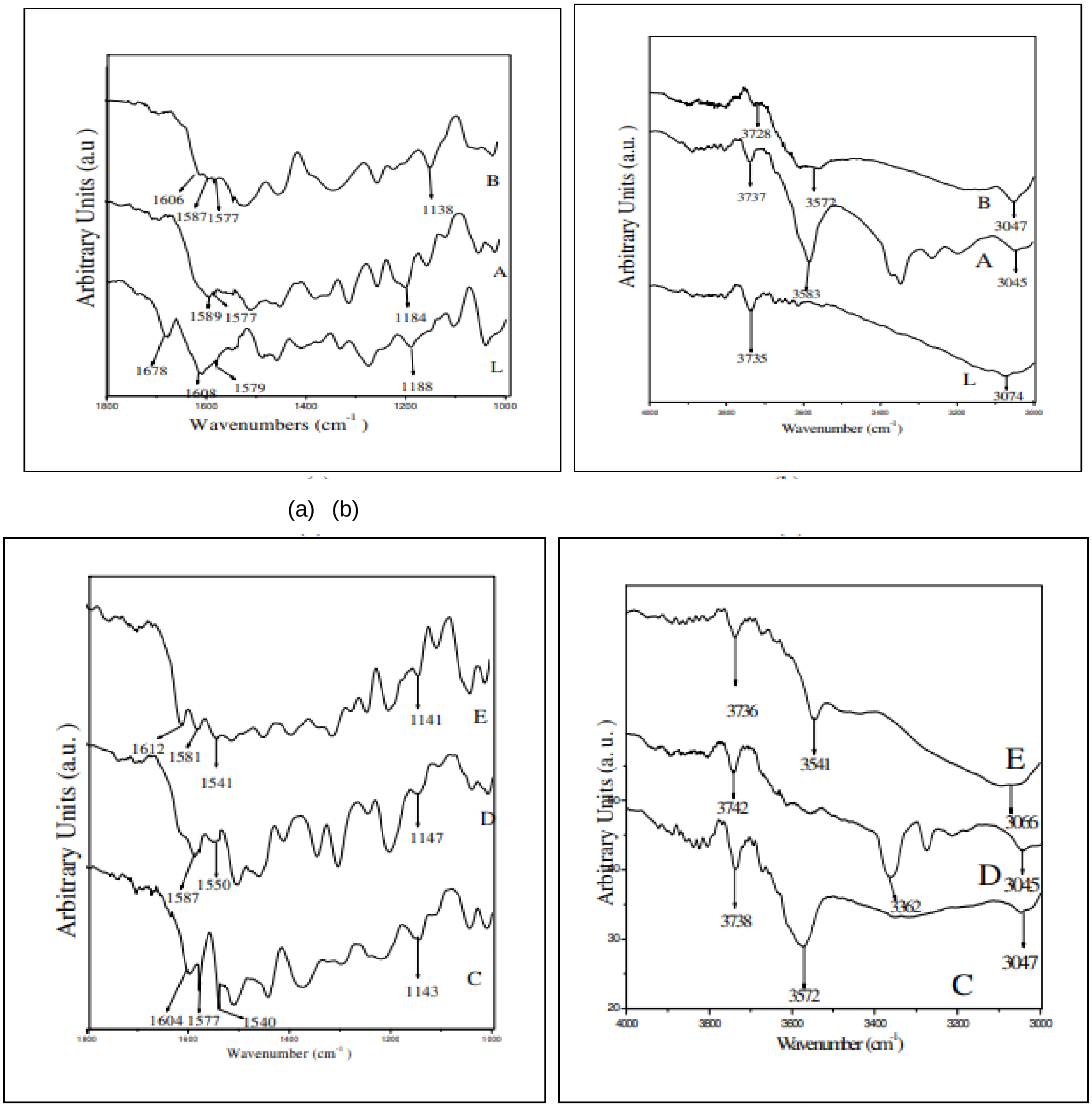


Figure 4.1 :absorption spectroscopy for β-diketone

Absorption Spectra for the Ligand (1) and Absorption Spectra for the Complexes 2= [Mn(L)2](H2O)2, 3 = [Fe(L)2](H2O)2, 4 = [Co(L)2](H2O)2, 5 = [Ni(L)2](H2O)2 & 6= [Cu(L)2](H2O)2.The ligand has three strong absorptions as seen The band of the shortest wavelength appearing at 265 nm may be attributed to π→π* transition of the aromatic ring moiety.In the spectra of metal β-diketone complexes the band of the longest wavelength shows an a obvious bathochromic shiftis relative to their free ligand while theto other two absorption peaks at 265 and 317 nm in the free ligand disappears or is observed as a shoulder with different intensity.

4.1.2 FT-IR SPECTRAL ANALYSIS OF LIGAND METAL COMPLEXES:



