SYNTHESIS OF COPPER COMPLEXES OF BENZOYL PYRAZOLIN WITH ORTHO AMINO PHENOL AND ORTHOAMINO THIO PHENOL – AN INTRODUCTION TO POTENTIOMETRIC STUDIES

BY

PRIYA V.S.

(07PCM13)

A Dissertation submitted to

Avinashilingam University for Women

Coimbatore-641043

In partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

APRIL – 2009

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Certified As Bonafide Research Work

R. Shyamala 30-4-09

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Head of the Department

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Signature of the

Guide

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CONTENTS

I. INTRODUCTION

Organometallic chemistry is the study of chemical compounds containing bonds between carbon and a metal. Organometallic chemistry combines aspects of inorganic and organic. Organometallic compounds are also known as organo-inorganics or metallogranics. The bonding interaction, by the journal organometallics must be ionic or covalent localized or delocalized between one or more carbon atoms of an organic group or molecule and a transition, lanthanide, actinide or main group metal atom. Despite this rather rigorous definition, the borderlines that distinguish organometallic chemistry from other branches containing main group metal atom.

Organometallic compounds thus include various hydrocarbon derivative, carbonyls, certain chelate complex carbides and related compounds, but do not include carbonates of the metal complex with organic amines and metallic salts of organic acids. Organometallic compounds have at least one carbon to metal bond, according to most definitions. This bond can be either a direct carbon to metal bond (σ bond) or a metal complex bond (π bond). Compounds containing metal to hydrogen bonds as well as some compounds containing non-metallic elements bonded to carbon are something included in this class of compounds. The common properties of organometallic compounds are insolubility in water, relatively high melting points, solubility in ether and related solvents, oxidizability and high reactivity. Example of organometallic compounds includes ferrocene, zeise's salt, tetracarbonyl nickel.

CONCEPT, STRUCTURE AND PROPERTIES

Organometallics compounds with bonds that have characters in between ionic and co-valent are very important in industry, as they are both relatively stable in solution and relatively ionic to undergo reactions. Organometallics find practical uses as stoichiometric and catalytically active compounds tetra

ethyl lead previously was combined with gasoline as an antiknocking agent. Organometallic compounds of the reactive metals such as lithium or zinc are extremely basic and may also act as reductants. Organo-transition metal derivatives have in general been of greatest interest not only due to their fascinating structural and bonding variations but also due to their potential applicability as catalytic and stoichiometric reagents along with their role in biological processes. There is hardly any other field of chemistry in which such a large variety of derivatives with novel types of bonding, structure and reactivity.

The 18 electron rule is helpful in predicting the stabilities of organometallic compounds. Organometallic compounds which have 18 electrons (filled s, p and penultimate d orbital) are relatively stable. The organo-transition metal chemistry is dominated by the presence of partially filled'd' orbital of suitable energy in the transition metal atom. The possibility of donation of these'd' electrons to suitable anti-bonding orbital of the ligands moieties, results in π-bond formation, conferring a special stability on such derivatives.

HISTORY

Early development in organometallic chemistry include Louise Claude cadet's synthesis of methyl arsenic compounds related to cacodyls, William Christopher Zeise's platinum-ethylene complexes, Edward frank land's discovery of $Ni(Co)_4$ and Victor Grignard's organomagnesium compounds. The abundant and diverse products from coal and petroleum led to Ziegler-natta fischer-Tropsch, hydroformylation catalysis, which employ carbon monoxide, hydrogen as ligands.

Recognition of organometallic chemistry as a distinct subfield culminated in the Nobel prizes to Ernst Fischer and Geoffrey Wilkinson's for work on metallocenes. In 2005 Yves Chauvin, Robert H. Grubbs and Richard R. Schrock shared the Nobel Prize for r 2 l catalyzed olefin metathesis.

CLASSIFICATION

Transition metal organometallics can be divided in to two broad classes.

- Sigma bonded organometallics and
- Pi –bonded organometallics.

In sigma bonded organometallic a single carbon atom of the ligand is attached directly to the metal through a sigma bond . Pi bonded organometallic, which are formed between a metal atom and ligands such as CO, RNC and other unsaturated molecules. These ligands in addition to the presence of a lone pair of electrons have in common the presence of low-lying vacant orbitals of correct symmetry to form Pi bonds by accepting electrons from transition metal d orbital, known as back bonding. These can be subdivided in to the following two types.

- In a large number of Pi bonded transition metals organometallics, generally the entire unsaturated hydro carbon molecule is involved in the electron donation, with no preferential bonding between the metal atom and any single carbon atom of the organic moieties. E.g- Ferrocene.

- Another type of ligands which form Pi bonded organometallics are carbon monoxide, carbene, carbine etc. In these derivatives only one carbon atom of the ligand is within the bonding distance of the metal.

APPLICATIONS

Until the 1950's, the organometallic chemistry was an unexplored area of chemistry. Tremendous interest in this field originated predominantly from the two discoveries of;

- Synthesis of ferrocene in 1952
- The low pressure catalytic polymerization of ethylene, discovered by Ziegler in 1952.

No area of chemistry has produced more surprise and challenges during the past few decades as organometallic chemistry. This field continues to be one of great excitement and research activity. Some organometallic compounds of transition metals with both saturated and unsaturated organic systems are of great utility as catalysts in organic chemistry and also in some industrial processes.

Example:-

- $RhCl_3(PPh)_3$ –Wilkinson's catalyst in the hydrogenation of olefins.
- Ferrocene when added to fuel oils promotes smokeless combination of the oil.
- A mixture of $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_2Cl$ is used as a catalyst for the polymerization of ethylene.
- $Co_2(CO)_8$ is used as the catalyst in the manufacture of aldehydes and alcohols from olefins.
- Cyclopenta dienyl manganese tri-carbonyl is an effective antiknock agent for petrol. It is more effective than $Pb(C_2H_5)_4$.

In the Heterogeneous polymerization of olefins with Ziegler-Natta catalyst, organometallic intermediate are involved.

