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SYNTHESIS, CHARACTERIZATION AND ENCAPSULATION OF BIPYRIDINE TRANSITION METAL COMPLEXES IN ZEOLITE Y

By: Alehegn Eskemech

Advisor: Dr. Yonas Chebude

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Synthesis, Characterization and Encapsulation of Bipyridine Transition Metal Complexes in Zeolite Y

Alehegn Eskemech

A Thesis Submitted to the Department of Chemistry in Partial Fulfillment of the Requirement for the Degree of Master of Science (Inorganic Chemistry)

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This is to certify that the thesis prepared by Alehegn Eskemech, entitled: Synthesis, Characterization and Encapsulation of Bipyridine Transition Metal Complexes in Zeolite Y and submitted in fulfillment of the requirements for the Degree of Master of Science (Inorganic Chemistry) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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Abstract:

Transition metal (M = Co(II), Ni(II) and Cu(II)) complexes have been synthesized by refluxing the metal chloride with ligand, 2,2’–bipyridine .Tris(2,2’-bipyridine)complexes of cobalt(II), nickel(II), and copper(II) have been encapsulated within the supercage of zeolite − NaY by the reaction of exchanged metal ion and flexible ligand that diffuses into the cavities. The hybrid material obtained and neat metal complexes have been characterized by FTIR, elemental analysis (CHN), UV−vis, magnetic susceptibility, molar conductance measurements, cyclic Voltammetry, TGA and Inductive Coupled Plasma (ICP) techniques. Infrared spectra of the complexes revealed that higher frequency shifts of varying magnitudes were observed in the (C=N) and lower in the (C=C) aromatic stretching vibrations from their ligand values. TGA was used to analyze the principal volatile thermal decomposition (fragmentation) products of 2, 2-bipyridne complexes (encapsulated and neat).The TGA and CHN data of intrazeolite complexes in comparison to those of the neat complexes suggest that the insertion of small amount of organic molecules(2,2-bipyridine) into the pores of the zeolite.

Keywords: Heterocyclic Ligand, Zeolite, Encapsulation, Flexible Ligand Method, 2, 2’-Bipyridine

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Table of Contents

List of Table

List of Figure

List Abbreviations

BPY	2, 2'-bipyridine
CHN	carbon, Hydrogen, Nitrogen
DCM	dichloromethane
DSC	dye-sensitized solar cell
FAU	faujasite
FT_IR	Fourier transformation infrared spectroscopy
ICP	inductively coupled plasma spectrometer
M	transition metal
MW	molecular weight
MY	transition metal exchange zeolite
NaY	type Y zeolite
Phen	1, 10-phenanthroline
TGA	Thermogravimetric analysis
THF	tetra hydro furan
ε	extinction coefficient
μ_{eff}	effective magnetic moment
χ_g	gram susceptibility
χ_m	molar susceptibilit

Introduction

1.1 Transition Metal Complexes

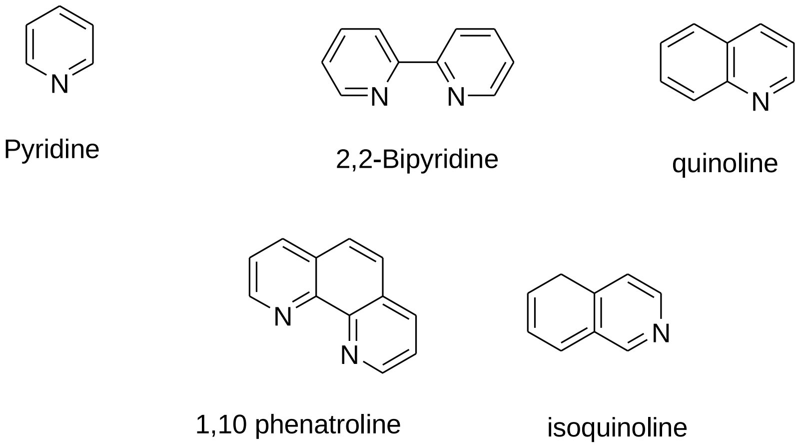
A transition metal complex is a species a consisting of a transition metal coordinated (bonded to) one or more ligands (neutral or anionic non-metal species) .Transition metal complexes are important in catalysis, materials synthesis, photochemistry, and biological systems. They display diverse chemical, optical and magnetic properties [1, 2]. Coordination complexes have always been a challenge to the inorganic chemists since they were identified in the nineteenth century. The chemistry of coordination compounds containing metal-nitrogen bonds has attracted increasing attention. The interest in these metal complexes, particularly those of bipyridine and its derivative, is due to their potential applications in homogenous catalysis, visible light photocatalysis[3,4], dye-sensitized solar cell (DSC)[5]and therapeutic agents(6) .

In part, the interest has also been due to the relevancy of the compounds in biochemistry and uses of complexes as antioxidant, oil additives, drugs and cosmetics, and coloring agents for plastics and as pesticides [7-10]. It is well known that N-donor ligands coordinate to a metal atom in different ways in different media depending on the diversified synthetic procedures. Complexes of nitrogen- nitrogen chelating ligands, nitrogen bridging and nitrogen semi bridging ligands with various metals are also been studied extensively [11-12]. The present study attempts to prepare complexes using cobalt, nickel and copper with some heterocyclic ligands viz, 2, 2- bipyridine outside and inside the zeolite Y.

1.2 Heterocyclic Compound

Heterocyclic compounds are organic compounds containing over carbon and hydrogen, hetero atoms such as oxygen, sulfur or nitrogen in the framework of the ring structure that can show both aromatic and aliphatic properties [13].

Heterocyclic compounds are very widely distributed in nature and are essential to life in various ways [14]. Most of the heterocyclics possess important applications in materials science such as dyestuff, fluorescent sensor, brightening agents, information storage, plastics, and analytical reagents. In addition, they have applications in supramolecular and polymer chemistry, especially in conjugated polymers. Moreover, they act as anticorrosive agents, photostabilizers, agrochemicals, copolymers, photographic developers, fluorescent whiteners, sensitizers, booster agents, antioxidants in rubber, and flavoring agents. Heterocycles are also of considerable interest because of their synthetic utility as synthetic intermediates, organic catalysts, and metal ligands in asymmetric catalysts inorganic synthesis [15, 16].The most common heterocyclic systems contain heteroatoms N, O or S and good examples of these are six-membered heterocycle pyridine and five-membered heterocycles pyrrole, furan and thiophene.Pyridine is one of the most common and best known heterocycles. It is an excellent polar solvent and act as a donor ligand in metal complexes. Aromatic nitrogen-containing heterocycles such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and related molecules are widely employed as ligands in coordinationand organometallic chemistry,especially in homogeneouscatalysis. Their interesting redox and photoredox chemistry means that they play a leading role in studies of electron and energy transfer[17]. Some interesting heterocyclic compounds are indicated below



Pyridine

2,2-Bipyridine

quinoline

1,10 phenatroline

isoquinoline

Figure 1.Some Examples of N-Heterocyclic Ligands

1.2.1 Chemistry of Bipyridine

Pure 2, 2'-bipyridine was synthesized for the first time in the late 19th century by distillation of copper picolinate. A more convenient synthesis was eventually achieved when Raney-nickel alloy was used as a catalyst. Since the preparation of the first 2, 2'-bipyridine complex in 1888, the derivatives of bipyridine have been widely employed in complexation experiments [18] .2, 2'-bipyridine is both a σ-donor and a π-acceptor. The lone electron pair of nitrogen can form a σ-bond with the central atom, while the aromatic system can take part in back-bonding.

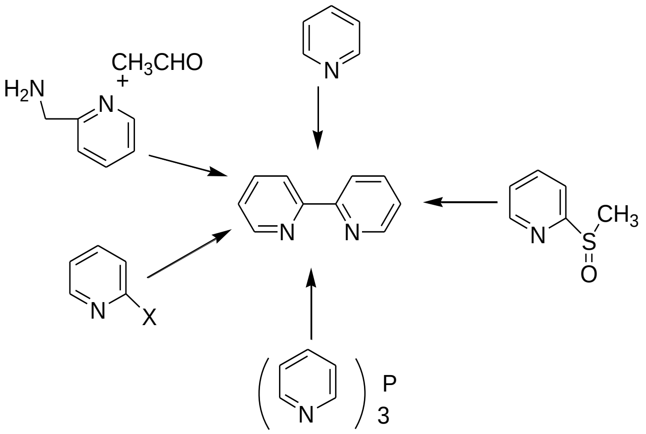


Figure 2 .Synthetic strategies towards 2,2 -bipyridine [18]

1.2.2 Metal Complexes of 2, 2-Bipyridine

2, 2- Bipyridine has two rings and two coordinating N atoms, and therefore it is very easy for this ligand to chelate a transition metal ion. Furthermore, the two aromatic rings of this molecule make the electrons more delocalized. As a result bipyridine complexes of transition metals usually possess properties of more interesting than those of pyridine complexes. Bipyridine ligand stabilizes soft metal ions, especially transition metal ions in low oxidation states [19]. Ligands with two or more donor atoms are able to form a chelate ring with metal atoms. 2,2'-Bipyridines,having two nitrogen donor atoms separated by two carbons, form five-membered rings, which are the most stable structures. The diimine part of the bipyridine delocalizes the electrons in the chelate ring.Diimines like 2, 2'-bipyridines and substituted bipyridine are undoubtedly among the most widely used ligands in coordination and supramolecular chemistry. The photophysical properties of their metal complexes are of special interest. In particular, electroluminescent chelate complexes have been shown to be useful in organic light emitting diodes (OLEDs).Ruthenium complexes of functionalized bipyridines are presently the most effective sensitizers for dye-sensitized solar cells (DSSCs) are of special interest as complex ligands in coordination and supramolecular chemistry [20].Moreover, the ability of bipyridines to form ionic and neutral guest compounds makes them useful precursors in supramolecular chemistry. Self-organization of bipyridine structures and metal cations often leads to the formation of helicates, which are supramolecular complexes formed between preorganized receptors and metal ions[21] Their long-lived, luminescent, charge-transfer state enables them to be used as sensitizers in photochemistry[22] .

In the "tris (bipy) complexes" three bipyridine molecules coordinate to a metal ion, written as $[M\ (bipy)_3]^{n+}$ (M = transition metal ion; Cr, Fe, Co, Ru, Rh and so on; bipy = 2, 2'-bipyridine). These complexes have six-coordinated, octahedral structures and two enantiomers. Polypyridyl complexes such as $Ru/Rh(bpy)_3{}^{+2}$ employed as visible light photocatalysts and absorb light in the visible region of the electromagnetic spectrum to give stable, long-lived photoexcited states [3, 4].The tris complexes of the first row transition metals in normal oxidation states (+2, +3) are best prepared by the reaction of a suitable metal salt with an excess of bpy in water, methanol or other organic solvent. The redo chemistry of polypyridyl complexes has been studied due to their potential applications as anticancer agents for structural changes in DNA and in solar energy conversion and water splitting [23, 24].

1.3 Zeolite

Zeolites are porous metal oxides, typically aluminosilicates, which contain extensive cavities and well-defined channel structures with, pore diameters in the 3-12Å range. Zeolites are crystalline minerals that are broadly present in nature and have been known to mankind for almost 250 years. In 1756 Axel Fredrick Crønstedt discovered the natural occurring mineral, nowadays known as stilbite, lost large amounts of steam upon heating. Therefore he named the material 'zeolite' which emerges from the classical Greek, where ζεω (zeo) means ‘to boil’ and λιθος (lithos) means ‘stone’ [25, 26]. Some of the more fundamental properties of zeolites were established over a period of 130 years beginning in 1840, when Damour reported that zeolites had undergone reversible dehydration with no apparent change in the transparency of the crystal form, and in 1858 Eichhorn observed the reversibility of ion exchange on zeolite minerals. In 1930, Taylor and Pauling determined the crystal structure of the zeolites and showed evidence of the presence of cavities in these structures; soon after in 1932 McBain established the term “molecular sieve” to describe the porous solid materials, and the ability of zeolite structure to act as sieves on a molecular scale. In 1945 Barrer reported the first classification of zeolite minerals based on the size and the rate of molecules absorbed: rapidly, slowly or not significantly at room temperature. In the early 1950s, Milton and Breck discovered the commercially vital synthetic zeolites A, P, X and Y.These zeolites were synthesized from readily available raw materials. At that time, only aluminum-rich zeolites could be synthesized. In 1967, Wadlinger and his co-workers introduced the first silica-rich forms of zeolite beta (BEA) [25].

Nowadays, zeolites are widely used in many applications due to their unique properties (thermal stability, acidity, hydrophobicity/hydroplicity of surfaces, ion-exchange capacity, low density and large void volume, uniform molecular sized channels, adsorption for gas and vapor and catalytic properties). Zeolites have found a broad range of industrial applications as catalysts, adsorbents, molecular sieves and ion exchangers. The major use of zeolites is as ion exchangers in laundry detergents, adsorbents, and in the separation of different isomers and gas-mixtures (petroleum refining, petrochemical, coal), moreover they are applied in water treatment processes such as water softening and purification from ammonia, heavy metals, radioactive species, dissolved or emulsified organic substances, toxic anions, odor and solids. They also can be exploited as mineral fertilizer additives, soil amendments for agricultural purposes, construction and building materials, cement additives, sorbents for oil spills, desiccant materials, water filtration adjuvant, domestic uses, carrier for pesticides, herbicides, animal feed additives, toxin binders, animal waste management, odor control, chemical spills[27,28,].

1.3.1 Structural Aspects of Zeolites

Zeolites are crystalline, micro porous, hydrated aluminosilicates that are built from an infinitely extending three dimensional network of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked to each other by the sharing of oxygen atoms [29]. Generally, their structure can be considered as inorganic polymer built from tetrahedral TO4units, where T is Si^{4+}or Al^{3+} ion. The structure formula of zeolite is based on the crystallographic unit cell [25]: $M_{x/n} [(AlO_2)_x (SiO_2)_y] .wH_2O$, where M is an alkali or alkaline earth cation, n is the valence of the cation, w is the number of water molecule s per unit cell, x and y are the total number of tetrahedra per unit cell. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation. Typically, these counter ions are elements from the IA and IIA groups of the periodic table. The cations can reversibly be exchanged for other ions possessing the same sign charge when aqueous passed through channels and voids. This replacement results in the narrowing of the pore diameter of the zeolite channels. The water may be removed reversibly by the application of heat.