(a) (b)

(c)(d)

Figure 4.2 :FT-IR spectral analysis of ligand metal complex

The metal β-diketone complexes this band decreased in intensity and most likelyoriginating from the metalation which increases the conjugation and delocalization of the aromatic ring with a formhexahydric ring. In the IR spectra there is a weak and broad absorption at 3074 cm−1 in the free ligand which would be due to the unsaturated vCH stretching vibration of the aromatic ring.

4.2 DICHLOROMETHANE

4.2.1CYCLIC VOLTAMMETRY OF DICHLOROMETHANE

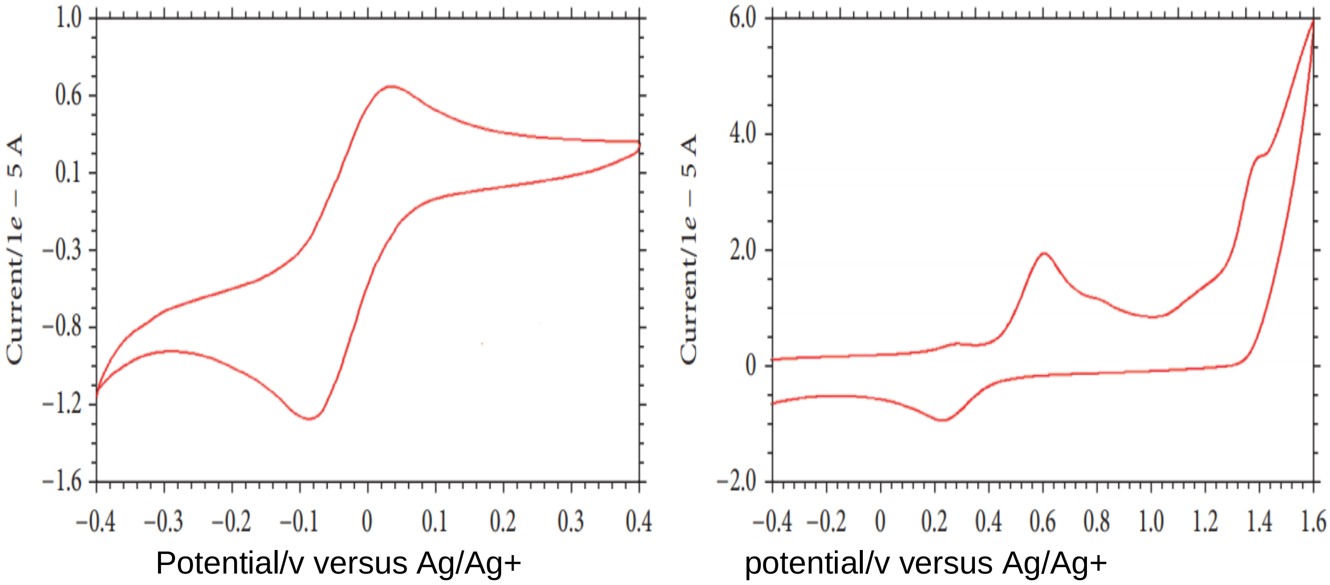


Figure 4.2.1: **cyclic voltammetry of dichloromethane**

Cyclic voltammogram of CuL2 and NiL2 in dichloromethane.Indicate that CuL2 undergoes one-electron reversible redox waves in potential range of 400 to −400 mV.