A catalyst speeds up a reaction by replacing the high energy barrier of an uncatalyzed process with a series of steps of much lower activation energy. Catalysts are of particular interest to industry because they speed up reactions as well as enabling them to occur with lower inputs of energy.

ORGANOMETALLICS IN INDUSTRY, BIOLOGY & ENVIRONMENT

In applications of some typical main group organometallic reagents, transition metal and their organometallic derivatives are also finding extensive applications in a large number of industrially and biologically important processes. Many biologically important reactions also take place with the aid of enzymes and in some of these organometallic species play important roles. Eg: - A cobalt atom lies at the core of the vitamin B_{12} coenzymes, which have been shown to play a predominant role in methylation reactions in the environment. Molybdenum and iron is essential constituent of nitrogen fixing enzymes in nature. One of the best known example in this direction can be cited as the role of chlorophyll (a Mg complex) as catalyst in the conversion of CO_2 and water in to carbohydrates.

The commercial usefulness of the organometallic derivatives of the main group elements, such as the tetramethyl and the silicon polymers. The use of transition metal organometallics as catalysts in a number of processes is growing at a phenomenal pace. Nitrogen fixation is another important process of promise in which organometallics are expected to play a vital role. Nitrogen is essential to life, but it is an inert gas which must be converted to a more amenable form before it can be used by plants and animals for their growth. This conversion, called nitrogen fixation, forms an essential part of the nitrogen cycle supply of usable nitrogen in soil, which would otherwise be lost to the atmosphere by de nitrification. The fixation of nitrogen by organometal species

is of great topical interest. Some organometallic compounds have been able to activate molecular nitrogen and form complexes.

Systematic investigations on the chemotherapeutic applications of organometallics began with the classical work of Paulehrlich on organoarsenials although some organomercurials have been off and on used before these in the treatment of syphilis and and other infectious diseases.

METAL COMPLEXES IN AGRICULTURE

A large number of organo mercury and tin compounds have been used as fungicides, algacides, herbicides and pesticides in agriculture. Triphenyl tin compounds have been used to protect sugarbeet seelindgs from leaf spot. Metals such as Fe, Cu, Zn, Mn and Mo are essential micronutrients for healthy plant growth. Deficiency in any of these metal nutrients leads to diseases in plants. Fe deficiency in a plant produces yellow leaves and consequently photosynthesis in the plant is affected. This disease is called ironchlorosis. This disease tends to occur in alkaline soil, when Fe (III) present in the soil is converted to insoluble $Fe(OH)_3$, which cannot be transported to the plant cells. Then the addition of soluble Fe (III)-EDTA complex to the soil eliminates this disease.

In food canning industries, chelating agents are used for food preservation traces of metal ions present naturally in fruits; fruit juices ..., tend to oxidize the food ingredients leading to food spoilage. This is prevented by chelating and stabilizing the metal ion oxidants.

II. BACKGROUND DISCUSSION

Heterocyclic compounds are organic compounds containing at least one atom of carbon and at least one element other than carbon such as sulphur, oxygen or Nitrogen with a ring structure[1]. About half of the known organic compounds contain at least one heterocyclic component. Organic chemistry has its origin in the study of natural products and this still remains it's most important role. Many heterocyclic compounds occur naturally and their functions are often of fundamental importance to living systems. Heterocyclic compound is found as key component in biological processes. For example nucleic acid, which are derivatives of pyrimidine and purine ring system, are the components required for photosynthesis and for oxygen transport in higher plants and animals. Nicotinamide, riboflavin and ascorbic acid are naturally occurring heterocyclic compounds.

The chemistry of heterocyclic compounds is as logical as that of aliphatic or aromatic compounds. Their study is of great interest both from the theoretical as well as practical stand point. Heterocyclic compounds occur widely in nature and in a variety of non- naturally occurring compounds. A large number of heterocyclic compounds are essential to life. Examples include such as alkaloids, essential amino acids, vitamins, dyes and hormones contain heterocyclic ring systems. Knowledge of heterocyclic chemistry is useful in biosynthesis and in drug metabolism. Nucleic acids are important in biological processes of heredity and evolution. There are a large number of synthetic heterocyclic compounds with other important application and many are valuable intermediates in synthesis[2].

PYRAZOLINE

Five membered ring system containing two nitrogen atoms adjacent to each other are called pyrazoles. Pyrazole[3-7] was first described by Buchner in 1889 who discovered it during the decomposition of pyrazole 3, 4, 5-tricarboxylic acid. The interest in pyrazoles stemmed from their application in drugs, dyes and as anesthetics. Pyrozoles have also been used as antioxidants in fuels, but their major applications have been in medical and agricultural fields. The di hydro pyrazoles are called pyrazolines. Pyrazoles are fused ring systems have found numerous applications in drug discovery. This species are of interest for at least three main reasons. The first of these is that such compound exhibit anti-inflammatory character, the second is that they boost at least two significant practical application as optical brighteners and fluorescent switches, the third application is that they are frequently used as starting materials for the synthesis of acyclic and cyclic compounds.