With the oxygen atoms distributed throughout the zeolite network, a rich variety of beautiful three-dimensional structures may be found. The two types of tetrahedral units can be arranged in a variety of ways and presented in different ratios – including the faujasite type zeolite, for instance, which is characterized by interconnected voids bounded by supercages with a diameter of 1.3 nm that can host cations and water molecules. As such water moves freely inside the structure, but the zeolite framework remains rigid. Figure 3 shows a tetrahedral structure that consists of a Si or Al atom in the middle and oxygen atoms at the corners. The oxygen at each tetrahedral corner is connected with another tetrahedron by straight lines that schematically represent the T-O-T bridges. These tetrahedrons are called primary-building units (PBUs) and combine to shape the secondary- building units or SBUs that give rise to the unique topology. As soon as SBUs are linked together, the sodalite like in zeolite Y or any other geometrical shapes can be formed [25, 26,].

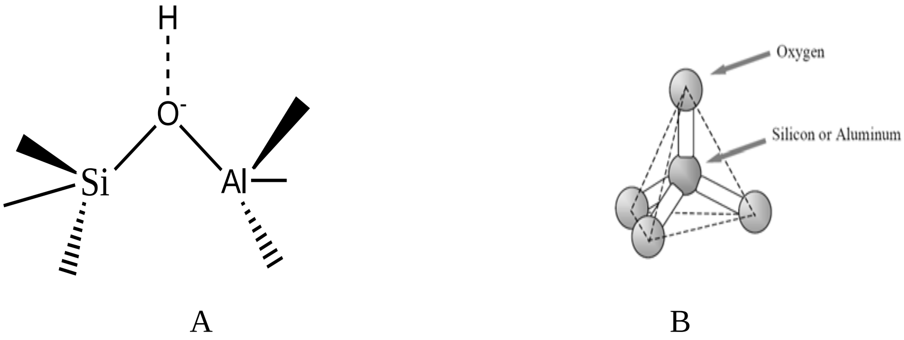


Figure 3 Chemical Structure of Zeolite (A) and Primary Building Unit of Zeolite Structure (B)

Zeolites A, X, Y are a group of zeolite which belongs to the faujasite type of zeolites. The aluminosilicates framework of zeolite A contains two types of polyhedra, a simple cubic arrangement of eight tetrahedra, (D4R) and other a truncated octahedron of 24 tetrahedra (sodalite unit). The zeolite X and Y contain a D6R secondary building units (double 6 ring, containing twelve silica alumina tetrahedral) and a sodalite unit. The sodalite unit has six 4-membered ring and eight 6-membered rings. Zeolite A is formed when the sodalite units are joined through the 4-membered ring (square) faces and zeolite X, Y are formed by joining of the hexagonal 6-membered faces of sodalite unit. Zeolite X and Y differ in their Si/ Al ratio which varies from 1.5 to 3 for zeolite Y and 1 to 1.5 for zeolite X. Zeolites have well defined pore system. The cavity of the sodalite unit is known as the β-cage while the large cavity (supercage) formed by the joining of the sodalite unit gives rise to α cage. The α cage diameter for zeolite Y is 13 Å and the α cage aperture is about 8 Å.

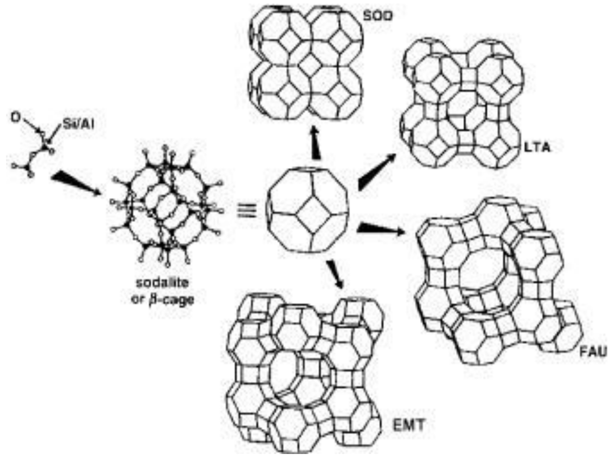


Figure 4 Structural Units of Zeolite (Sodalite Unit, Zeolite A and Zeolite Y)

1.3.2 Zeolite encapsulated metal complexes

The polyhedral cavities in zeolite Y inscribe a cavity of substantial dimensions that they could be able to hold clusters of small molecules in addition to the appropriate numbers of exchangeable cations. Proper choice of complex molecule of correct size that fit securely within the ≈ 13 Å supercages of zeolite Y ensures that the molecule cannot escape through the ≈ 7 Å ring opening of the supercage [30].

Over the past decade, the encapsulation of transition metal coordination complexes and organometallics within the voids of microporus zeolite has attracted attention, since it provides a simple way of coupling the reactivity of the metal complex with the robustness and stereochemistry of the host zeolite. The encapsulation approach is convenient and ideal because the complex once formed inside the cages of the zeolite is too large to diffuse out and is not lost in the liquid phase during the reaction. The topology of the voids has a profound influence on the encapsulated complexes, resulting in a constrained chemistry occurring inside such small cavities. The space constraints imposed by the zeolite matrix lead to a change in the geometrical parameters, electronic properties, reactivity's, and redox behavior of the complexes in comparison to the neat complexes in solution, which in turn has led to the wide applications of these hybrid materials in heterogeneous catalysis. These hybrid catalysts offer the advantage of shape selectivity and site isolation, as provided by the zeolite matrix, while retaining the solution reactivity of the metal complex [31, 32].

Many coordination complexes can be formed with in the zeolite pores by simple reaction of the exchangeable cations with various organic molecules. A variety of transition metal complexes have been successfully encapsulated in zeolites and show improved catalytic properties in the oxidation of different types of organic substrates .Typical complexes that have been incorporated are metal phthalocyanine complexes, metal porphyrin complexes and metal Schiff base complexes[30,33,34]. Several methods have been developed for encapsulation of transition metal complexes inside the three-dimensional pore structure or the supercage of zeolite.

1.3.2.1 Flexible ligand method

This method was first introduced by Heron in the synthesis of encapsulated complexes of bis(salicylaldehyde)ethylenediamine(salen) in the cavities of faujasite [35,436,37]. In this approach, the ligand must be able to diffuse freely through the zeolite pores having an advantage to complex with a previously exchanged metal ion and or synthesis of the metal complex in situ in the zeolite cavity by reaction of the ligand with the exchanged metal cations. The shaped complex becomes too large and rigid to escape from the cage. This method takes advantage of the flexibility of the ligand which enables it to enter the cavities of the zeolite host material through the restricting windows.

The bipyridine is able to enter the pores of zeolite due to possible free rotation around the carbon-carbon sigma bond. The ligand gets access to larger cages where they react with the transition metal ions previously introduced into the lattice. Once the ligand has entered the zeolite cage and complexed with previously exchanged transition metal ions, the complex adopts a suitable geometry and cannot diffuse out of the zeolite pores. The salen complexes of Fe(III),Co(II),Mn(II),Rh(II) and Pd(II) are already synthesized by this method[35,438,39]. A similar method was adopted for the synthesis of bipyridyl complexes of Fe (II),Mn(II), Cu(II) and Ru(II)[40]. The encapsulated complexes prepared by this technique exhibit good catalytic activity and the catalysis have been reported to depend upon the transition metal ion and the nature of the Schiff base ligands .The flexible ligand method was also adopted for the synthesis of highly selective bis and tris-coordination complexes.

In this work,$[M(bpy)_3]^{2+}$ were synthesized using a flexible ligand technique, where the supercages of these zeolite Y are doped with M^{2+}(M= Co, Ni and Cu)ions and, subsequently, with the ligand 2,2-bipyridine through the windows of the zeolite structure.

1.3.2.2 Ship-in-a-bottle synthesis

The ship-in-a-bottle method was first suggested by Romanovsky and his coworkers to encapsulate transition metal phthalocyanine in zeolites [41]. This method of encapsulation involves the synthesis of the metal complex from smaller components of the ligand within the zeolite voids or assembling it from smaller species around the transition metal ions. This procedure was adopted for the synthesis of phthalocyanine complexes of cobalt, nickel, copper, iron, and manganese [42, 43]. The bipyridine complexes of Fe (II), Co (II), and Ru(II) were already synthesized by this method[44,45,46].

1.3.2.3 Zeolite synthesis methods

Zeolite synthesis method is one of the recent methods for synthesizing zeolite encapsulated complexes. In this method, a zeolite structure is synthesized around the pre-formed complex .The newest zeolite synthesis method has the obvious advantage that the nature of the intrazeolite species is well-defined and no free ligand need to be removed. However, there is a heterogeneous distribution of metal complex in the precursor gel and the complexes cannot be evenly distributed within the zeolite crystals, which have a direct effect on the loadings of the metal complex in the zeolite host. The transition metal complexes which are stable under the conditions (at the temperature, hydrothermal and pH) of zeolite synthesis are included in the synthesis mixture. Metal phthalocyanine, porphyrins and amino acids provide examples of such encapsulated catalysts [47].

2 Objective

2.1 **General objectives**

The main objective of the present work is to synthesize and characterize transition metal complexes of Co (II), Ni (II) and Cu (II) with ligand (BPY) in the supercages of zeoliteY.

2.2 Specific objective

To synthesize and characterize zeolite encapsulated Transition metal, Co (II) Ni (II) and Cu (II) complex catalyst.

To study the redox potentials of the neat complex and the encapsulated metal complex using cyclic voltammetry

3 Experimental

3.2 Materials and Reagent

3.2.1 Reagents

All chemicals used are analytical reagent grade. The chemicals were 2,2-bipyridine, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, NaYzeolite (FAU, CBV100, Si/Al=2.83) in powder form were obtained from zeolyst international.

3.3 Solvents

All the solvents used in this work are distilled before use. The solvents were ethanol, methanol, acetone, THF, diethyl ether, double distilled water, acetonitrile**,** dichloromethane.

3.4 Instrumentation

The IR spectra of the ligand, the neat metal complex, the metal exchanged zeolite and zeolite encapsulated transition metal complex were recorded using KBr pellets on Perkin-Elmer BTXFT-IR Spectrometer. Electronic spectra were obtained using a SPECTRONIC GENESYS 2pc UV/VIS spectrophotometer. The uv-vis spectra of the metal complexes were determined in acetonitrile and methanol. The percentage composition of the elements (CHN) of the complexes was determined using an elemental analyzer and the complex was analyzed for its metal (Co, Ni and Cu) content with ICP. Magnetic susceptibility was measured at room temperature (22 and 20^{o}C) with a Sherwood Scientific MSB-Auto magnetic balance. The conductances of the metal complexes (~ 10^{-3}M solution) were determined in H_2O at room temperature using an EC 214 Bench conductivity meter. The cyclic voltammograms of neat and encapsulated complexes are recorded on an electrochemical analyzer CHID760, and 0.1 MTBAP (tetra butyl ammonium phosphate) in acetonitrile is used as the supporting electrolyte. The zeolite modified glassy carbon working electrode (ZME) is prepared by dispersing 50 mg of M LY and 50mg of graphite powder in 200 µmL of DCM and300 µmL of THF . A 10mg of polystyrene (as binder) is added and small portion of this dispersion is coated on glassy carbon, and dried in air. The Ag/AgCl/KCl (saturated) is used as a reference electrode. The cyclic voltammogram of neat complexes are taken in solution mode, using 0.01 M solution of the metal complexes with 0.1 M acetonitrile solution of TBAP as supporting electrolyte. Thermogravimetric analyses were done on TGA thermo analyzer in the range between 20-900°C at a rate of 20°/min.

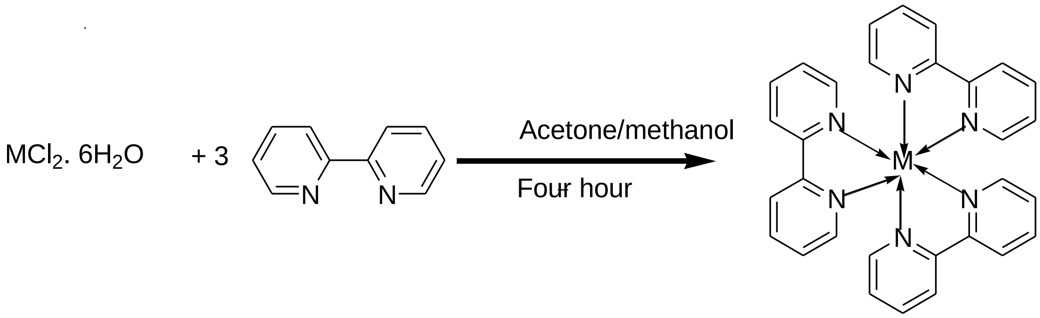
3.5 Methods

All metal complexes of 2, 2-bipyridine were synthesized by refluxing the metal chloride solution (using appropriate solvent) with the ligand, bipyridine.

3.5.1 Preparation of the Tris (2, 2-bipyridine) M (II) Complex, Where M = Co, Ni, and Cu

An overview of the prepared metal compounds is provided in Scheme 2. Metal complexes were prepared by following the procedure reported in the literature [5, 48].

Co (2, 2'bipyridine) was prepared by dissolving 0.25g (1mmol) $CoCl_2.6H_2O$ in acetone (20ml) and, then adding slowly 0.53g (3.35mmol) of 2, 2' bipyridine, which was previously dissolved in acetone (20ml). The mixture (the red solution) was refluxed for four hours with continuous stirring. After the solution had cooled at room temperature for 24 hours, it was concentrated with Rota vapor and red precipitate was filtered, washed with (50:50) diethyl ether and chloroform several times. The red complex was dried under the dessicator and stored for further use. The pink complex of nickel and light greenish-blue complex of copper were obtained following the same procedure using 0.25g(1mmol)of $NiCl_2 \cdot 6H_2O$ and 0.17g (1mmol) of $CuCl_2.2H_2O$ in the case nickel and copper complexes, respectively in methanol and acetone. The percentage yield of the metal complexes (Co, Ni and Cu) obtained was 65.5, 76.9 and 74.4% respectively.