4.3 SCHIFF BASE LIGAND

4.3.1 FT-IR SPECTRAM OF SCHIFF BASE LIGAND

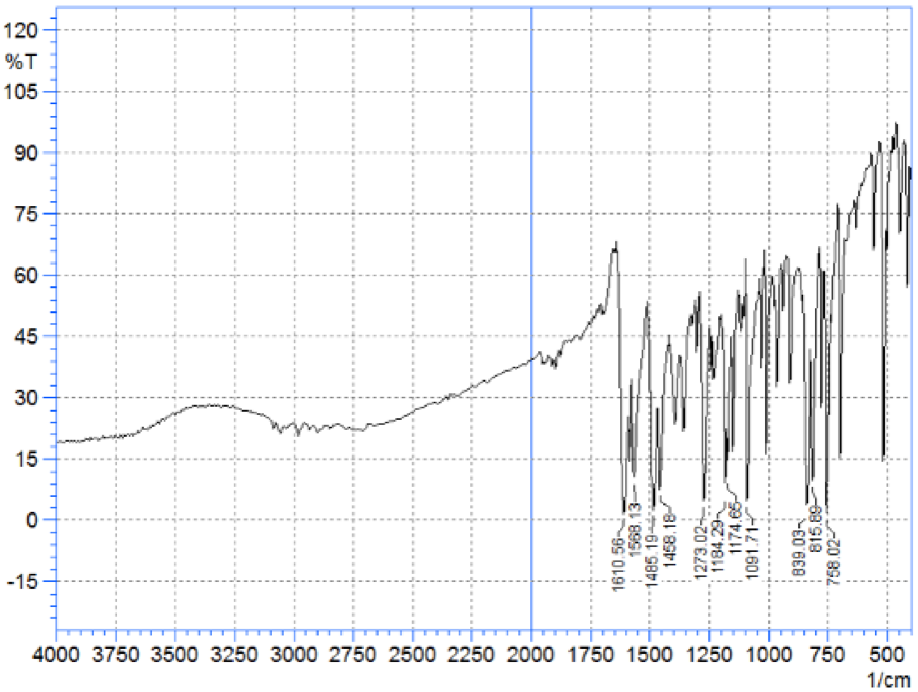


Figure **4.3.1 FT-IR spectrum of Schiff base ligand**

FT-IR spectroscopy is a powerful tool for assigning geometry to the coordination chemistry. the operational classes and their FT-IR frequencies of Schiff base ligand and its Co(II) and Mn(II) complexes are listed in Table 1, Figures 1,2 and 3. They were recorded in wave number 4000-400 cm-1**.**