Pyrazolinones have extensively been studied for their antipyretic and analgesic activities. Various pyrazolinones have been claimed to be effective as germicide and fungicides **[E.Afsah *et al* .,1978]**[8]

Heterocyclic five membered carbonyl compound 5- pyrazolone possess significant fungicidal activity against the rice blast pathogen pyricularia oryzae which is responsible for the fatal blast disease of the rice crop. Further it has been observed that the replacement of the carbonyl oxygen atom by sulphur enhances the fungicidal activity markedly **[A.S.Mittra *et al*., 1978]**[9]

Pyrazolone derivatives have often shown therapeutic activities and have been used as **dyes [V.S.Jolly *et al.,* 1978]**[10]

A new synthesis of 4-acyl-1-phenyl-3-methyl-pyrazolines-5 is by condensation of acid chlorides or anhydrides with 1- phenyl -3- methyl-pyrazolone -5 in dioxane, catalyzed by suspended calcium hydroxide,have been

found to produce the 4-acylated derivatives directly and in good yields. [**Bror skytte Jensen .,1959]**[11]

A facile synthesis of 5,5[1]-(1,4-phenylene)bis(3-aryl-2-pyrazolines) has been achieved by the cyclo addition reaction of hydrazine hydrate with bis-substituted chalcones which in turn were prepared by the Claisen – Schmidt condensation of p-substituted acetophenone with terephthaldehyde. Condensation of 5,5[1]-(1,4-phenylene)bis(3-aryl-2-pyrazolines) with w-bromo alkoxy phthalimides afforded the titled compounds. Some of which exhibited significant anti malarial as well as anti-microbial activity. [**Neelam Dhakar *et al*., 2008]**[12]

1, 3, 4-oxadiazolinium salts react with ethyl cyano acetate in the presence of triethyl amine to yield 1-substituted 3-amino pyrazole-4-carboxylic ester. An open chain intermediate has been isolated and a mechanism is proposed involving initial attack at C-2 of the oxadiazole ring. The reaction was extended to the synthesis of 3-amino pyrazole-4-carbonitriles ethyl pyrazole-4-carboxylates, 4-acyl-pyrazoles and a 3-acetoxy pyrazole from oxa diazolium salts and malono nitrile, β-ketonic ester, β-diketones and ethyl malonate, respectively. Application of these reagents to oxadiazolo [3, 2-a] pyridinium salts gave derivatives of pyrazolo [1,5-a] pyridine **(S.R. Dando *et al,* 1971)**[13]**.**

3-amino-1-phenyl-2-pyrazolin-5-one condensation with aldehydes in the presence of glacial acetic acid giving the corresponding diarylidene (diferrocenylidene)- iminopyrazolone derivatives. The reaction of with hydrazine, phenylhydrazine'chloroceyl chloride and quinaldine ethiodide have been investicated [**KH.M.Hassan *et al.,* 1978]**[14]

Structural studies on the oxovanadium (IV), Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates of 4-formalozime-3-methyl-1-phenyl-2-

pyrazolin-5-one are reported. The chelates have been isolated in the solidstate and characterized by elemental analyses,spectral data,room temperature, magnetic moment and conductivity measurements.[**Y.M.Patel *et al.*,1981]**[15]

Complexes of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Fe(II) and Zn(II) with 4-benzoyloxime-3-methyl-1-phenyl-2-pyrozolin-5-one have been prepared and characterized on the basis of conductivity, infrared and electronic spectral measurements in conjunction with magnetic susceptibility measurements. **[A.K.Rana *et al.*, 1981]**[16]

Complexes of Co(II),Ni(II),Cu(II) and Zn(II)with Schiff bases derived from condensation of cinnamaldehyde with 4-amino-3-ethyl-5- mercapto-s-triazole and 4-amino-5-mercapto-3-n-propyl-s-triazole have been prepared. These complexes have been characterized on the basis of elemental analyses, NMR,IR ,electronic spectral data, magnetic and thermal studies.[**A.Kumar *et al* .,1999]**[17]

A series of new pyrazolines and isoxazoles have been synthesized from 4- acetylthioanisole, with aryl aldehydes through alpha, beta-unsaturated ketones. The structures of the newly synthesized compounds have been confirmed on the basis of elemental analysis and spectral studies. The newly synthesized compounds have been tested for their analgesic and anti-inflammatory activity. Some of the compounds exhibited encouraging results.[**Grisha.M *et al*., 2009]**[18]

A simple, efficient and environment friendly procedure is developed for the synthesis of 1-substituted-3,7-dialkyl-4H-pyrazolo[4,5-f][1,2,4] triazolo [3,4-b] [1,2,4] thiadiazepines by condensation of 1-amino-2-mercapto-1,3,4-triazoles and 5-chloro-4-formyl-1,2-pyrazoles in the presences of N,N-dimethylformamide as an energy transfer medium, p-TsOH as catalyst and basic alumina as solid support under microwave irradiation. The products are

obtained in good to moderate yields and are in a state of high purity. [**Monika Gupta *et al.*, 2009]**[19]

Derivatives of 5-pyrazolone are *known* to possess antipyretic as well as analgesic properties. It is also known that certain alpha-substituted imides are used as sedatives **[Basil *et al.*, 1978]**[20]

A series of donor substituted 1,3,5-triaryl-2-pyrazoline fluorophores were structurally characterized by X-ray analysis, and their photophysical properties studied by steady-state absorption and emission spectroscopy**.[Liuchun yang *et al*., 2003]**[21]

A negative ion mass spectra and photo electron spectra of substituted pyrazoline were studied. A correlation between the ionization energy of the highest occupied molecular orbital and the yield of ion was found. Isomerisation of molecular negative ions was studied by resonance electron capture mass spectrometry**.[Furley I.I *et al*.,2000]**[22]

The pyrazoline nucleus is of pharmacological interest and has been proved to be a fertile source of antibacterial, antiamoebic, anticancer and medicinal agents.[**Archita Bapna *et al* ., 2008**][23]

Organic pyrazoline dyes were adopted due to their appropriable characteristic. Possibility of the further luminescent material parameters increase while performance dye molecules in the white nanostructured zeolite matrix by components are mixing and laser annealing was proposed. Experimental results with 60 percent of quantum yield again and relaxation time quadruple decrease was obtained. Using the received materials in plotting the identification. Luminescent elements based on the optical disc cover procedure have been determined. [**I.V.Beliak *et al*., 2007]**[24]

The photochemical behavior of 3-pyrazolyl-2-pyrazoline derivative, a newly synthesized biologically active compound has been studied in micellar solutions of anionic sodium dodecyl sulphate, cationic acetyl tri methyl ammonium bromide[CTAB] and non ionic P-tert-octyl phenoxypolyoxyethanol micelle using steady state and time-resolved fluorescence spectroscopy technique.[**Paltu Banerjee *et al*.,2008**][25]