Scheme 1.Synthesis of Metal Complexes of 2, 2’- Bipyridine (M= Co,Ni and Cu)

3.6 Synthesis of Zeolite Y encapsulated metal complexes

The encapsulated transition metal complexes of cobalt, nickel and copper, here represented as MLY, are synthesized following the general “flexible ligand” method

3.6.1 Synthesis of cobalt, Nickel and copper ion exchanged zeolite

The metal exchange zeolites (CoY, NiY and CuY) were prepared by following the procedure reported in the literature [31, 49].

The transition-metal-exchanged zeolites (Co^{2+}−Y, Ni^{2+}−Y, and Cu^{2+}−Y) are prepared by stirring a mixture of NaY (2.0 g) and 0.1 mmol of individual metal chlorides ($CoCl_2\cdot 6H_2O$ in the case of Co^{2+}−Y, $NiCl_2$. $6H_2O$in the case of Ni^{2+}−Y and $CuCl_2\cdot 2H_2O$ in the case of Cu^{2+}−Y) in 100 mL of distilled water for 24h at room temperature. The mixtures so obtained are washed with distilled water until the filtrate gives no white precipitate with $AgNO_3$ solution. The metal-exchanged zeolites, dried at 150c° for 8h. Finally light pink color product for cobalt exchanged and very light green for nickel and gray for copper exchanged zeolite was obtained.

3.6.2 Synthesis of cobalt, Nickel and Copper complex of bipyridine inside the zeolite NaY (MLY, M = Co^{2+},Ni^{2+} and Cu^{2+}).

Metal 2, 2’- bipyridine encapsulated within zeolite-Y was prepared by following the procedure reported for 1,10-phenatroline in the literature (31).The encapsulated metal bipyridine(MLY) complex is prepared by mixing dry metal exchanged zeolite Y (Co^{2+}−Y, Ni^{2+}−Y, and Cu^{2+}−Y)with a stoichiometric excess of 2,2-bipyridine to get zeolite-encapsulated tris-(2,2’–bipyridine) complexes of cobalt, nickel, and copper.

0.13 g of 2,2-bipyridine was dissolved in absolute ethanol (60ml) and then added to the previously exchanged CoY (0.62 g) and NiY (0.41g) and CuY(1.63g),0.26g of bpy with continuous stirring. The solution was refluxed for four hours, cooled to room temperature and then the precipitate was filtered and dried at 60^0C for 8h. The powders (pale white for cobalt, light greenish for nickel, and gray for copper) obtained were subjected to Soxhlet extraction for several hours using methanol and diethyl ether as solvents. The color of the samples remained the same after Soxhlet extraction.

4 Results and Discussion

4.2 IR spectra of Co (II), Ni (II) and Cu (II) complexes of 2, 2'-bipyridine

The IR spectra (appendix 1-4) of the free ligand and its metal complexes are recorded in 4000-400 cm^{-1} range. The IR spectra of metal complexes are interpreted by comparing them with the free ligand, in order to characterize their structures and modes of coordination of the ligand, (table 1).The spectrum of the free ligand (2,2-bipyridine)exhibits a medium broad band at 3435cm^{-1} ,which has been assigned to O-H stretching frequency of water. In the spectra of all metal complexes (Co, Ni and Cu (II)), this band appears as a strong and broad band,(3412,3401 and 3389cm^{-1}) ,which supports the presence of lattice water molecules in the ligands and all metal complexes. The most characteristic ring vibrations (C=C) and (C=N) in free 2,2-bipyridine appear at 1453 and at 1578 cm^{-1}. The aromatic ring stretching vibration(C=N) found 1578cm^{-1} in the 2,2-bipyridine shift to higher frequencies ,(1598, 1599, and 1599 cm^{-1}) of Co BPY, Ni BPY and Cu BPY complexes respectively, suggesting the coordination of bipyridine nitrogen[50].This shifting can be attributed to the delocalization of the electron density of the metal ion into the π-system of the ligand while the C=C stretching bands around 1453 in 2,2-bipyridine shifted to lower frequency (1443 and 1442cm^{-1})of the respective complexes . The symmetric out-of - plane mode/ deformation of the C-H group observed at 757 cm^{-1} in the uncoordinated 2, 2' bipyridine appear at ÷778cm^{-1} in CoBPY ,780 cm^{-1} NiBPY and 774cm^{-1} CuBPY. On complex formation most of the bands in the IR spectrum of the ligand 2,2'-bipyridine undergo frequency shift and in many cases intensity changes (see appendix).

Table 1. IR spectra of Co, Ni and Cu (II) complexes of BPY

Compound	νH_2O(cm^{-1})	νC=C(cm^{-1})	νC=N(cm^{-1})	νC-H(cm^{-1})
BPY	3435	1452	1578	757
CoBPY	3412	1443	1598	778
NiBPY	3401	1442	1599	780
Cubpy	3389	1443	1599	774

4.3 FTIR spectra of the CoY, NiY, CuY and CoLY, NiLY and CuLY

A comparative study of the IR bands of the ligand and the neat and encapsulated complexes were carried out .The IR spectra of the exchanged and zeolite encapsulated complexes are given in the appendix (4-6) and the IR frequencies are presented in Table 2. The spectra are dominated by the peaks due to the zeolite. The stretching due to the zeolite OH group is spread over the region from 3500-3700 cm^{-1} .The band due to the bending vibration of H_2O molecules in zeolite lattices is also displayedat1643cm^{-1}in all the spectra(exchanged and encapsulated)[51,52]. The ligand absorption at 1578cm^{-1} due to νC=N is shifted to higher region in case of all neat metal complexes. Up-on encapsulation this band is not visible, since it is overlapping with the bending frequency of the water on the zeolite. The stretching frequency C=N of the bipyridine , seen in the region 1578cm^{-1}might have shifted to higher regions in the encapsulated complexes, though this is not clearly visible in the case of all the encapsulated complexes, possibly because it gets merged with other peaks. The shift of the band is not seen in the spectra of the complexes as it is masked by the broad band of the zeolite. Therefore, evidence for bipyridine linkage in the zeolite encapsulated metal complex, could not be obtained. Framework vibrations are observed in the spectral range between 1250 and 400cm^{-1},symmetric stretching modes, antisymmetric stretching modes, bending modes of the [(Si/Al) O_4] tetrahedral.

For cobalt encapsulated, the bands at 459, 576, 722 and 788 cm^{-1} as well as 1021 cm^{-1} are attributed to T–O bending mode, double ring, symmetric stretching and asymmetric stretching vibrations, respectively. For Ni encapsulated 459, 576, 722 and 791 cm^{-1} as well as 1021 cm^{-1} and for copper 457 576, 722 and 790 cm^{-1} as well as 1021cm^{-1} are attributed to T–O bending mode, double ring, symmetric stretching and asymmetric stretching vibrations, respectively. No shift was observed upon inclusion of [M([BPY)] complexes, further substantiating that zeolite framework remains unchanged. The IR bands of metal exchanged zeolite appear almost at the same position as those of the parent zeolite NaY. Therefore the zeolite framework remains unaffected on ion exchange using the metal salt solution of low concentration used in the present study.

Table 2 .The IR absorption data of the exchanged and encapsulated complexes (cm-1)

Compound	ν(OH)	ν(OH) δ	ν(T-O)as	ν(T-O)sy	ν(T-O)δ
CoLY	3448	1643	1021	722,788	459,576
NiLY	3436	1639	1021	722 , 791	459, 576
CuLY	3454	1635	1021	722 , 790	457 ,576
CoY	3436	1639	1019	790	458
NiY	3448	1640	1021	791	459
CuY	3444	1637	1021	790	457

δ =bending, as= asymmetric stretching, sy= symmetric stretching

4.4 Elemental Analysis

The experimental values of the chemical composition (C, H, and N) of the complex of bipyridine show a good agreement with their theoretical values. Hence the results suggest that the syntheses of Co, Cu and Ni (BPY) complexes were successful. The elemental analyses also show that the complexes are hydrated. The metal content of the neat and encapsulated complex of bipyridine were determined by ICP. The elemental analysis of the encapsulated complexes show that small amount/ percentage of carbon, nitrogen and hydrogen as compared to the neat complexes, confirms the insertion of small amount of bipyridine into the pores of the zeolite. The metal to nitrogen ratio of the neat and the encapsulated complexes of cobalt and nickel show similar ratio and can be taken as an evidence of the successful encapsulation were. However, the C/N ratio of copper encapsulated complex (CulY) is higher than the neat complex. This is may be the unreacted copper which is present on the zeolite surface.

Table 3 .Elemental analysis data of the neat and encapsulated metal complexes.

Compound	C (%)		H (%)		N (%)		C/N(calc)	M%(calc)	M/N
	found	calc	found	calc	found	calc			
[Co(BPY)3]Cl_2.6H_2O	50.25	50.99	4.91	5.01	11.84	11.89	4.24(4.28)	14.1(8.34)	1.19
[Ni(BPY)3]Cl_2.6H_2O	51.24	50.99	4.92	5.01	11.81	11.89	4.33(4.28)	9.4(8.33)	0.79
[Cu(BPY)3]Cl_2.3H_2O	47.83	50.27	4.32	3.97	11.09	11.73	4.31(4.28)	14.7(10.5)	1.25
CoLY	5.75	---	1.50	---	1.34	---	4.29	1.6	1.19
NiLY	4.44	---	2.51	---	1.04	---	4.26	1.1	1.05
CuLY	6.27	---	2.51	---	1.53	---	4.09	3.9	2.5

L=BPY=$C_{10}H_8N_2$

4.5 UV-Vis spectra

The uv visible spectra of bipyridine and the complexes of bipyridine were recorded in acetonitrile and methanol (10-^{3}M) in the range from 900 to 250 nm and the results are given in table 4 and appendix 7.The free (2, 2'- BPY) bipyridine showed absorption bands at 236.8nm and 281 nm which have been assigned as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, transitions respectively corresponding to C=C and C=N of the bipyridine system. Up-on complexation, the absorption band shifts to the higher wave length / red shift, which show that the formation of bond is through nitrogen of bipyridine.

The spectra of Cobpy exhibited the bands at 240.6 nm and 296.4 nm which is a shift to higher wave length assigned as charge transfer band. The visible absorption spectra at490nm assigned as MLCT and 516 nm assigned as $^{4}T_{l}g \rightarrow {}^{4}A_{2g}$, which is typical of a d-d transition, corresponds to high spin octahedral geometry.

The spectra of NiBPY exhibited the bands at 244nm and 296.8 nm which are shifted to higher wave length assigned as charge transfer bands. In the visible spectrum of complex the [Ni (BPY)] complex, three peaks are observed(one strong and two weak peaks) at 518nm(16), 784nm (ε_{max}= 10.1 molar^{-1}cm^{-1}) and(859 nm) (ε_{max}= 7.9 molar^{-1}cm^{-1}),which are assigned to ($^3A_2g \rightarrow {}^3T_1g$ (F)) and ($^3A_2g \rightarrow {}^3T_1g$(F)), $^3A_2g \rightarrow {}^3T_2g$ d–d transition confirming octahedral geometry around Ni(II) complex. The literature value for Ni complex is (518,786 and 850nm, which is in good agreement [48]. Similarly, the electronic spectra of Cu(II) complexes show two intense bands, at 239 and 296 nm, which are assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$,transitions of the organic ligand, which is a shift to the higher wavelength. In the visible region it shows an absorption band at 668, 746 nm and weak band at 833 nm which is assigned to $^2A_{1g} \rightarrow {}^2B_{1g}$ $^2B_{2g} \rightarrow {}^2B_{1g}$ $^2E_g \rightarrow {}^2B_{1g}$, transitions suggesting distrorted octahedral geometry of Cu(II) complex[53].

Table 4. Summary of the electronic transitions of Co, Ni, and Cu bipyridine complexes

Compound	Band position(L)	Assignment	Suggested geometry	{ε_{max}}
BPY	236.8, 281	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$		1,320 and 1,040
CoBPY	490, 516	$^4T_{2g} \rightarrow {}^4A_{2g}$ $^4T_{lg} \rightarrow {}^4A_{2g}$	octahedral	28
NiBPY	518 ,784 ,859	$^3A_2g \rightarrow {}^3T_1g$(F),$^3A_2g \rightarrow {}^3T_1g$, $^3A_2g \rightarrow {}^3T_2g$	octahedral	16,10.1, 7.9
CuBPY	668,746, 833	$^2A_{1g} \rightarrow$2B1g, 2B2g$\rightarrow {}^2B_{1g}$, $^2E_g \rightarrow {}^2B_{1g}$	octahedral	13.85

4.6 Molar conductivity

The conductivity measurements were made using EC214 conductivity meter for each complexes in water (1.0×10^{-3} M). Molar conductivity is a method of testing the degree of ionization of the complexes, the molecular ions that a complex liberates in solution (in case of presence anions outside the coordination sphere) .The molar conductivity values for the complexes suggest a 1:2 electrolyte type (three ions) indicating that the counter ions Cl^- is in the outer coordination sphere. The molar conductivity values of cobalt, nickel and copper (II) complexes are172, 149 and 126 Scm^2mol^{-1} respectively.

4.7 The magnetic moments, μ_{eff} (B.M.) measurements

The magnetic moments of all complexes were measured at room temperature (20 and 22^0C) using solid samples, which show that the gram susceptibility, $\chi_g =$ 3.642, 5.193 and $2.188*10^{-6}$ g/cm^3 for cobalt (II), nickel (II) and copper (II) respectively (table 5). The effective magnetic moment, taking the diamagnetic corrections in to account is 2.5, 2.9 and 1.8 BM of the respective metal. The magnetic moment of [Co (BPY)] complex is 2.5 BM, which corresponds to 1.7 unpaired electrons and it suggests that the formation of octahedral complexes. The [Ni (BPY)] complexe has a magnetic moment of 2.70 B.M, which corresponding the magnetic moment of two unpaired electrons. This also supports of octahedral geometry of the nickel complexe. The [Cu (BPY)] complex has a magnetic moment of 1.75 B.M, which corresponds with the magnetic moment.of one unpaired electron, and corresponds to octahedral Cu (II) complexes.