4.3.2 CYCLIC VOLTAMMETRY OF SCHIFF BASE LIGAND

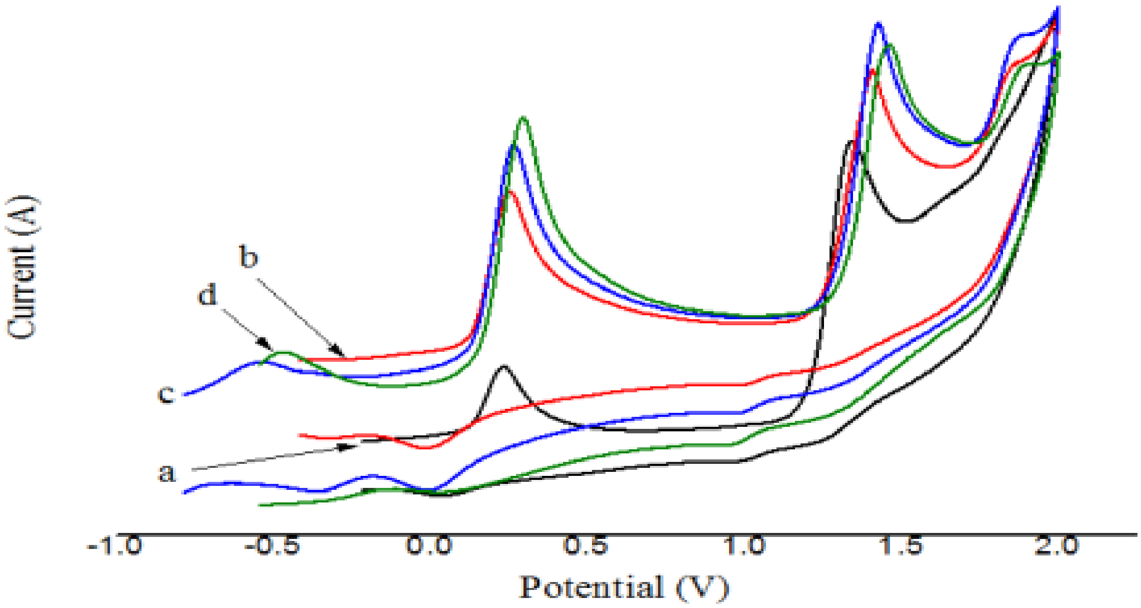
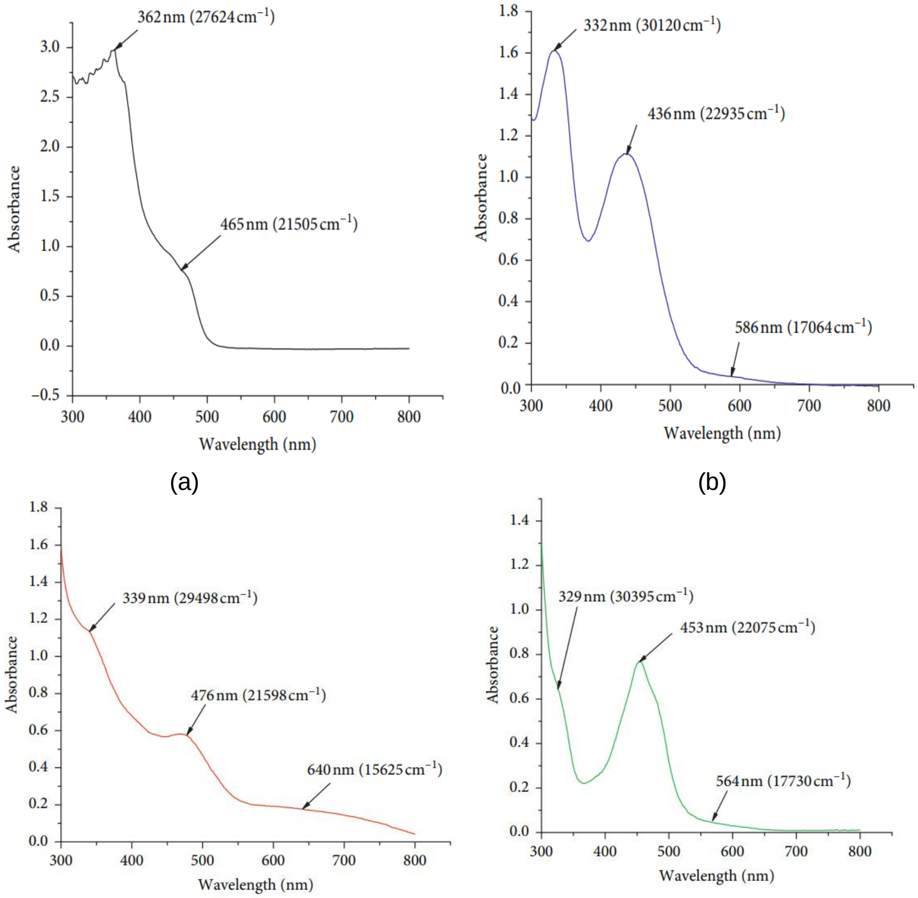