Pyrazolone derivatives play an important role and they are substructures of numerous pharmaceutical agrochemicals, pigments, dyes, chelating as well as, extracting agents. Research on 4-acy pyrozolone derivatives has also received considerable attention because they have potential to form different types of co-ordination compounds due to tautomeric effect of enol form and keto form. Therefore 4-acyl pylazolone derivative are widely used in biological, analytical and extraction metallurgy applications. **[Jianping *et al*., 2005]**[26]

The reaction of diphenylacetalene with μ-1,2-[3,3-bis (methoxy carbonyl)-4-phenyl-1-pyrazoline]-hexa-carbonyldiiron gives tetra phenyl cyclobutadiene tri-carbonyliron; possible intermediates have been isolated , and the structure of the initial cyclo adduct has been determined by x-ray analysis [**H. Kisch *et al*, 1975]**[27]

Pyrazolines and isoxazolines have gained importance due to their varies chemotherapeutic properties celecoxib, a pyrazole derivative and veledecoxib an isoxzole derivative are now widely used in the market as anti-inflammatory drugs**.[V.Padmavathi *et al*., 2008]**[28]

The reaction of enones containing trifluromethyl groups with semicarbazide in basic media proceeds unequivally to give pyrazolidine-1-carboxamides. The direction of the reaction of the enones with thiosemicarbazide depends on their structure, the reaction products are

pyrazolidine and 2-pyrazoline-1-carbothioamides. An enone containing a CF_3 group and a ethoxy group capable of replacement react with semicarbazide to give 2-pyrazoline-1-carboxamide and with thio semicarbazide to give the double addition product, 5-(1-thiosemicarbazido)-2-pyrazoline-1-carbothiamide [**V. Sanin *et al.*,1997]**[29]

Condensation of 1-(P-formylphenyl)-3,5-diphenyl-2-pyrazoline with 4-acetyl-N-phenyl naphthalamide and a mixture of 3- and 4-acetyl-7H-benzimidazo [1,2-b] benz-[de]isoquinoline-7-ones and subsequent heating of the products with phenyl hydrazine were used to synthesize luminophores with orange-red luminescence that have high quantum yields in aromatic solvents. Intramolecular transfer of the electronic excitation energy is observed for these compounds in toluene **[T.P. Zubanova *et al.*, 1982]**[30]

1-pyrazolines which contain a spirocyclo propane fragment at the adjacent azo group, react selectively with acetyl (benzoyl) chloride or acetic anhydride in the presence of $AlCl_3$ to give high yields of the corresponding 1-acyl-3-(2-chloroethyl)-2-pyrazolines, adducts of electrophilic 1,5-addition of acyl chlorides to the conjugated azo cyclo propane system [**O.M. Nefedov *et al.*,1994]**[31]

Pyrazoles are quite popular in the field of medicine and agro chemistry. A number of pyrazole derivatives have been reported to possess interesting biological activities like anti-inflammatory, antimicrobial and antiprotozoal activities. In addition, pyrazole is found widely as a core structure in a large variety of compounds that exhibit important biological activity**.[V.S.Taile *et al.*,2008]**[32]

Pyrazoline exhibit a plethora of bioactivities antibacterial, antitumor,antidepresant, antifungal,insecticidal, antidiabetic, anti amoebic and molluscidal activity. In addition Pyrozolines are also used in the treatment of

parkinson's, alzheimer's disease and cerebral edema. Besides being biologically active they are also used extensively as useful synthons in organic synthesis. **[Neetu Gupta *et al*; 2008]**[33]

Pyrazolones are used as starting materials for the synthesis of biologically of condensed heterocyclic systems **[H.S.Joshi *et a*l; 2007]**[34]

SCHIFF BASES

A Schiff base named after Hugo Schiff is a functional group that contains a carbonitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, but not hydrogen. Schiff bases are simply derived from the condensation of the aldehydes or ketones by the elimination of water. Schiff base compounds are widely studied and used, attracting much attention in both organic syntheses of such compounds are still common among modern synthetic protocols Schiff bases and the relevant transition metal complexes are still found to be of great interest in inorganic chemistry although this subject has been studied extensively.

Schiff base complexes with metal ions have been studies because of their biological and pharmaceutical activity, such as antitumour, antibiotics, antiviral and antioxidative activity. Schiff bases and their metal complexes have been prepared because of their interesting and important properties like high ability to bind toxic heavy metal ions and exhibit catalytic activity.

In the reaction between a nucleophile and a carbonyl group, the carbon atom changes hybridization from sp^2 to sp^3. Addition reactions with primary amines give imnes[35] that are stable under an inert atmosphere. In the presence of oxygen or water, such imines will readily hydrolyze however with an aryl group or certain stabilizing alkyl substituents on nitrogen, the imine formed is stable to oxygen and water and is called a Schiff base. Carbonyl compounds differ in their reactivity towards amines. Some react in a short time to give

imines in good to excellent yields other react only after a prolonged time and the reaction equilibrium may not be favourable.

Schiff base form complexes with several transition metals such as Fe, Co, Cu, Mn, Ni, Cr etc. All transition metal exhibits a strong tendency for formation of complexes with different ligands due to small size, high charge density, variable oxidation states, and a variability of vacant d-orbital to accept the electron.