Table 5 Summary of magnetic moments of bipyridine metal complexes

Compound	Mw g/mol	χ_g 10-^{6} g/cm^{-3}	X_m $10^{-3}g/mol^{-3}$	μ_{eff} B.M	n
CoBPY	707	3.6	2.57	2.5	1.7
NiBPY	707	5.2	3.67	2.9	2
CuBPY	606	2.2	1.32	1.8	1

Mw = molecular weight, χ_g = gram susceptibility, χ_m = molar susceptibility μ_{eff} = effective magnetic moment and n= unpaired electron

4.8 Cyclic voltammetry of the neat and encapsulated complexes

Cyclic voltammetry (CV) is a very useful electroanalytical technique. Many inorganic compounds contain elements that may take on several different oxidation states. The CV experiment can provide important information about the oxidation state of an element in a compound and provide helpful information about the influence of the zeolite on the formation and reactivity of the complexes within the host cavities. Cyclic voltammogram of CoBPY in ACN-0.1 mol dm ^{3} in tetra butyllammonium perchlorate (TBAP) solution , shows a couple of peaks with values of E_{pc} =0.122 V and E_{pa}=0.55 V , $E_{1/2}$ = 0.33V. This redox process, when associated with a cathodic peak, is the reduction of Co^{+2} to Co^{+1} and. When associated with anodic peak, is the oxidation of Co^{+1} to Co^{+2}. Thus, by comparing this voltammogram to the data obtained with neat metal complexes, it appears that the zeolite-encapsulated complexes (Epc= 0.25 V and Epa= 0.53 V, $E_{1/2}$= 0.28 V) show electrochemical behavior which is very similar to that of the dissolved species in solution and peaks are broadened (appendix11 and 12). Similarly the cyclic voltammogram of nickel complex (NiBPY) in solution shows a redox couple at peaks at E_{pc}= -1.42 V and E_{pa}= -1.15 V ($E_{1/2}$= -1.286 v), that can be attributed to the Ni^{+2}/Ni redox process (appendix 13). The cyclic voltammogram of the Ni LY modified electrode does not show redox behavior in 0.1 M TBAP supporting electrolyte solution. This shows that interior molecules of NiLY are maybe inaccessible in 0.1 M TBAP solution. The cyclic voltammogram of neat complex(CuBPY) also shows a couple of peaks with values of E_{pc} (cathodic) peak at -0.175 V and E_{pa}(anodic) peak at 0.133V , $E_{1/2}$= -0.021V (appendix14). This redox process associated with the cathodic peak is reduction of Cu^{+2} to Cu and the anodic peak is oxidation of deposited copper metal to copper cations (Cu/Cu^{+2}) .Up-on encapsulation in Zeolites, the reduction potential is altered towards more negative value (0.28 V for Co, and -0.119 V for Cu encapsulated) and peaks are changed as shown in the appendix. The alteration of peak potential towards more negative value upon encapsulation indicates the stabilization of M^{+2} oxidation state in zeolite cages. This may be due to interaction with zeolite matrix. The alteration of peak potentials indicates that the metal complex is not having the same geometry as in the neat complex but undergoes distortion inside the zeolite matrix.

Table 6 .The redox potential values for encapsulated and neat complexes.

Samples	E_{red}	E_{oxd}	$E_{1/2}$ vs Ag/AgCl
CoBPY	0.122	0.55	0.33
NiBPY	-1.42	-1.15	-1.28
CuBPY	-0.175	0.133	- 0.2
CoLY	0.25	0.53	0.28
NiLY	---	---	---
CoLY	-0.37	0.131	-0.119

$E_{1/2}$= ($E_{pa+}E_{pc}$/2, where $_{Epa}$ = anodic current and E_{pc} = cathodic current

4.9 Thermo gravimetric analysis (TGA) results of the neat metal complex, and encapsulated metal complexes.

Thermoanalytical curves for NiBPY demonstrate patterns typical of multistep processes (appendix 9). Analysis of gaseous products and mass loss (14%) reveals 6 molecules of crystallization H_2O are released gradually in the initial stage, between 40 and 147 °C. There is a 21.3% mass loss which corresponds to the loss of 2, 2-bipyridine in the range of 147 and 202 c^o. The second stage, in the temperature range of 202 – 353 °C, is related to the decomposition of one bipyridine ligand (found 22.7%, calc. 22%). Between 353 and 476 °C (353-402 and 402-476 °C), the debipyridation decomposition process takes place and 23% mass loss, which corresponds to the loss of other bipyridine. Some stages of bipyridine decomposition shows the release of bipyridine through debipyridination decomposition [54].There is further small mass loss above 476°C; at each point there is a residue comprising of NiCl2 (19.3%). Finally release of Cl_2 and the remaining 9.8% is a residue comprising of Ni. Total weight loss is 90.2%, calc, 91.7% .Whereas as shown in appendix 9, the Ni encapsulated in zeolite NiLZ, only 26.8% weight lose was recorded,indicating the zeolite enhances the stability of the metal complex.

Similarly, the thermal decomposition of CoBPY proceeds in multi stages (appendix 8). In the temperature range of 34–118°C corresponds to the loss of crystallization of five water molecules (found: 15%, calc.:12.5%). The second stage, in the temperature range of 118–174 °C, is related to the decomposition of the one bipy moieties (found 22 %, calc.22%). The third stage, in the temperature range of 174-252°C, is related to the consecutive decomposition of the one H_2O and 0.5 mole bipy moieties (found 16.48%, calc 14.5%) . In the temperature range, (252-346 °C.) shows 11.2% mass loss indicating rerelease of other 0.5 mole bipy. Fourth and fifth stage also shows the release of bipyridine through debipyridination decomposition [54] (22%) which corresponds to libration of 1mole bipyridine. Finally release of Cl_2 and remaining 11% is the metal .The overall weight loss (expt., 89 %, clad. 87.1%) agrees with the proposed assignments. In contrast to the high weight(%) lost in the neat complex, the CoBPY encapsulated in zeolite NaZ showed lower weight(%) lost measured as 25.4 % .).

As indicated in (appendix 10), the thermal decomposition of the Cu complex, TGA curve is well-defined, consisting of three stages. In the first step, dehydration of the complex occurs in the temperature interval 35 – 96◦C with mass loss of 7.2 % corresponds to three water molecules. Between 96 and 182 °C, 34.5 %(cacl: 35.5%) of mass loss occurred, indicating of the rerelease 1.5mole bipyridine. The third stage takes place in the temperature range 182 and 400 °C with 34.4%(35.5%) mass loss which shows the release of other 1.5mole bipyridine and there is further mass loss above 400°C and the liberation of the Cl_2 maybe occur .the remaining a residue accounts only 2.6% indicates the metal copper may melt/ decompose at high temperature. The total mass loss is (exp 97.3%.; calc 87.1 %).

In summary, rapid weight loss of the neat complexes was observed around 400^0C, indicative of decomposition of coordinated ligand. Although, the extent of total decomposition of the neat complexes is different ranging from 89% in CoBPY to 97% in CuBPY, the extent of total weight lost in the encapsulated complexes is almost similar indicating the zeolites were able to stabilize regardless of the type of the metal in the complex. The total weight loss of nickel, cobalt and copper encapsulated metal complexes were 25.3, 26.4 and 26.8 % respectively. As compared to the neat complexes, the mass loss of the encapsulated complexes decreases highly, which indicates that the zeolites helped to stabilize the metal complexes. Transition metals are known for their instability and the result of this research is promising in finding ways to stabilize and use them for different applications Finally the constant curve of the thermogram was observed, suggests the formation of final decomposition products corresponding to the metal.

Table 7 .Thermal decomposition data for neat and encapsulated metal complexes.

Compound	Temperature °C	Mass loss (%) Found	Mass loss (%) calc	Gaseous product
CoBPY	34-118	13	12.5	5H2O
	118-174	22	22	1BPY
	174-252	16.48	14.5	1H_2O,0.5moleBPY
	252-346	11.2	11	0.5mole BPY
	346-632	20.67	22	1BPY
NiBPY	40 -147	14	15.2	6H2O
	147-203	21.3	22	1BPY
	203-353	23.4	22	1BPY
	353-402	11.3	11	0.5moleBpY
	402-476	12.3	11	0.5moleBPY
CuBPY	35-96	7.2	7.3	3H2O
	96-182	34.5	35.5	1.5moleBPY
	182-400	34.4	35.5	1.5moleBPY

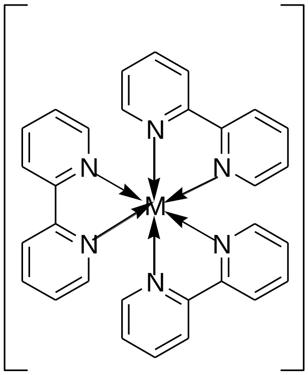
Compound	Temperature/ °C	Weight loss (%)
CoLY	23-318	18.2
	318-900	8.2
NiLY	23-312	19
	312-900	6.34
CuLY	23-318	17.86
	318-900	8.94

L= BPY= 2,2 bipyridine , Y = zeoliteY ,MLY= Encapsulated complexes

5 Conclusion

Tris (2,2 bipyridine)complexes of cobalt(II),and nickel(II), were synthesized and characterized using elemental analyses, conductance measurements, magnetic susceptibility, cyclic voltammetry,TGA and spectroscopic studies. Tris (2, 2 bipyridine) complexe of cobalt (II), was encapsulated within the supercage of zeolite by flexible ligand method and characterized by FT-IR, CHN TGA, and ICP analysis. The elemental analytical results for carbon, hydrogen and nitrogen are very close to the calculated values Conductance values indicate that the complexes are 1:2 electrolyte types. Infrared shifts of relevant bands of the ligands in the complexes indicate that both are coordinated to the metal ions. UV-vis spectra confirm octahedral geometry for the complexes. The TGA and CHN analysis of intrazeolite complexes in comparison to those of the neat complexes confirm that the insertion of small amount of organic molecules (2, 2-bipyridine) into the pores of the zeolite.

The proposed structure of the complexes is given below



Cl_2 $.nH_2O$

M=Co,Ni and Cu

6 References

1. F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry 6th ed., *Wiley, New York*, **1999**.
2. N. Akhmetov, Inorganic Chemistry, *MIR publications*, Soviet Union/Moscow **1973**.
3. Tehshikp.Yoon.,Visible Light Photocatalysis:The Development of Photocatalytic Radical Ion Cycloadditions, *ACS Catal*, **2013**, 3, 895−902.
4. Tehshik P. Yoon, Michael A. Ischay And Juana Du,Visible light Prafulla M .Sabale, J. Patel and Y. Patel, Metal Complexes: Current Trends and Future Potential Photocatalysis as a greener approach to photochemical synthesis, *NCHEM*,**2010**,2,527-532.
5. Jesse P. Nolan, Timothy W. Jones, Scott W. Donne, Gregory J. Wilson, Tuning the Electrochemistry of Homoleptic Cobalt4,4-Disubstituted-2,2-Bipyridine Redox Mediators, *Electrochimica Acta* ,**2013** ,108 ,690–*697. IJPCBS, **2012**, 2(3), 251-265.*
6. A. Choudhary, R. Sharma, M. Nagar, M. Mohsin and H. S. Meen , Synthesis, Characterization and Antioxidant Activity of Some Transition Metal Complexes with Terpenoid Derivatives. *J. Chil. Chem. Soc*., **2011,** 4, 56.
7. M.Azam, I.Warad, S. Al-Resayes, M. Zahin, I. Ahmad, and M.Shakir. Syntheses, Physico-Chemical Studies and Antioxidant Activities of Transition Metal Complexes with a Perimidine Ligand. *Z. Anorg. Allg. Chem*. **2012**, 1–7.
8. A.A,Warra,.Transition Metal Complexes and Their Application in Drugs and Cosmetics – A Review *, J. Chem. Pharm. Res*., **2011**, 3(4):951-958.
9. I. Kuz´ Niarska-Biernacka, K. Biernacki, A.L. Magalhães, A.M. Fonseca, I.C. Neves, Catalytic.Behavior of 1-(2-Pyridylazo)-2-Naphthol Transition Metal Complexes Encapsulated In Y Zeolite, *Journal of Catalysis*, **2011,** 278 , 102–110.

10. F.Tellez,H.Lopez-Sandoval, S.E.Castillo Blum and Barba Behens, Coordination Behavior of Benzimidazole, 2-Substitued Benzimidaziloles and Benzothiazoles, Towards Transition Metal Ions, *ARKIVOC* ,**2008**, 245-275
11. S.P.Sovilj, G.Vuèkoviæ, V.M. Leovacand D.M. Minic,Dinuclear Copper(II) Complexes of N,N’,N’’,N’-Tetrakis(2-pyridylmethyl)1,4,8,11 tetraazacyclotetradecane and Some N,S or N,O Bidentate Ligands, *Polish J. Chem.*, **2000**, 74, 945–954.
12. J.A .Joule and K. Mills, Heterocyclic chemistry, 5th Edition, *John Wiley & Sons*, 2010.
13. S.yadav,Devrakash and Senthilkumar G P.Benzothiazole: Different Methods of Synthesis and Diverse Biological Activities, *JPSDR*, **2011**, 3,(1),01-07.
14. R.Dua, S.Shrivastava, S.K.Sonwane and S.K.Srivastava.Pharmacological Significance of Synthetic Heterocycles Scaffold, *Advan. Biol. Res*, **2011,** 5(3), 120-144.
15. D.M. Badgujar, M.B.Talawar, S.N.Asthana and P.P.Mahulikar.Novel Synthesis of Biologically Active Nitro Hetrocyclic Compounds. *J SCI IND RES*,**2008,** 67,54-57.
16. S.Conejero, P.Lara,M. Paneque, A. Petronilho, Manuel L. Poveda,O.Serrano, F. Vattier, E.Alvarez, C.Maya, V.Salazar, And E. Carmona. Monodentate, N-Heterocyclic Carbene-Type Coordination Of 2, 2’-Bipyridine and 1,10-Phenanthroline to Iridium, *Angew. Chem. Int. Ed*.**2008**, 47 , 4380 –4383
17. George R. Newkome,Anil K. Patri, E. Holder, and Ulrich S. Schubert, Synthesis of 2,2-Bipyridines:Versatile Building Blocks for Sexy Architectures and Functional Nanomaterial, *Eur. J. Org. Chem.* **2004**, 235-254.
18. Bhakti S. Kulkarni, A.Tanwar and S.Pal. Reactivity Descriptors and Electron Density Analysis For Ligand Chemistry: A Case Study of 2, 2 ′-Bipyridine and Its Analogues.*J .Chem.Sci*., **2007**,119,489-499.