***Figure* 4.3.2 cyclic voltammetry of Schiff base ligand**

The cyclic voltammograms of the Schiff base ligand at different scan ratesa (0.05 Vs-1), b (0.1 vs-1), c (0.2 Vs-1) and d (0.5 Vs-1). The exhibited three irreversible redox peaks of oneelectron transfer may be to the formation of anions and cations species due to a reduction and oxidation process corresponding to an irreversible electron transfer.

4.4 LIGAND H_2L_1

4.4.1CYCLIC VOLTAMMETRY OF LIGAND H_2L_1



(a) (b)

(c)(d)

Figure **5.6 cyclic voltammetry of ligand H_2L_1**

Electronic spectrum of ligand H2L1 and its corresponding complexes,exhibit one oxidation peak at 0.603 V corresponding tooxidation of Co(II) to Co(III) and a reduction peak at −0.474 V corresponding to the reduction of Co(III) to Co(II).When this cyclic voltammogram is compared to that of the ligand a disappearance of the azomea as group reductio

CHAPTER 6

SUMMARY AND CONCLUSION

The present study is the some metal complexes undergos oxidation and reduction. Stebilitiy of the complexes is only carrying out cyclic voltammetry and its study to understand the metal and ligand of it is a coordinate complexes.

The application of the ligand to perform a conversion is studied by the conversion of β-diketone,chlorosalicykidenanline, Nickel and Copper, cobalt is betadiketone is potentially bidentate ligand its coordinate. Transition metal complexes have been prepared and characterized by physical spectral and analytical data. The infrared data conforming that, the coordination of metal ions with Schiff base ligand introduced via the nitrogen atom of azomethane and oxygen atom of the phenolic group.The Co(II) complexes appeared two irreversible oxidation peaks. All complexes had a deviation of current and potential to more anodic values when the cyclic sweep was done at different scan rates. Cyclic voltammetry studies on the ligand and its metal complexes reveal that the redox systems Co(III),Co(II) and Cu(II)/Cu(I) displayedreversible processes

REFERENCES:

1. Z. Lu, L.Yang, J. Inorg. Biochem., 95, 31(2003).

2. J. Z. Wu, H. Li, J. G. Zhang, H. Xu Ju, Inorg. Chem. Commun., 571, (2002).

3. J. D. Lee 5th Eds Concise Inorganic Chemistry. 195, (1996),

4. O. G. Khudina, Y. V. Burgart,N. V. Murashova, V. I. Saloutin, Russian J. Org. Chem., 39, 1421 (2003).

5. G. Aromi, P. G amez and J. Reedijk, Coordination Chemistry Reviews, 252, 964(2008).

6. S. T. Heller, S. R. Natarajan, Org. Lett.,8, 2675(2006).

7. D. Simoni, F. P. Invidiata, R. Rondanin, S. Grimaudo, G. Cannizzo, E. Barbusca, N. A. Porretto, F. D. lessandro, M. Tolomeo, J. Med. Chem., 42, 4961(1999).