The Schiff bases and complexes synthesized from biologically active tridentate amino acid have been evaluated for their anti bacterial activity against bacterial species such as Escherichia coli, staphylococcus aureus. [**Zahid H. chochan *et al*., 1997]**[36]

Schiff base have gained prominence as pharmacologically important substances. They have anticancer or antituberculostatic activity. Anticancer schiff base have been prepared by the condensation of aniline with substituted benzaldehyde. Pyrimidine schiff base were synthesized as possible anticancer agents. In view of marked pharmacological importance of this class of compounds, it would be of interest to investigate the Schiff bases having a pyrazolone nucleus. **[Sundar Rao *et al*, 1977]**[37]

synthesis of iron complexes of the tetradentate ligand, bis(2,5-dihydroxy acetophenone) ethylene diamine and a fifth anionic ligand and characterized by spectroscopic techniques. The complex exhibit a broad visible band with maximum wave length in the 550-605nm range, which is assigned to the phenolate→Fe charge transfer transition.[**Sharma *et al.*,1994**][38]

The synthesis and characterization of several hexa co-ordinated ruthenium (III) Schiff base complexes of the type [RuX(Eph3)2(L)] (E=P orAs; X=Cl or Br; L=anion of the Schiff bases derived by the condensation of salicylaldehyde or o-hydroxy acetophenone with benzoyl hydrazine or p-

chlorobenzoyl hydrazine) are reported. An octahedral geometry has been proposed for all these complexes. **[R. Karvembu *et al.*, 2003]**[39]

Infrared , NMR and UV-visible spectra of a series of substituted 2-hydroxy-1-naphthaldehyde Schiff bases were used to investigate enol-imine and keto amine tautomeric equilibrium. They were synthesized and studied by elemental analysis. From the IR spectra of the model compounds it was possible to assign the IR absorption for the C-N and the C-O groups in both keto-amine and enol-imine forms. [**Huseyin Unver, 2001]**[40]

Pure bis-imine Schiff bases are readily accessible in high yield typically>95%. When aliphatic diamine\ aldehyde condensation reactions are carried out under solvent free condition or in poly (propylene)[PPG] as a recyclable reaction medium with negligible waste. [**Colin L. R Raston *et al.*, 2005]**[41]

Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represent an important series of widely studied organic ligands. Schiff bases and the relevant transition metal complexes are still found to be of great interest in inorganic chemistry, although this subject has been studied extensively. Schiff bases and their metal complexes exhibit biological activity as antibiotics, antiviral and antitumor agents because of their specific structure. [**Mohan N.Patel *et al*, 2004**].[42]

Many Schiff bases and their corresponding metal complexes have been extensively studied; relatively few water soluble azo-linked Schiff bases and their metal complexes have been reported. **[Mehmet T uencel *et al,* 2006]**[43]

Synthesis and characterization of six new Schiff‘s, potential hexadentate ligands, containing amide group and Pyridine rings with shallow structures are described. The two step reaction involving ring opening of isatoic anhydride

with Pyridine aldehydes proceed smoothly to give Schiff's bases containing pyridine rings in high purity and better yields **[K.Suresh *et al* ,2003]**[44]

SCHIFF BASE COMPLEXES WITH TRANSITION METALS

The interest in the synthesis and characterization of transition metal containing Schiff bases lies in their catalytic and biological activity in many reactions. The tetra dentate Schiff base complexes related to synthetic, biological and catalytic activities. Schiff base and their metal complexes play an important role in biological processes namely respiration, cell division, photosynthesis etc.

Transition metals have a tendency to form complex with several natural and anionic ligands. These ligands possess invariable lone pairs of electrons and they donate it to the transition metals for the formation of complex compounds. Transition metal form complexes due to small size, high positive charge density , variable oxidation states and vacant (n-1)d orbitals. Schiff base derivatives of various transition metals have been investigated for their pharmaceutical, biological and catalytic activities. Schiff bases have also been used in the determination of metal ions and in the solvent extraction of metals. Presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, transport and storage of matter in living organisms.

Complexes of Co (II) and Ni (II) with new Schiff bases derived from 4-amino-5-sulfanyl-1,2,4-trizoles and glyoxal, biacetyl or benzyl have been prepared. All have the stiochiometry ML $(H2O)_2$ with L Co-ordination via the 2 imine nitrogen and two thialato sulfurs in an overall octahedral geometry. **[Mallikarjun S.Yadawe *et al*., 1997**][45]

Treatment of pyrazoline obtained from acetyl acetone and benzoyl hydrazine with nickel(II) causes the ring opening and formation of a neutral

complex with a trianionic tetra dentate ligand, a square planar nickel(II) complex is formed [**Samudranil pal *et al.*,2004]**[46]

Novel mixed ligand Nickel (II) complexes having octahedral stereochemistry of 3-methy-1-phenyl-2-pyrazoline-5-one were studied by **[Ram C. maurya *et al*; 1991]**[47]

Bis{1-[2,(N,N-dimethylamino)ethylamino] ethaniminato} di copper (I,II) per chlorate,$[Cu_2(C_6H_{13}\ N_3)_2]ClO_4$, is a product of the reaction of $[(H_3CCN)_4\ Cu]\ ClO_4$ with a substituted triazine ring system. The complex is a copper (I)/copper (II) compound in which each Cu atom has a square planar co-ordination environment; the Cu-Cu distance is 2.4552A^o. The two Cu atoms are bridged by an amidate ligand which was apparently formed in a ring cleavage reaction of the triazine ring. Each atom has a two folded axis perpendicular to the Cu-amidate plane, bisecting the Cu-Cu bond. [**Thomas Gallauner *et al.*, 2002]**[48]

A series of amino acid complexes of Co, Cu, Ni which have antifungal, antibacterial have been synthesized and characterized by spectral studies [**Zahid. H.Chochan *et al*., 2006]**[49]

Several new hexa-coordinated ruthenium (III) complexes of the type $[Rux(Eph_3)(LL^1)]$ [x=cl,Br; E=P ,Ar; LL^1 = anthacac, anthdibm, 2-amtpacac] have been synthesized by reacting with tetra dentate Schiff bases**. [K.Natarajan *et al;* 2001]**[50]

New complexes of $Mn,^{11}$,Co^{11},Ni^{11},Cu^{11} and Cd^{11} with bis (acetophenone) ethylenediamine and 5-Chlorosalicylideneaniline have been prepared and characterized on the basis of elemental analysis, magnetic measurements, electronic and i.r.spectra. **[Nilesh H.Patel *et al.,* 2004]**[51]]