19. Valery N. Kozhevnikov, Olga V. Shabunina, Dmitry S. Kopchuk, Maria M. Ustinova,Burkhard Konig, Dmitry N. Kozhevnikov.Facile, Synthesis of 6-Aryl-3-Pyridyl-1,2,4-Triazines as A Key Step Toward Highly Fluorescent 5-Substituted Bipyridines And Their Zn(II) And Ru(II) Complexes, *Tetrahedron*, **2008,** 64**,** 8963–8973
20. Henrique E. Toma, Koiti Araki.Supramolecular Assemblies of Ruthenium Complexes and Porphyrins. *Coordination Chemistry Reiews, 2000***,** 196**,** 307–329.
21. Simone D. Inglez, Francisco C. A. Lima,Mariana R. Camilo, Juliana F. S. Daniel, Evania D. A. Santos, Benedito S. Lima-Neto,And Rose M. Carlos,Tuning Of Photochemical and Photophysical Properties of [Ruii(2,2'-Bipyridine)$_2$L$_x$] Complexes Using Nonchromophoric Ligand Variations, *J. Braz. Chem. Soc,* **2010**. 21, (1), 157-168.
22. Smita Ghosh,Vithal A Kawade, Avinash V Sapre and Avinash S Kumbhar, Pulse Radiolytic Studies On Ci S-Dichlorobis(1,10-Phenanthroline-,6-Dione)Cobalt(III) Complex, *J. Chem. Sci*., **2010**, 22, (2), 225–232.
23. W. T. Eckenhoffa, W.R. Mcnamarab, P. Duc, R. Eisenberg, Cobalt Complexes As Artificial Hydrogenases For The Reductive Side Of Water Splitting. *Biochimica et Biophysica Acta*, **2013,** 1827, 958 – 973.
24. H.V. Bekkum, E.M. Flanigen, P.A. Jacobs and J.C. Jansen. Introduction to Zeolite Science and Practice. 2nd Edition. *Elsevier, Amsterdam*, **2001.**
25. R. Szostak, Molecular Sieves: Principles of Synthesis and Identification,2nd Edition, *New York-USA: Van Nostrand Reinhold, **1998***
26. T. Fertu And M.Gavrilescu, Application of Natural Zeolites As Sorbents in The Clean-Up of Aqueous Streams, *EEMJ,* **2012**, 11(4), 867-878.
27. Y.Yangxin , Z.Jin and Andrew E. Bayly, Development of Surfactants and Builders in Detergent Formulations, *Chin. J. Chem. Eng.,,* **2008**, 16(4) 517 -527

28. R.Xu,W. pang, J. Yu, Q. Huo, and J. Chen, Chemistry of Zeolites and Related Porous Materials; Synthesis and Structure, *John Wiley and Sons*, **2006.**
29. Kusum K. Bania, D. Bharali, B. Viswanathan, and Ramesh C. Deka , Enhanced Catalytic Activity of Zeolite Encapsulated Fe(III)-Schiff-Base Complexes for Oxidative Coupling of 2-Napthol, *Inorg. Chem*., **2012**, 51, 1657− 1674.
30. Kusum K. Bania and Ramesh C. Deka, Influence of Zeolite Framework on the Structure, Properties, and Reactivity of Cobalt Phenanthroline Complex: A Combined Experimental and Computational Study, *J. Phys. Chem. C* , **2011**, 115, 9601 –9607.
31. M.SalavatiNiasari,Z.Salimi,M.Bazarganipour,F.Davar,Synthesis,Characterization and Catalytic Oxidation of Cyclohexane Using A Novel Host(Zeolite-Y)/Guest (Binuclear Transition Metal Complexes) Nanocomposite Materials, *Inorganica Chimica Acta* , **2009**, 362 3715–3724.
32. Geoffrey A. Ozin and S. Ozkar, Zeolates: A Coordination Chemistry View of Metal-Ligand Bonding in Zeolite Guest-Host Inclusion Compounds. *Chem. Mater*. **1992,** 4(3), 511-521.
33. Dennis H. Leung, D. Fiedler, Robert G. Bergman, and Kenneth N. Raymond, Selective C H Bond Activation by a Supramolecular Host–Guest Assembly, *Angew. Chem. Int , Ed.,***2004,** 43 , 963 –963.
34. J. Basset, R. Psaro, D. Roberto,R.Ugo,Modern Surface Organometallic Chemistry, *Welly-VCH*, **2009**.
35. N. Herron, David R.Corbin .Inclusion Chemistry with Zeolites: Nanoscale Materials by Design: Nanoscale materials by design, 1995.
36. J,cejka, H.v. Bekkum, Zeolites and Ordered Mesoporous Materials: Progress and Prospects, 1st Edition ,*Elsevier*, **2005 .**
37. T.H. Bennur,D. Srinivas, P.Ratnasamy, EPR Spectroscopy of Copper and Manganese Complexes Encapsulated In Zeolite, *Microporoue and Mesoporous Materials*, **2001,** 48, 111-118.

38. A. Mobinikhaledi, M. Zendehdel, P. Safari, Synthesis And Characterization Of Some Novel Transition Metal Schiff Base Complexes Encapsulated In Zeolite Y:Effective Catalysts For The Selective Oxidation Of Benzyl Alcohol, *Reac Kinet Mech Cat* ,**2013**, 110:497–514

39. Stefan H. Bossmann, S. Jockusch, P.Schwarz, B.Baumeister, S. Gob, C. Schnabel, L.Payawan, Jr, Megh R.Pokhrel, M.Worner, Andre M. Braun and Nicholas J.Turro, Ruthenium (Ii) Tris Bipyridine /Titanium Dioxide Codoped Zeolite Y Photocatalysts:Photocatalyzed Degradationof The Model Pollutant 2,4- Xylidine, Eviedince For Percolation Behavior,*Photochem.Photobiol.sci*., **2003**,2,477-486.

40. Mario G. Clerici and Oxana A. Kholdeeva.Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and industrial Applications, *John Wiley and Sons,inc,hoboken New jersey*, **2013**.

41. N. Ohata, Y.Ito,D. Gomibuchi, H. Kitamura, Y. Funahashi, T. Ozawa,H. Masuda.,Nickel Phthalocyanine Complex Encapsulated In To Nanopores Of Faujasite Zeolite, *Advanced Maerials Research* **2006**, 11,281-284.

42. Y. Tanamura,T. Uchida,N. Teramae,,M. Kikuchi,K. Kusaba,and Y Onodera, Ship-in-a-Bottle Synthesis of CopperPhthalocyanine Molecules within Mesoporous Channels of MCM-41 by a Chemical Vapor Deposition Method, Nano Lett., **2001**,1(7), 387-390.

43. Carol A. Bessel and Debra R. Rolison,Topological Redox Isomers: Surface Chemistry of Zeolite-Encapsulated Co(salen) and[Fe(bpy)3]2+Complexes, J. *Phys. Chem. B*,**1997**, 101, 1148-1157.

44. Stefan H. Bossmann, N Shahin, Hieu L.Thanh, A.Bonfill, M.Worner and Andrem, M. Braun, [Fe(BPY)3]^2/Tio$_2$ Codoped Zeolites: Synthesis, Characterization And First Application In Photocatalisis,*Chemphyschem*, **2002**,3,401-407.

45. P. Laine, M. Lanz, and G. Calzaferri, Limits of The in Situ Synthesis of Tris (2,2′Bipyridine)Ruthenium(II) In The Supercages of Zeolite Y, *Inorg. Chem*. **1996**, 35, 3514-3518

46. P. Barbaro, F. Liguori, Heterogenized Homogeneous Catalysts For Fine Chemicals Production: Materials and Processes, *Springer*, **2010.**

47. Douglas A. Vander Griend, Daniel Kwabena Bediako, Michael J. Devries, Nathan A. DeJong, and Lee P. Heeringa, Detailed Spectroscopic, Thermodynamic, and Kinetic Characterization of Nickel(II)Complexes with 2,2′-Bipyridineand 1,10-PhenanthrolinenAttained via Equilibrium-Restricted Factor Analysis, *Inorg. Chem*. **2008**, 47, 656−662.

48. K. Mori, K. Kagohara, and H.Yamashita, Synthesis of Tris(2,2 ′-Bipyridine)Iron(Ii) Complexes In Zeolite Y Cages: Influence Of Exchanged Alkali Metal Cations On Physicochemical Properties And Catalytic Activity. *J. Phys. Chem. C*, **2008,** 112, 2593-2600.

49. D. Czakis-Sulikowska and j. Kaluzna-Czapliñska., Thermal Properties of Complexes of Mn(Ii),Fe(Ii),Co(Ii),Ni(Ii).With.2,2’-Bipyridineor 4,4’-Bipyridine And Thiocyanates, *J.Therm. Anal. Cal., **2000**.62, 821-830.*

50. Antonio M. Fonseca, S. Gon¸Alves, P. Parpot And Isabel C. Neves, Host–Guest Chemistry of The (N,N’-Diarylacetamidine)Rhodium(III)Complex In Zeolite Y. *Phys.Chem.Chem.Phys*,**2009**, 11, 6308– 6314.

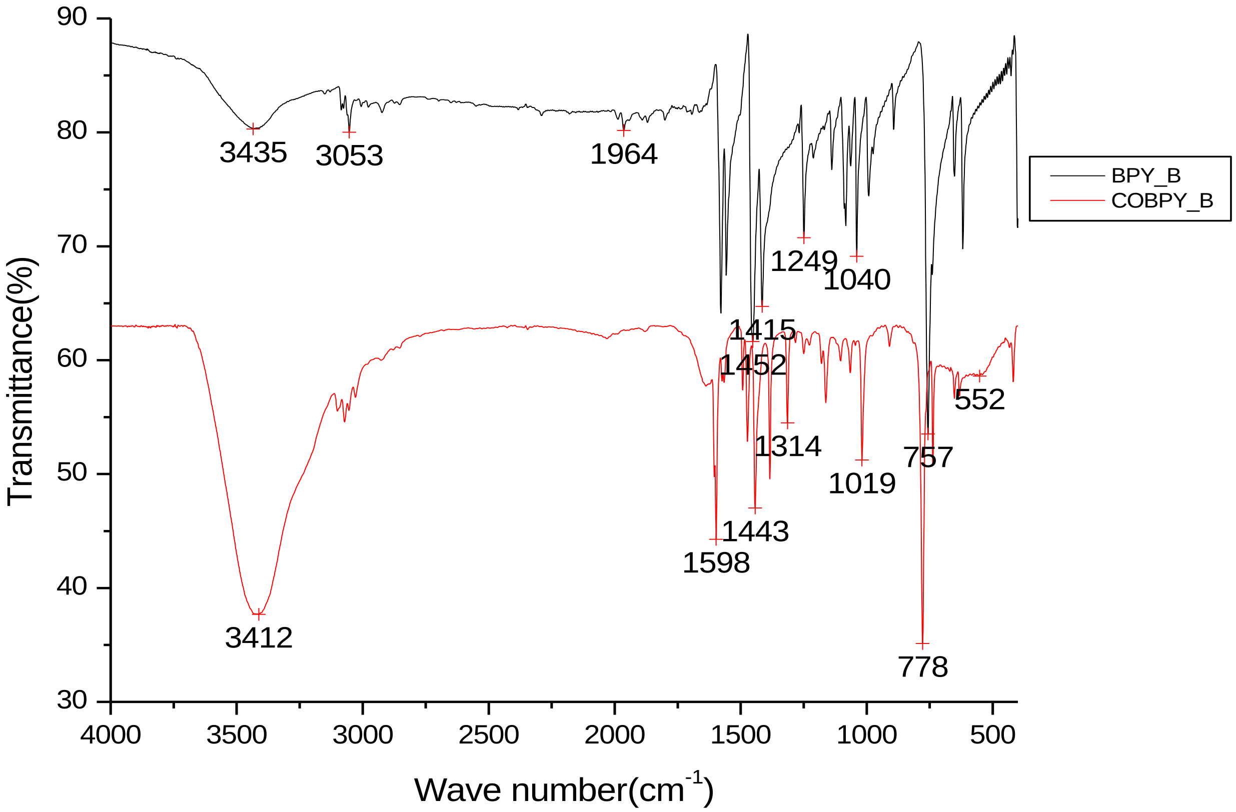
51. C. Teixeira, P. Pescarmona, M. A. Carvalho, Antonio M. Fonsecaand Isabel C. Neves.Host(beta zeolite)–guest (copper(II)–methyladenine complex)nanomaterials: synthesis and characterization . New J. Chem., **2008**, 32, 2263–2269.

52. Oladipo M. Adelaide, Olayiwola O. Abidemi and Adeoye D. Olubunmi, Synthesis, Characterization and Antibacterial Studies of Some Copper (II) Complexes Of 2,2’ Bipyridine And 1.10-Phenanthroline ., Journal of Chemical and Pharmaceutical Research, **2013**, 5,8:69-73.