8. H. Valizadeh, M. Amiri, E. Khalili, Molecular Diversity, 16(2), 319(2012).

9. L. Tang, S. Zhang, J. Yang, W. Gao, J. Cui, T. Zhuang, Molecules, 9, 842(2004).

10. R. Kumar, Y. C. Joshi, ARKIVOC, 9, 142(2007).

11. O. G. Kuzueva, Y. V.Burgart, V. I.Saloutin, O. N.Chupakhin, 37, 1130(2001).

12. L. Tchertanov, J. F. Mouscadet, J. Med. Chem., 50, 1133(2007).

13. Manuel, A., R. Silva and Luis M. Santos, J. Chem. Thermodynamics, 38, 817 (2005)

14. K. Binnemans, Chem. Rev. 107, 2592(2007).

15. R. Karvembu, K. Natarajan, Polyhedron, 212, 219(2002).

16. Huaqiang Zeng, JianmingXie, P. G. Schultz, Bioinorg. Med. Chem. Let, 16, 5356(2006).

17. Narendra A. Bhise, Shalini T. Dengle, Suresh T. Gaikwad and Anjali S. Rajbhoj Der Pharma Chemica, 8(19), 338(2016).

18. J. Charette, G. Neirynck. P. Teyssie, J. Phys. Chem.65, 735(1961).

19. R. Sultan, K. Gadamsetti, S. Swavey, Inorg. Chim. Acta. 359, 1233(2006).

20. D. Z. Ma, Y. Q. Wu, X. Zuo, Materials. Letters, 59, 3678

21. Singh HL. Synthesis, spectroscopic characterization, and 3D molecular modeling of lead(II) complexes of unsymmetrical tetradentate Schiff-base ligands. Res Chem Intermed. 2011;37(8):1087–101.

22. Garg BS, Nandan Kumar D. Spectral studies of complexes of nickel(II) with tetradentate schiff bases having N2O2 donor groups. Spectrochim Acta - Part A Mol BiomolSpectrosc. 2003;59(2):229–34.

23. Ziessel R. Schiff-based bipyridine ligands. Unusual coordination features and mesomorphic behaviour. Coord Chem Rev. 2001;216–217:195–223.

24. Cozzi PG. Metal-Salen Schiff base complexes in catalysis: practical aspects. Chem Soc Rev [Internet]. 2004 Sep 10;33(7):410–21. Available from:

25. Gupta KC, Sutar AK. Catalytic activities of Schiff base transition metal complexes. Coord Chem Rev. 2008;252(12–14):1420–50.

26. Costes JP, Shova S, Wernsdorfer W. Tetranuclear [Cu-Ln]2 single molecule magnets: Synthesis, structural and magnetic studies. Dalt Trans. 2008;(14):1843–9.

27. Ran X, Wang L, Lin Y, Hao J, Cao D. Syntheses, characterization and biological studies of zinc(ll), copper(ll) and cobalt(ll) complexes with Schiff base ligand derived from 2-hydroxy- 1-naphthaldehyde and selenomethionine. Appl Organomet Chem. 2010;24(10):741–7

28. Orio M, Jarjayes O, Kanso H, Philouze C, Neese F, Thomas F. X-Ray structures of copper(II) and nickel(II) radical salen complexes: The preference of galactose oxidase for copper(II). AngewChemie - Int Ed. 2010;49(29):4989–92.

29. Sengupta P, Ghosh S, Mak TCW. A new route for the synthesis of bis(pyridine dicarboxylato)bis(triphenylphosphine) complexes of ruthenium(II) and X-ray structural characterisation of the biologically active trans-[Ru(PPh3)2(L1H)2] (L1H2=pyridine 2,3- dicarboxylic acid). Polyhedron [Internet]. 2001;20(9):975–80. Available from:

30. Boghaei DM, Mohebi S. Non-symmetrical tetradentate vanadyl Schiff base complexes derived from 1,2-phenylene diamine and 1,3-naphthalene diamine as catalysts for the oxidation of cyclohexene. Tetrahedron [Internet]. 2002 Jun 24 [cited 2019 Oct 16];58(26):5357–66. Available from: https://www.sciencedirect.com/science/article/pii/S0040402002004817

31. Liu Z, Anson FC. Rate enhancements in the four-electron reduction of O2 by mixtures of vanadium(III) Schiff base complexes and decamethylferrocene in acetonitrile. J Mol CatalA Chem [Internet]. 2002;186(1):43–51. Available from:

32. Mersal GAM, Majid A, Adam A, Hassan RF, Refat MS. Spectral and cyclic voltammetric studies of glyceryl guaiacolate drug in pure form and in situ chelation with some different transition metals. J Mol Liq [Internet]. 2017;237:128–40. Available from: http://dx.doi.org/10.1016/j.molliq.2017.04.086

33. Tadavi SK, Rajput JD. Synthesis, crystal structures, biological screening and electrochemical analysis of some salen-based transition metal complexes. Res Chem Intermed. 2017;

34. Tadavi SK, Yadav AA, Bendre RS. Synthesis and characterization of a novel schiff base of 1,2- diaminopropane with substituted salicyaldehyde and its transition metal complexes: Single crystal structures and biological activities. J Mol Struct [Internet]. 2018;1152:223–31. Available from: https://doi.org/10.1016/j.molstruc.2017.09.112

35. A. J. L. Pombeiro J. A. McCleverty. Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds: NATO Advanced Research Workshop. A. J. L. Pombeiro and J. A. McCleverty, editor. Amsterdam-New York: Kluwer Academic Publishers; 1993. 311 p.

36. Ebara N. Benzylideneaniline. III. Anils of Substituted Benzaldehydes. Bull Chem Soc Jpn. 1961;34(8):1151–8.

37.Cross S, Com III, Lig S, Wang M. Structure, Magnetic Properties, Mössbauer and Catalase-like Activity of Spin Crossover Iron(III) Complexes with Salicylaldimine Ligands. J Chinese Chem Soc. 2002;49:825–32.

38. LIU J, Wu B, Zhang B, LIU Y. Synthesis and Characterization of Metal Complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with Tetradentate Schiff Bases. Turk J Chem [Internet]. 2006;30:41–8. Available from: http://journals.tubitak.gov.tr/chem/abstract.htm?id=8061

39. Y.K.1 G, S.C. A, S.P. M, Ram N. Synthesis, Characterization and Antimicrobial Studies of Some Transition Metal Complexes of Schiff Bases. Res J Chem Sci [Internet]. 2012;2(4):68–71. Available from: www.isca.in

40. Utthra PP, Kumaravel G, Raman N. Screening the efficient biological prospects of triazole allied mixed ligand metal complexes. J Mol Struct [Internet]. 2017;1150:374–82. Available from: https://doi.org/10.1016/j.molstruc.2017.09.002

41. S. Nica, M. Rudolph, I. Lippold, A. Buchholz, H. G¨orls, and W. Plass, "Vanadium(V) complex with Schiff-base ligand containing a flexible amino side chain: synthesis, structure and reactivity," Journal of Inorganic Biochemistry, vol. 147, pp. 193–203, 2015.

42. L. Xiang and H. Jean-Rene, "Recent developments in penta-, ´ hexa- and heptadentate Schiff base ligands and their metal complexes," Coordination Chemistry Reviews, vol. 389, pp. 94–118, 2019.

43.J. Rangaswamy, H. Vijay Kumar, S. T. Harini, and N. Naik, "Synthesis of benzofuran based 1,3,5-substituted pyrazole derivatives: as a new class of potent antioxidants and antimicrobials—a novel accost to amend biocompatibility," Bioorganic & Medicinal Chemistry Letters, vol. 22, no. 14, pp. 4773–4777, 2012.

44. E. M. McGarrigle and D. G. Gilheany, "Chromium- and Manganese-salen promoted epoxidation of alkenes," Chemical Reviews, vol. 105, no. 5, pp. 1563–1602, 2005.

45. Z. Guo, R. Xing, S. Liu et al., "Antifungal properties of Schiff bases of chitosan, N-substituted chitosan and quaternized chitosan," Carbohydrate Research, vol. 342, no. 10, pp. 1329–1332, 2007.