Nickel(II) complexes of the Schiff base, 2,3-dimethy-4-formly1-(benzhydrazide)-1-phenyl-3-pyrazoline-5-one with the formulate $[Ni(L)_2(NO_3)](NO_3)$ and$[Ni(L)_2 (ClO_4)]$ ClO_4, have been synthesized and characterized by elemental analyses, electrical conductance in non aqueous solvents, infrared and electronic spectra as well as magnetic susceptibility measurements **[K.C.Raju *et al.,* 2005]**[52]

A series of anti-bacterial and anti-fungal amino acid derived compounds and their Co(II), Ni(II), Cu(II), and Zn(II) metal complexes have been synthesized and characterized by their elemental analyses, molar conductance, magnetic moment IR and electronics spectral measurements. The magnetic moment data suggested for the complexes to have an octahedral geometry around the central metal atom. The electronic spectral data, elemental analyses and NMR spectral data of the ligands and their metal complexes agree with their proposed structure **[M. Arif *et al*., 2006]**[53]

Coordination complexes of Cr(III), Mn(III), and Co(III) with Schiff base derived from 3-substituted phenyl 4-amino -5-mercapto -1,2,4-trizoles and anisaldehyde, veratraldehyde, salicylaldehyde ,2-hydroxyacetophenone have been prepared and characterized by elemental analyses electrical conductance, magnetic moments electronic, IR, NMR, FAD mass studies **[Vinod *et al.,* 2006]**[54]

A new Schiff base ligand has been synthesized from the reaction of 5-amino-1,10-phenanthroline with formyl benzo-15-crowm-5.The ligand reacts with Co(II),Ni(II),Cu(II) salt to characterized by FTIR,NMR,UV-vis, electrical analysis, mass spectra[**Ibrahim Erder *et al.,* 2006**][55]

Some novel mixed –ligand, ternary carboxylate complexes of cobalt (II)with Schiff base having general formula [Co(OOCR](SB)] have been sythesised by the substitution reaction of anhydrous cobalt II acetate. The

isolated products have been characterized by elemental analysis, molar conductance and magnectic moment measurements and spectral (IR, electronic, and FAD mass) data[**Balram *et al.,* 2006]**[56]

A new schiffbase has been synthesiszed from 4-aminophenyl benzimidazole and 2,2,1 –dihydropyrollidene - N –aldehyde and its complexes with Zn(II), Cd(II), Hg(II) halide have been prepared. Physicochemical properties of these metal complexes have been investigated using elemental analysis ,molar conductance ,proton NMR and IR Measurements .All the complexes have been screened for their biological activities **[S. Rekha *et al.,* 2006]**[57]

Cobalt II, Nickel II & cobalt complexes of some aroylhrdrazone Schiff'sbase derived from isoniazide with p-hydroxy benzaldehyde,2,4-dihydroxy Benzaaldehyde are prepared and characterized .metal complexes are analysed by thermal studies, electronic spectral data, IR spectra data **[Boraey 2005]**[58]

Two new Schiff base ligands and their mononuclear complexes with 1:2 metal Ligand ratio have been prepared from acetate salts of Co (II)' Cu(II), Ni(II) &Zn in ethanol .The ligand and their complexes have been established by micro analysis like C^{13} and H^{1} NMR spectra. Antimicrobial activities of the ligands and their complexes have been tested against six different micro organism three are yeast and three are bacteria. [**yilmaz *et al* .,2003]**[59]

The synthesis and characterization of several hexa - coordinated ruthenium(III) complexes of the type $[RuX_2(EPh_3)(L)$ { E=P or As; X= Cl or Br; L=Monobasic tridentate ligand derived by the condensation of o-phenylene diamine or ethylene diamine with salicyladehyde or 0-hydroxy acetophenone are reported. An octahedral geometry has been proposed for all the complexes. The new complexes were found to be effective catalysts for the

oxidation of benzylacohol and cyclohexanol to benzaldehyde and cyclohexanone. **[K.Saridha *et al.*, 2005]**[60]

SCHIFF BASE COMPLEX WITH COPPER

Among the transition metals copper are the most important of all metals, occur most abundant in the earth's crust. Copper-mediated synthetic organic reactions have been continuously and actively studies from 19th century. Preparation and characterization of novel copper complexes are useful in several aspects. In the copper mediated synthetic organic reactions, ligand co-ordinated to copper play frequently an important role. Preparation and characterization of the corresponding copper complexes permit to elucidate the ligand effect on the reactions, which gives a guide to the choice of proper ligand for the reaction. Several of the copper complexes may be useful as a copper reagent in organic synthesis.

Copper is an element in the periodic table that has the symbol Cu with atomic number 29. It is a ductile metal with excellent electrical conductivity. It finds extensive use as an electrical conductor, thermal conductor and as a building material as a component of various alloys. Copper is an essential nutrient to all higher plants and animals. In animals it is found primarily as a cofactor in various enzymes and pigments. In sufficient amounts of copper can be poisonous and even fatal to organisms. Copper (II) sulphate forms a blue crystalline pentahydrate which is perhaps the most familiar Copper compound in the laboratory. It is used as a fungicide, known as Bordeaux mixture.