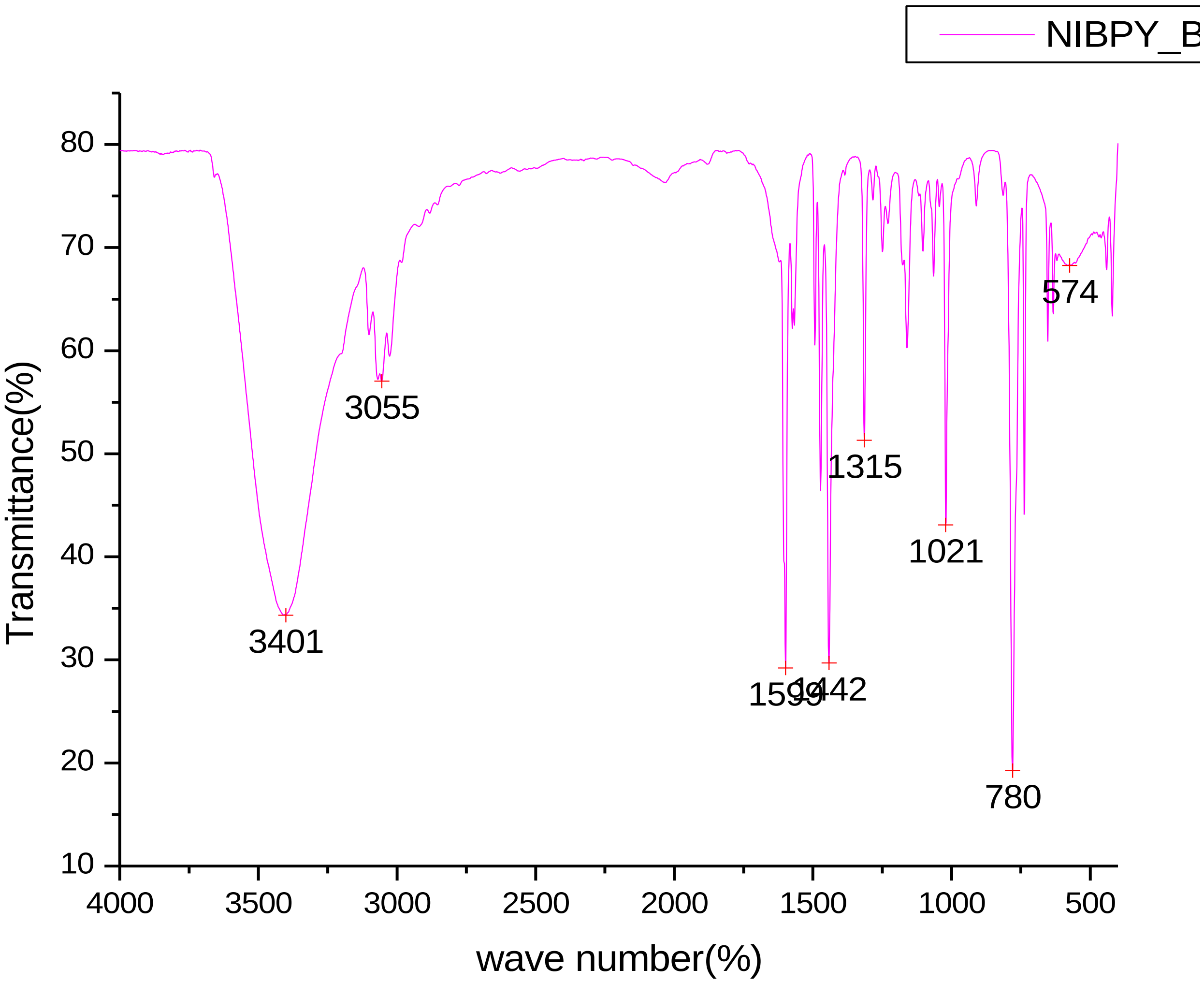
53. P. Naumov, V. Jordanovska, O. Grupèe, B. Boyanov And G. Jovanovski, Thermal Behaviour of The N-Donor Adducts of Metal Saccharinates I. 2,2’-Bipyridine Saccharinato Complexes Of Co(Ii), Ni(Ii),Cu(Ii), Zn(Ii) And Pb(Ii), *J.Therm. Anal. Cal.,* **2001**. 65, 59-67.

7 Appendices

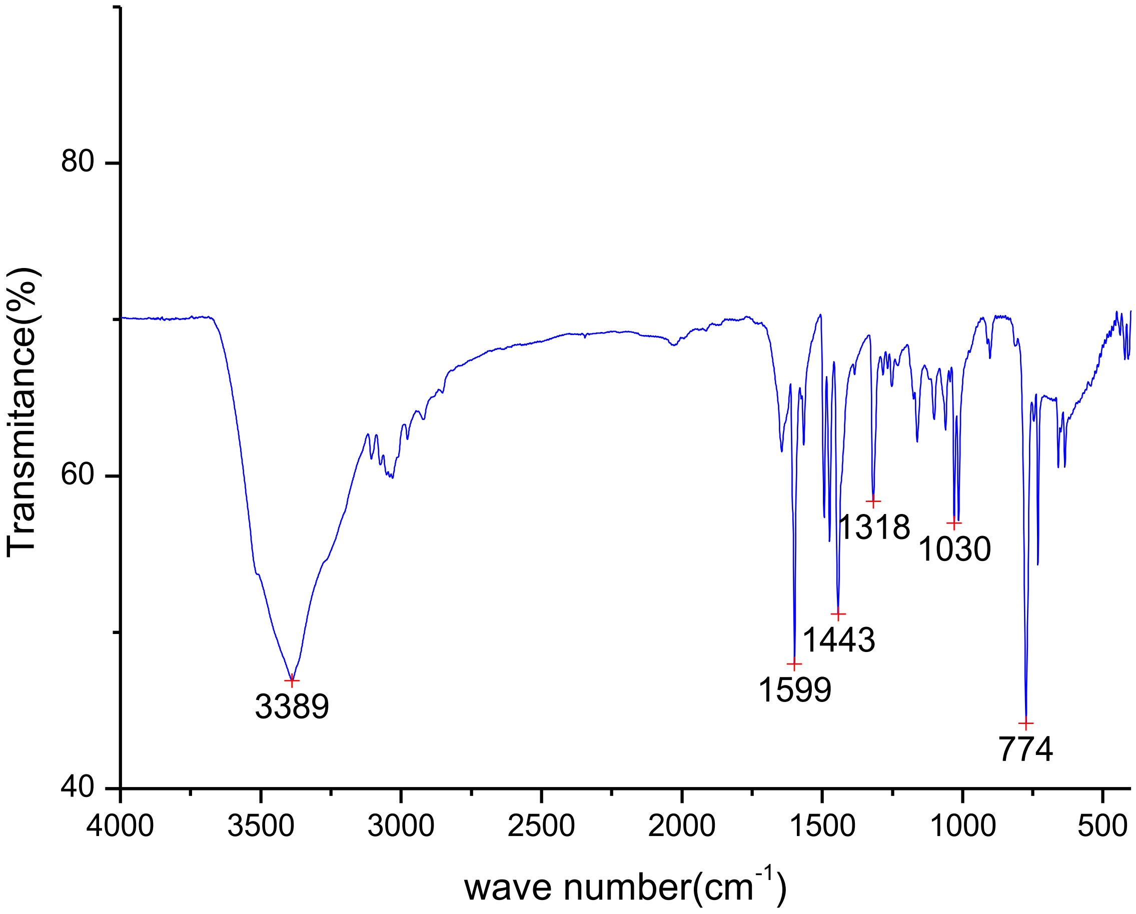
Appendix 1 FT-IR spectra of BPY and CoBPY