46. M. Amjad, S. H. Sumrra, M. S. Akram, and Z. H. Chohan, "Metal-based ethanolamine-derived compounds: a note on their synthesis, characterization and bioactivity," Journal of Enzyme Inhibition and Medicinal Chemistry, vol. 31, no. 4, pp. 88–97, 2016.

47.L. Jian, L. Tingting, C. Sulan, W. Xin, L. Lei, and W. Yongmei, "Synthesis, structure and biological activity of cobalt (II) and copper (II) complexes of valine-derived Schiff bases," Journal Inorganic Biochemistry, vol. 100, pp. 1888–1896, 2006.

48. H. Zahid, M. Arif, A. Muhammad, and T. Supuran, "Metalbased antibacterial and antifungal agents: synthesis, characterization, and in vitro biological evaluation of Co(II), Cu(II), Ni(II), and Zn(II) complexes with amino acid-derived compounds," Bioinorganic Chemistry and Applications, vol. 2016, Article ID 083131, 13 pages, 2006.

49.G. Elif, C. Selma, A. Dilek, and K. Hulya, "Two tridentate Schiff base ligands and their mononuclear cobalt (III) complexes: synthesis, characterization, antibacterial and antifungal activities," Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 94, pp. 216–222, 2012.

50. P. Ikechukwu and M. Fanyana, "Cu(II) complexes of tridentate Schiff base ligand: synthesis, characterization and biological evaluations," Medicinal Chemistry, vol. 7, no. 11, pp. 1–32, 2017.

51. Rauf, A.; Shah, A.; Khan, A. A.; Shah, A. H.; Abbasi, R.; Qureshi, I. Z.; Ali, S. Spectrochim. Acta, Part A., 2017, 176, 155-167.

52. Mohamed, G. G.; Omar, M. M.; Hindy, A. M. Turk. J. Chem., 2006, 30, 361-382.

53. Ismail, T. M. J. Coord. Chem., 2006, 59(3), 255-270.

54. Nanjundan, N.; Narayanasamy, R.; Geib, S.; Velmurugan, K.; Nandhakumar, R.; Balakumaran, M. D.; Kalaichelvan, P. T. Polyhedron., 2016, 110, 203-220.

55. Ashassi-Sorkhabi, H.; Shabani, B.; Aligholipour, B.; Seifzadeh, D. App. Surf. Sci., 2006, 252, 4039-4047.

56. Ehteshamzade, M.; Shahrabi, T.; Hosseini, M. G. App. Surf. Sci., 2006, 252, 2949-2959.

57. Dadgarnezhad, A.; Sheikhshoaie, I.; Baghaei, F. Asian J. Chem., 2004, 16, 1109-1118.

58. Shokry, H.; Yuasa, M.; Sekine, I.; Issa, R. M.; El-Baradie, H. Y.; Gomma, G. K. Corros. Sci., 1998, 40(12), 2173-2186.

59. Dey, R. K.; Jha, U.; Singh, A. C.; Samal, S.; Ray, A. R. Anal. Sci., 2006, 22(8), 1105-1110.

60. Sabry, S. M. J. Pharm. Boimed. Anal., 2006, 40(5), 1057-1067.

61. Okochi, M.; Ohta, H.; Taguchi, T.; Matsunaga, T. Electrochim. Acta., 2005, 51(5), 952-955.

62. Salimi, A.; Mamkhezri, H.; Mohebbi, S. Electrochem. Commun., 2006, 8(5), 688-696.

63. Gholivand, M. E. B.; Ahmadi, F.; Rafiee, E. Electroanalysis (N. Y. N. Y.)., 2006, 18(16), 1620-1626.

64. Liu, G.; Cogan, D. A.; Owens, T. D.; Tang, T. P.; Ellman, J. A. J. Org. Chem., 1999, 64(4), 1278-1284.

65. Love, B. E.; Ren, J. J. Org. Chem., 1993, 58(20), 5556-5557