Three dissymmetrical Schiff base have been prepared by the condensation of 2-hydroxyacetophenone/ethylene diamine and several aldehydes. The electronic transition with in these Schiff base molecules and the effects of solvents of different polarities on these transitions have been investigated with uv visible spectra. Schiff bases complexes binary 1:1 and

ternary 1:1:1 with transition metal Co(II),Ni(II), Cu(II) and Zn(II) have been synthesized and characterized [**Rabie *et al.*, 2007]**[61]

The electrochemically generated dianion reacts with M^{11} trifluoromethane sulfonate to afford the corresponding (1/1) complexes. $[Co^{11}L_3]$,$Ni^{11}L_3]$ and $[Cu^{11}\ L_3]$ respectively. These complexes have been characterized by spectroscopic and electrochemical techniques. ESR studies were carried out and the environment of Co^{11} and Cu^{11} ions were studied and found to high-spin distorted octahedral geometry in $[Co^{11}L_3]$ and tetrahedrally distorted square-planer symmetry in $[Cu^{11}L_3]$. **[Alain *et al*., 2000]**[62]

Synthesis of Schiff base 4-hydroxy salicylaldehyde-p-amino acetophenone Oxime starting from P-aminoacetophenone oxime and 4-hydroxy salicylaldehyde complexes of this ligand with Co(II), Cu(II),Ni(II) and Zn(II) were prepared with a metal ligand ratio of 1:2.[**Eradalcanpolat *et al*., 2007**][63]

Mono and binuclear Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of Schiff base ligands derived from 7 formyl-8-hydroxy quinoline with diaminonaphthalane were prepared. The results show that the Co(II),Zn(II) and Cd(II) complexes are tetrahedral; Ni(II) complexes are octahedral Cu complexes are tetragonally distorted, octahedral or square planar. [**Tarek M.A.Ismail *et al*;2004**][64]

Synthesis and structural characterization of distorted pentagonal bipyramidal Co(II), pseudo-octahedral Ni(II) and Cu(II) complexes of the type $[ML(NO_3)_2]$ {L=N-(2-pyridylethyl) Pyridine-2-methyl ketimine} are reported. All the complexes exhibit d-d transitions in the visible region. [**Sumanta Kumar padhi *et al*., 2007**][65]

Two new five co-ordinated Cu(II) complexes, $Cu(L)\ Cl_2$, CH_3OH and $Cu(L)\ Cl_2\ CH_3OH$ and $Cu(L)Br_2$ flexidentate ligand (L) 2-pyridineal diazine have been synthesized and characterized **[Ruma Karmakar *et al.*,2007]**[66]

Two new one-dimensional azido bridged chital copper (II) co-ordination polymers, $[\mu\text{-}1,1,3\text{ -}N_3]_2\ \{Cu_2(R\text{-}L)_2\ (N_3)_2\}]_n$ (R=L=R-2-(N-(2-Hydroxy butyl) carbaldimino) pyridine) have been synthesized and characterized [**Jain-Qing tao *et al*.,2007]**[67]

Synthesis, spectral, co-ordination and thermal aspects of N,N^1-polymethylene bis(1-phenyl-3-methyl-4-trifluoro acetylimino-2- pyrazoline-5-ol) oxo vanadium alkyl back bones ranging from two to four carbons have been characteristized on the basis of elemental analysis, magnetic moments, molar conductivity measurements, spectra(FTIR, ESR, UV-Visible) and thermal studies**.[C.K. Modi *et al* .,2005]**[68]

POTENTIOMETRY

Potentiometry involves measuring an electrical potential that is related to a component in which one is interested. For example many communities fluoridate water supplies to enhance the durability of tooth enamel. One convenient way to measure fluoride concentration is to use an electrode where the potential depends upon the concentration of fluoride. Potentionmetric electrodes are usually fast, portable and do not require extensive training to operate. Many strategies have been explored to create electrodes in which the electrical potential varies with the concentration of some species. The most common electrodes in use is the glass membrane pH electrode. The heart of the glass membrane P^H electrode is the glass membrane which ideally only allows H_3O^+ ions to become incorporated in its inner and outer layer.

Many types of membranes have been developed to detect a wide variety of analytes, but the electrical potential across that membrane is the signal that must be measured. In order to measure most reasonable pH meters are capable of acquiring signals from different types if ion selective electrodes[69].

The application of potentiometry includes pollution monitoring in effluents and natural water. Such as Cl, K, Ca, CN in soils, plant material, fertilizers and feed stuffs, fluoride in drinking water, skeletal and dental studies, biomedical laboratories- Ca, K, Cl in body fluids and in electroplating of F and Cl in etching baths.

Keeping the above view in mind we have prepared tetra dentate Schiff base ligands of pyrazolone derivatives and their corresponding copper complexes.

The new copper complexes synthesized are characterized by spectral and subjected to potentiometric studies by preparing the ion-selective membranes by using complexes. In this potentiometric studies, we have studied the electrode response, effect of pH and its interference study.

III. EXPERIMENTAL

The experimental work consist of various chemical reactions,which involves pure solvents and reagents. All the solvents were freshly distilled before use. Pyrazoline derivatives were freshly prepared by standard procedures and then the pyrazoline Schiff bases were synthesized by condensation reaction. The copper complexes of new Schiff bases were prepared by using previously prepared starting complex $CuCl_2$ $(PPh_3)_2$. One of the newly synthesized Cu (II) complexes was subjected to potentiometric studies. Melting points were determined from Joshibha instrument. Double beam FTIR were recorded form systronic pc based double beam spectrophotometer 2202, double beam UV were recorded form systronic double beam UV spectrophotometer, elemental analysis were done from Sophisticated Test and Instrumentation Center, Cochin. Potentiometric studies were carried out using [Equiptronics MODEL EQ 602] instrument.

MATERIALS REQUIRED

The chemicals required for this work includes 1-phenyl-3-methyl-2-pyrazolin-5-one [Aldrich], 1,4-Dioxane (S-d fine chemicals), Calcium hydroxide (S-d fine chemicals), Benzoyl chloride [Reachem] Hydrochloric acid [LR Grade, Hi-pure chem] $CuCl_2.6H_2O$[s-d fine chemicals], Triphenyl phoshine [Loba chemie], ortho-Amino phenol [Loba chemie], ortho amino thiophenol[Loba chemie].

1. Preparation of 4 benzoyl-1-phenyl-3-methyl-2-pyrazolin-5-one [BP]

It was prepared by condensation of 7.5gm of 1-phenyl-3-methyl-2-pyrazolin-5-one[70] by dissolving in 40ml of 1, 4 dioxane by the application of heat; about 6g of Ca $(OH)_2$ and 1.5 ml of benzoyl chloride were added in drop wise in 1 minute. Then the reaction mixture was refluxed 45 minutes. Then the flask was filtered and was poured in to HCl (200ml, 2N). The solution was kept in freezer for 2days to form yellow crystals.