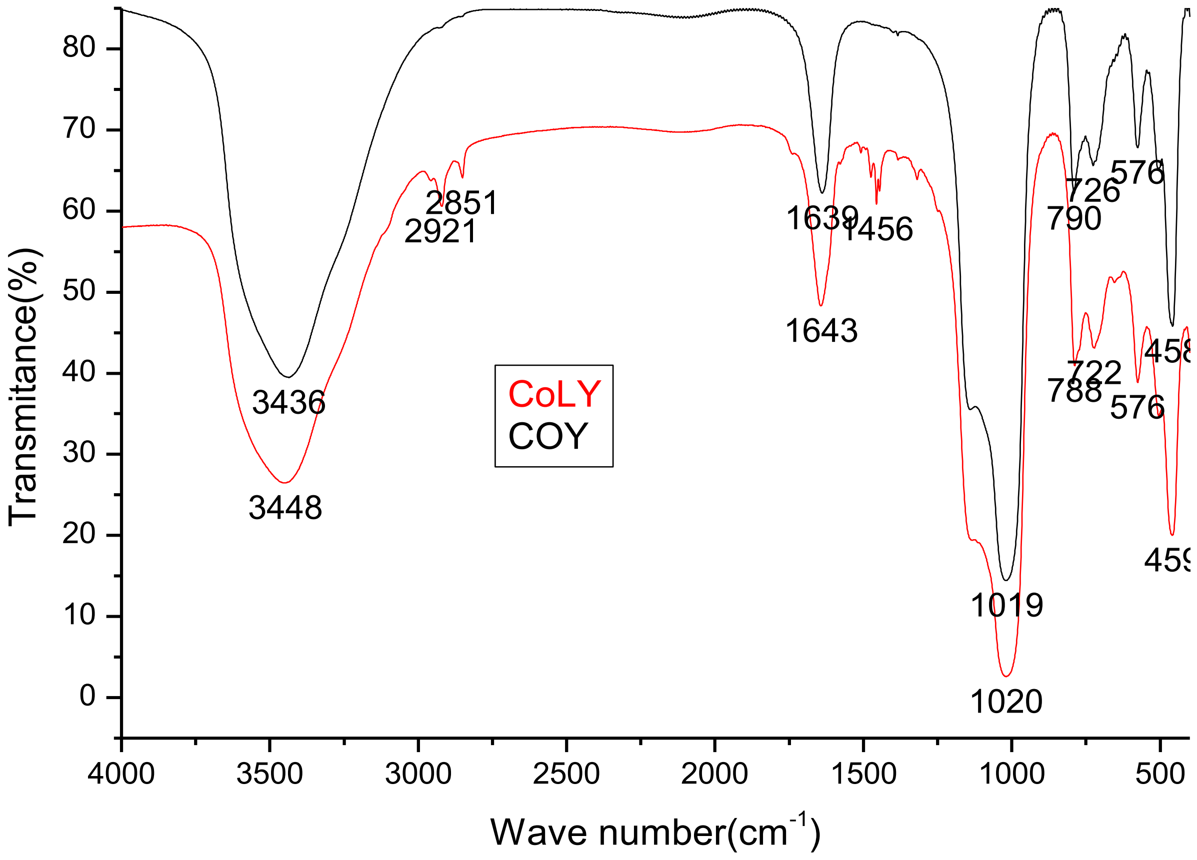
Appendix 2 FT-IR spectrum of NiBPY



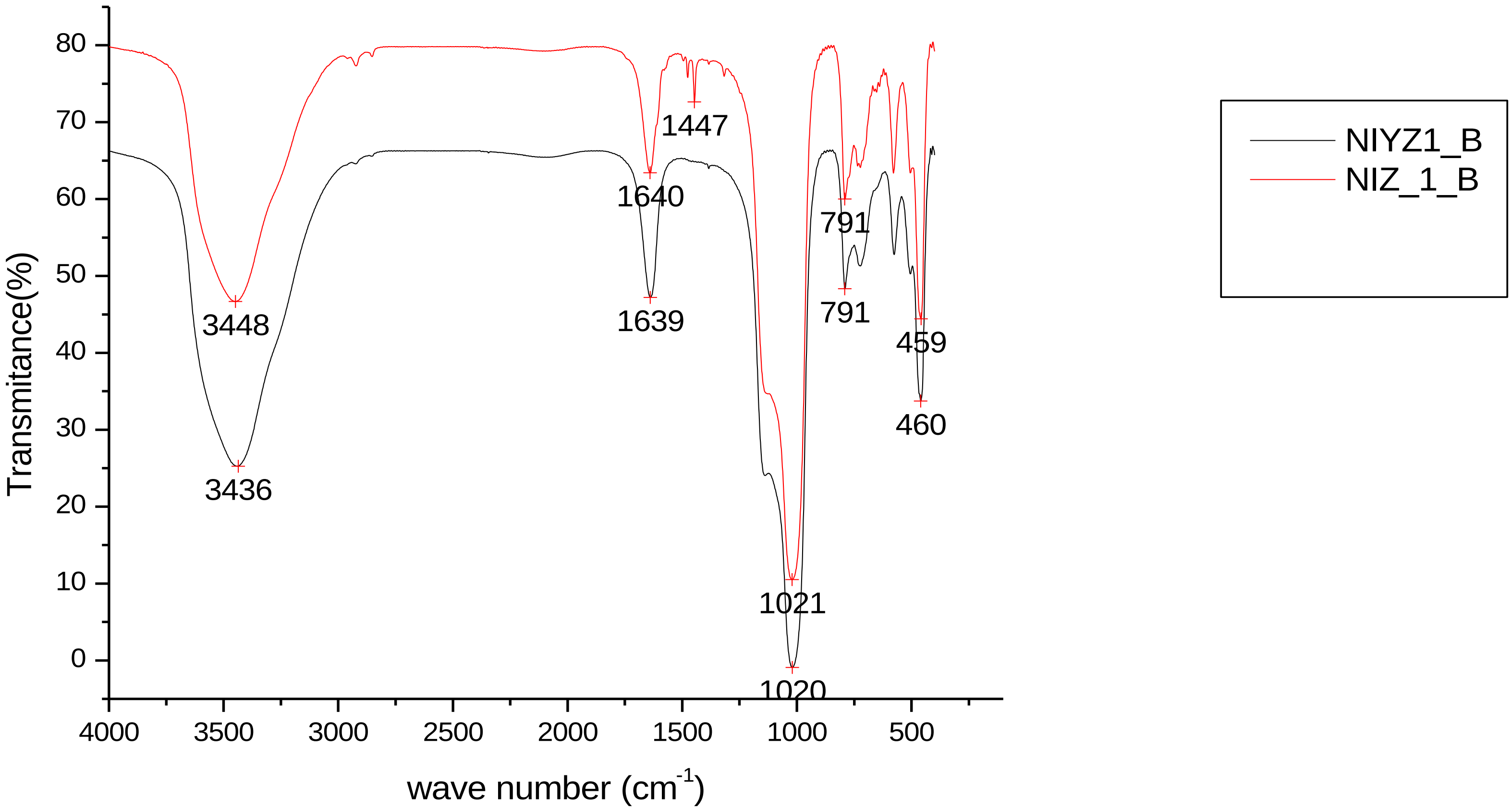
Appendix 3 FT-IR spectrum of CuBPY



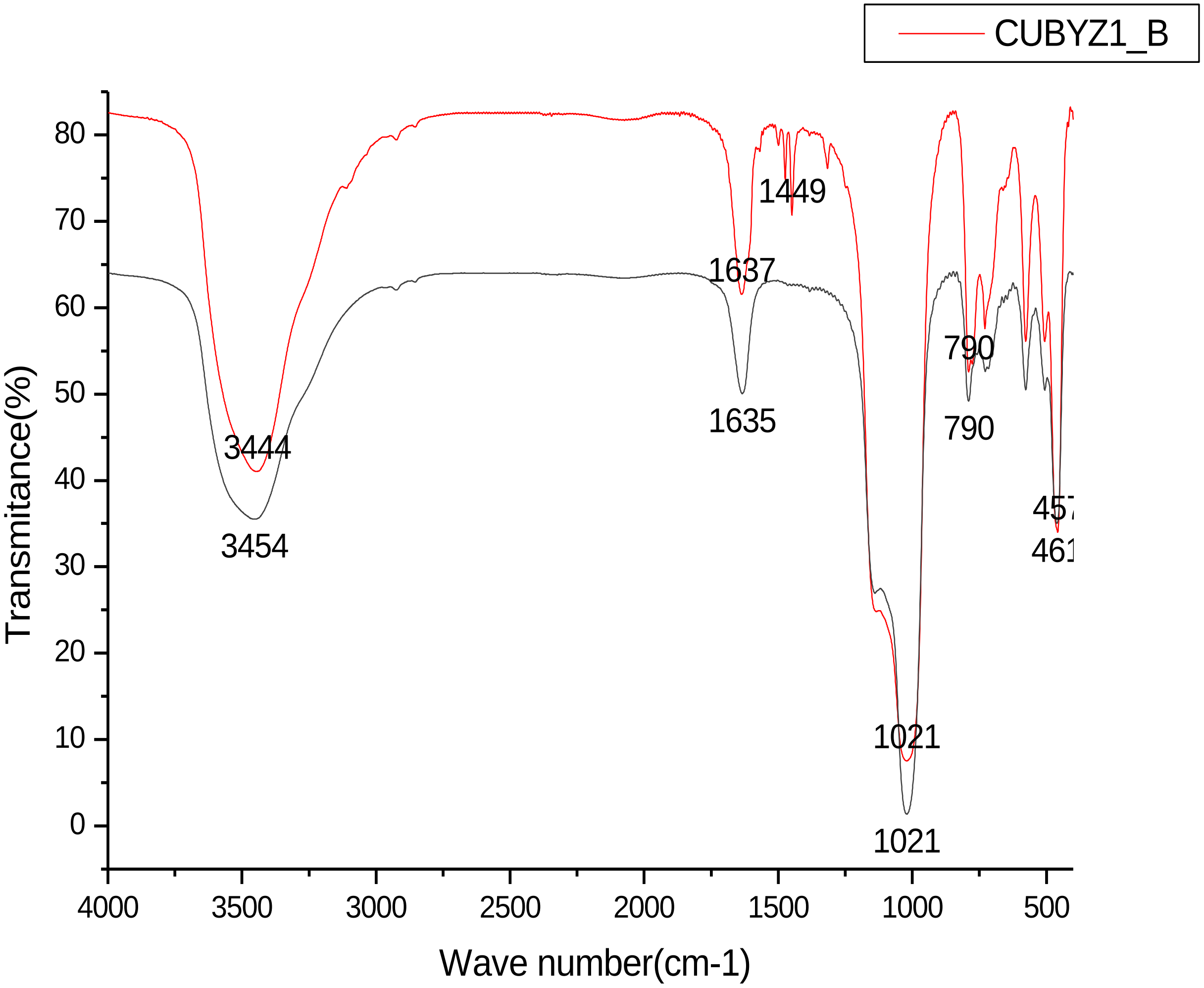
Appendix 4 FT-IR spectra of CoY and CoLY



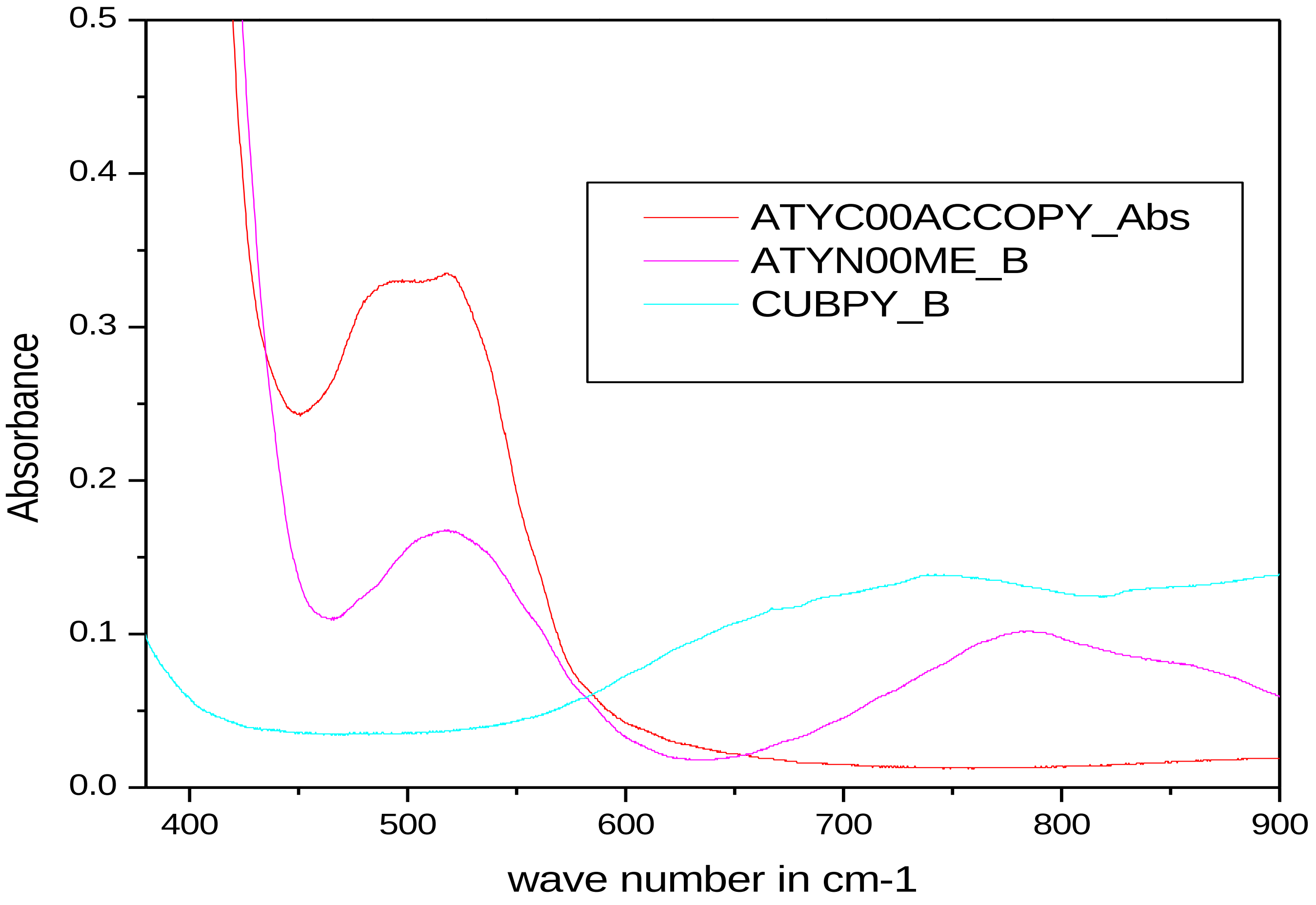
Appendix 5 FT-IR spectra of NiY and NiLY



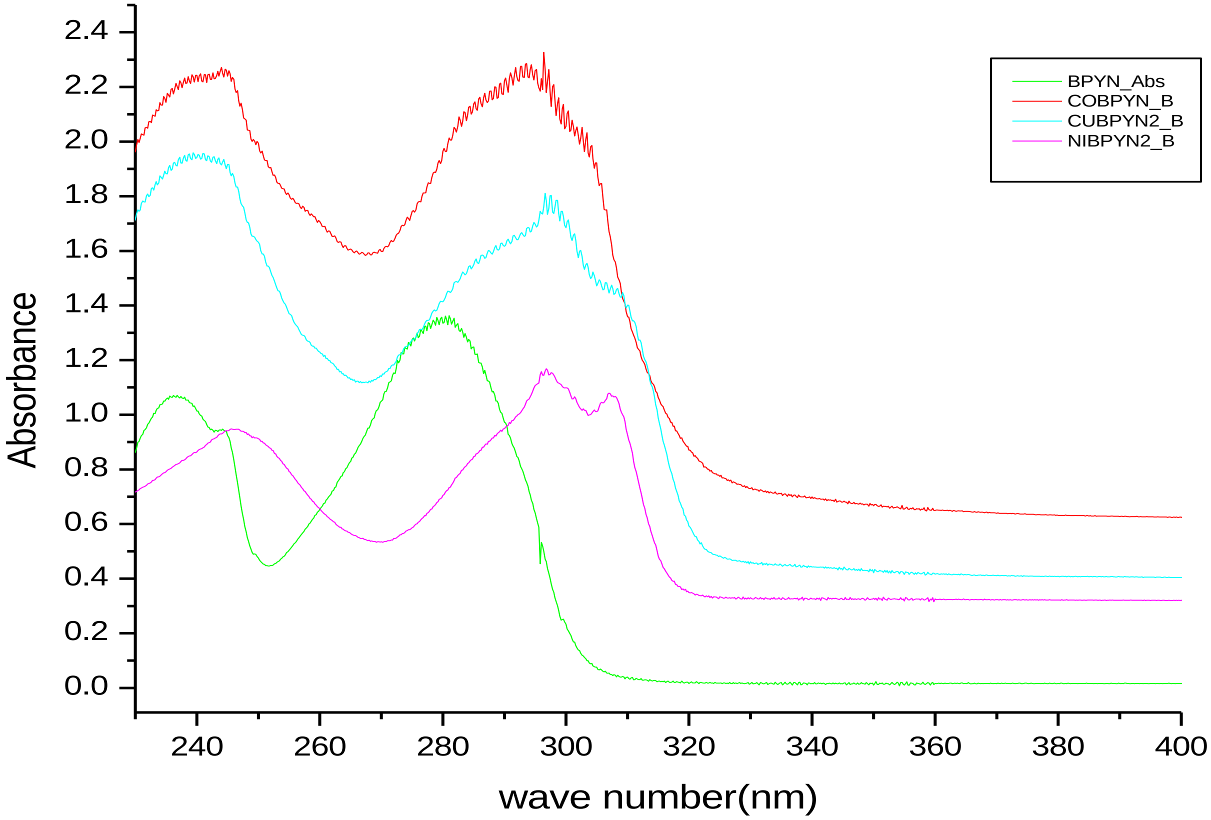
Appendix 6 FT –IR spectra of CuY and CuLY



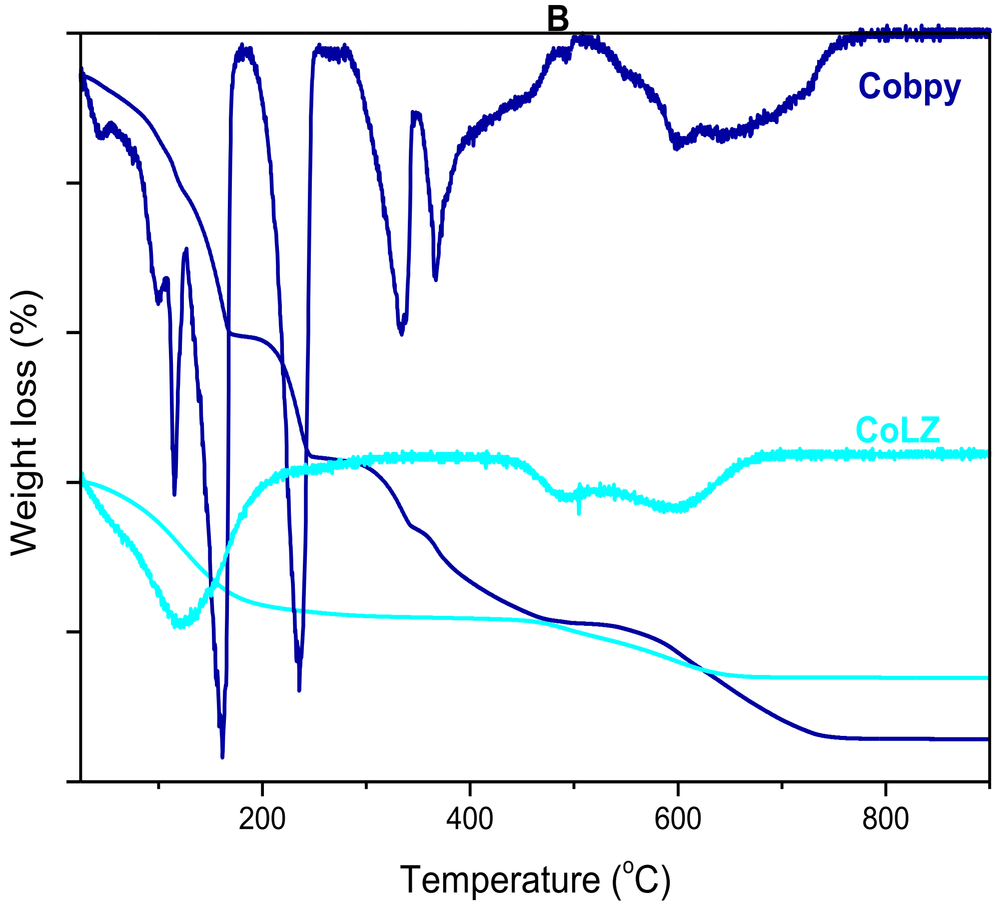
Appendix 7(A) Uv -Vis spectra of BPY, CoBPY, NiBPY and CuBPY



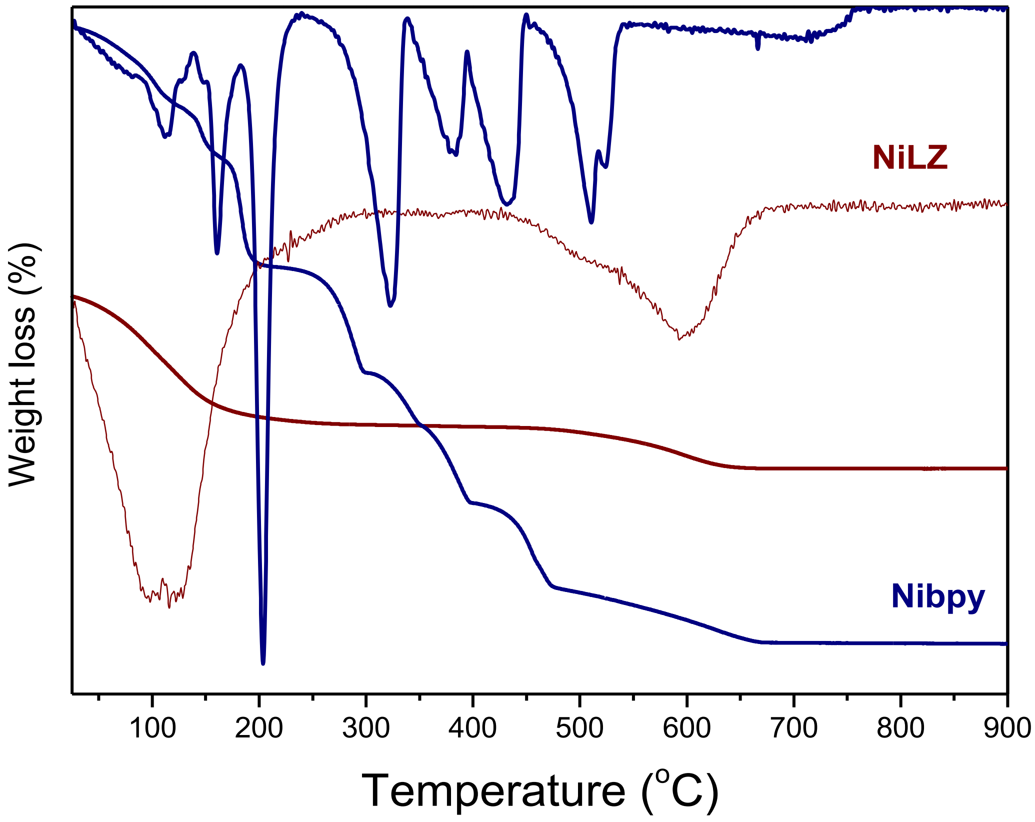
Appendix 7Appendix 8 TGA curve of CoBPY and CoLY (B) Uv -Vis spectra of BPY, CoBPY, NiBPY and CuBPY



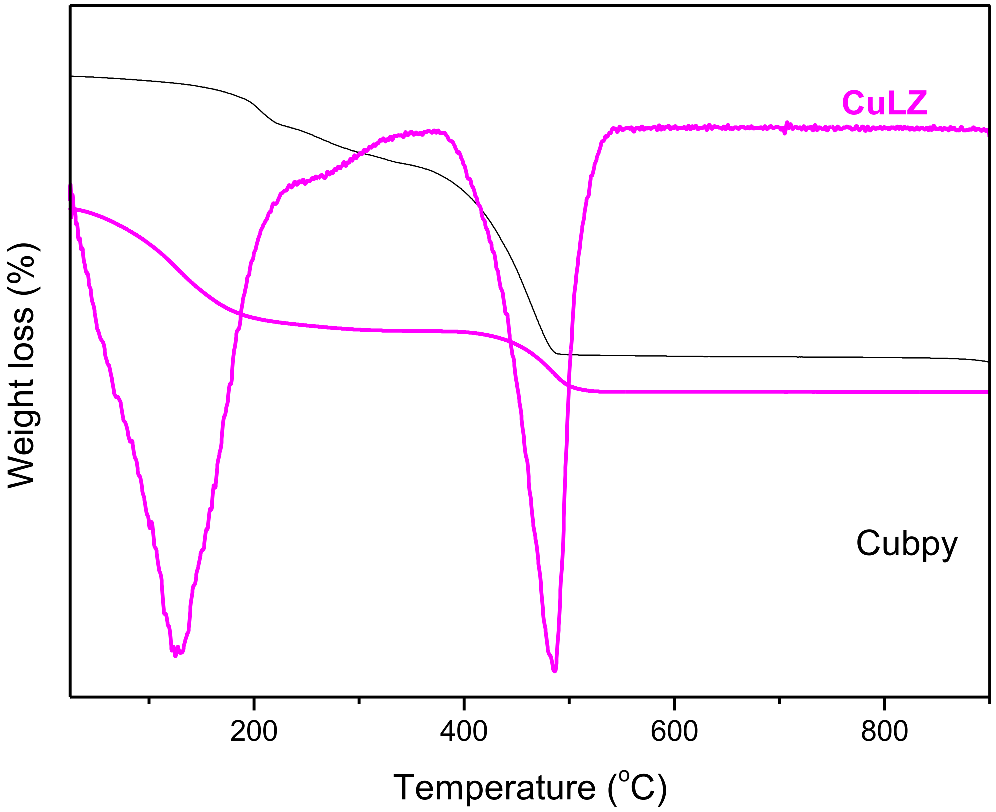
Appendix 8 TGA cuve of CoBPY and CoLY



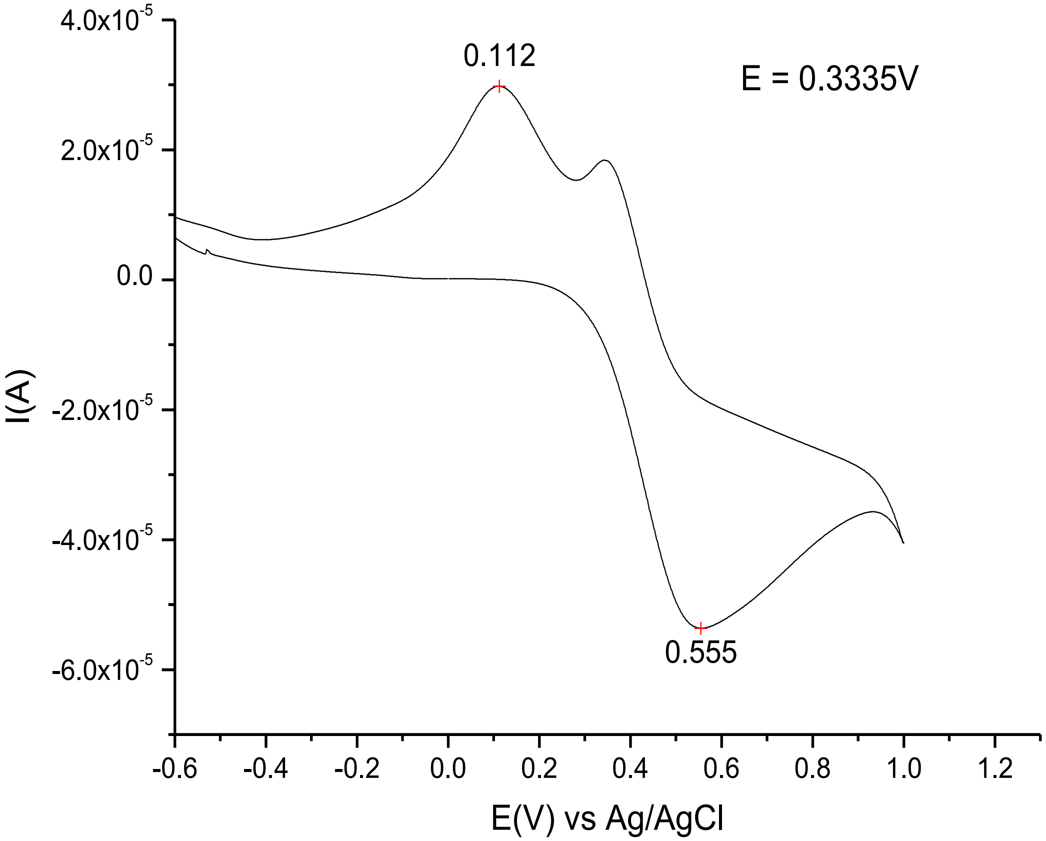
Appendix 9TGA curve of NiBPY and NILZ



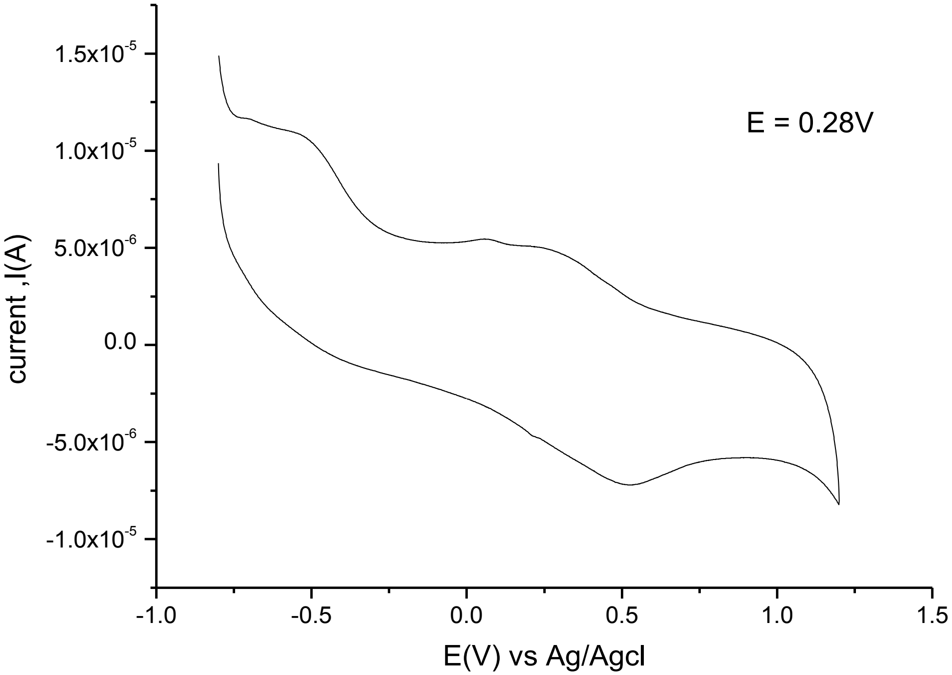
Appendix 10 TGA curve of CuBPY and CuLY



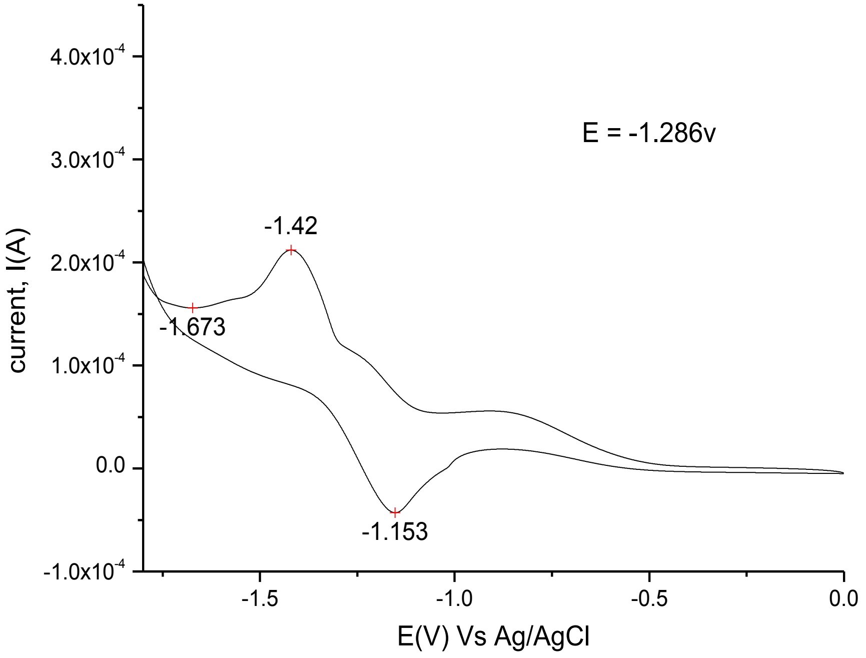
Appendix 11 cyclic voltagram of CoBPY ACN-0.1 mol dm-3 TBAP solution



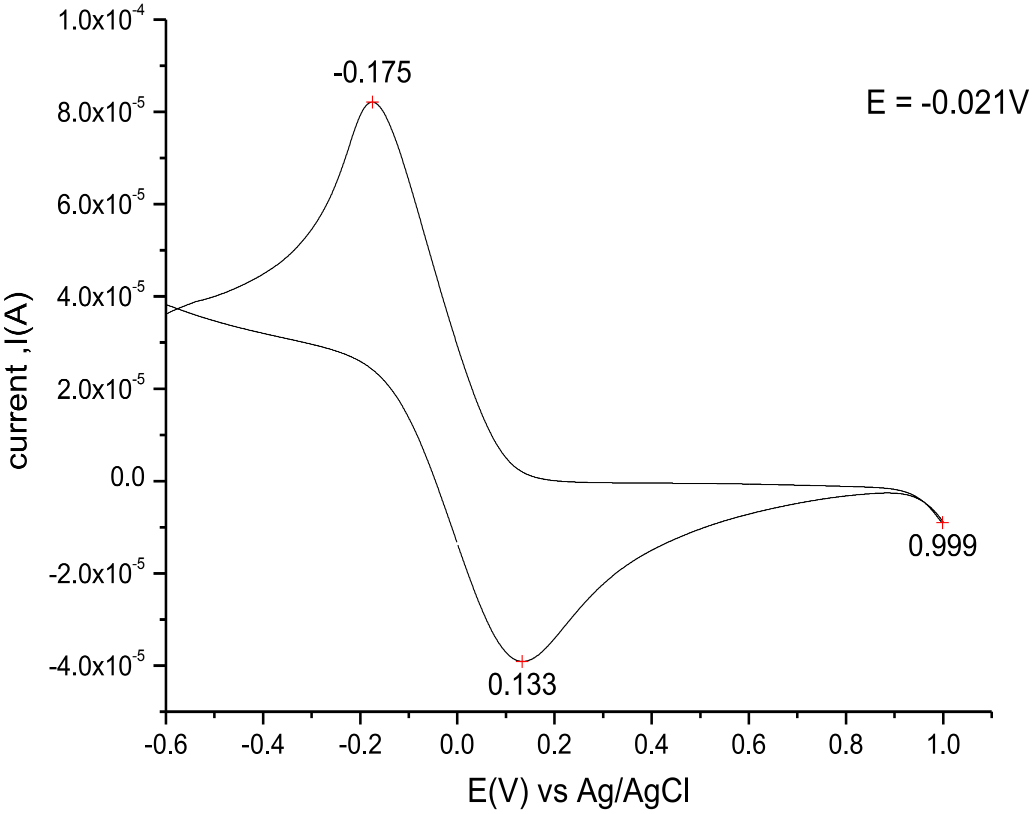
Appendix 12 cyclic voltagrame of graphite-Y/CoBPY electrode in ACN-0.1 mol dm-3 TBAP solution



Appendix 13 cyclic voltagram of NiBPY in ACN-0.1 moldm-3 TBAP solution



Appendix 14 cyclic voltagram of CuBPY in ACN-0.1moldm-3 TBAP solution



Appendix 15 cyclic voltagrame of graphite-Y/CuBPY electrode in ACN-0.1 mol dm-3 TBAP solution