Colour	-	yellow
Yield	-	73%
Melting point	-	148^{o}C

2. PREPARATION OF NEW SCHIFF BASES

i) Preparation of N(1-phenyl-3-methyl -4-benzoyl-5-hydroxy-1,2-pyrazolin)-o-Amino phenol imine [BPOAP]

To a solution of 1-phenyl -3-methyl-4-benzoyl-5-one [0.844mg, 3mmole] in 30ml of ethanol added o-Aminophenol [0.327mg, 3mmole] and refluxed over water bath for about 5 hours. The resulting solution is kept as such for about two days. The Schiff base was separated as shiny yellow crystals. It was filtered washed with petroleum ether and dried

Colour	-	yellow
Yield	-	70%
Melting point	-	230-232^{o}C

ii) Preparation of N(1-phenyl-3-methyl -4-benzoyl-5-hydroxy-1,2-pyrazolin)-o-Amino thio phenol imine[BPOATP]

To a solution of 1-phenyl -3-methyl-4-benzoyl-5-one [0.556mg, 2mmole] in 30ml of ethanol ,added o-Amino thiophenol [0.5ml, 4mmole] and refluxed over water bath for about five hours. The resulting solution is kept as such for about 3days. The Schiff base was separated as shiny brownish yellow crystals. It was filtered washed with petroleum ether and dried.

Colour	-	Brownish yellow
Yield	-	68%
Melting point	-	95^{o}C

1. **Preparation of starting Copper complex (Dichloro-bis-[triphenyl phosphine Copper (II)] [$CuCl_2(PPh_3)_2$]**

To a warm solution of $CuCl_2.6H_2O$ (0.8524g, 0.005mol) a hot solution of triphenyl phosphine [2.623g, 0.01mol] in minimum amount of ethanol was added slowly with constant stirring to give a white precipitate. The reaction mixture was boiled for 5 minutes and kept at room temperature for 24 hours. The precipitate was filtered, washed with dry acetone and dried in a vaccum desiccators (H_2SO_4; KOH) the complexes was further washed with petroleum ether [60-80^{0}c] to remove traces of free triphenyl phosphine.

Colour	-	Dirty white
Yield	-	85%
Melting point	-	174^{o}C

2. PREPARATION OF NEW COPPER COMPLEXES WITH THE NEWLY PREPARED SCHIFF BASES

i) Preparation of N(1-phenyl-3-methyl -4-benzoyl-5-hydroxy-1,2-pyrazolin)-o-Amino phenol imine Copper complex [BPOAPCu]

To a solution of $CuCl_2$ $(PPh_3)_2$[71,72] [0.196mg, 0.3mmole] in 30 ml dry ethanol added BPOAP [0.109mg, 0.3mmole] and refluxed over water bath for about three hours. The resulting solution mixture is reduced 10ml. The copper complex was separated as shiny yellow crystals. It was filtered, washed with petroleum ether and dried.

Colour	-	Yellow
Yield	-	82%
Melting point	-	178-185^{o}C

ii) Preparation of N (1-phenyl-3-methyl -4-benzoyl-5-hydroxy-1,2-pyrazolin)-o-Amino thio phenol with Copper complex [BPOATPCu]

To a solution of $CuCl_2(PPh_3)_2$ [0.196mg, 0.3mmole] in 30 ml dry ethanol, added BPOATP [0.109mg, 0.3mmole] and refluxed over water bath for about six hours. The resulting solution is reduced to 10 ml. The copper complex was separated as bluish black powder. It was filtered, washed with petroleum ether and dried.

Colour	-	Bluish black
Yield	-	82%
Melting point	-	270^{o}C

POTENTIOMETRIC STUDIES

PREPARATION OF [BPOAPCu] MEMBRANE ION SELECTIVE ELECTRODE

A number of membranes were prepared using varying amount of epoxy resin as binding material. About 0.2g of powdered BPOAPCu complex was thoroughly mixed with epoxy resin (Huntsmen advanced material, India Pvt. Ltd.) and the paste was applied on Whatmann filter paper no.42. This was spread uniformly over the filter paper to obtain 0.9mm thickness of the electro active material with matrix. This was left in air to dry for 48 hours to get an electro active membrane. A circular piece of this membrane was fixed with the tube filled with saturated solution of Copper sulphate and reference Copper metal wire was inserted (diameter 0.5mm and length 12cm) through other end of the glass tube in such a way that it remains dipped in saturated solution of Copper sulphate already filled in this glass tube. This complete assembly will work as an ion selective electrode of Cu^{2+}ion. The entire electrode system for the measurement can be represented as;

Internal reference electrode (Cu wire)	Internal reference solution (1M $CuSo_4$ solution)	Ion selective membrane	Sample solution	External reference electrode (SCE)

The ion selective electrode was connected to one terminal of a digital potentiometer. The other terminal was connected to the reference electrode [saturated calamol electrode]. The ion selective electrode was immersed in the sample solution of $CuSO_4$ and the reference standard calomel electrode is immersed in saturated KCl solution. These solutions are connected using potassium nitrate-agar salt bridge

The following studies are conducted to ensure the efficiency of the electrode.

- The electrode potential of a series of standard solutions copper (II) had been measured to determine the electrode response
- The electrode potential of standard copper(II) solution in a series of varying concentration of propanol had been measured to determine the effect of solvent
- The electrode potential of standard copper(II) solution of varying pH has been measured
- The interfering study of various cations and anions has been measured.

The water used in this study was doubly distilled water. The electrode has to be rinsed in the doubly distilled water after every measurement to prevent contamination carry over on the electrode.

IV. RESULTS AND DISCUSSION

Schiff base derived from (1- phenyl 3 methyl-4- benzoyl pyrazolin-5-one) with ortho amino phenol and ortho amino thio phenol present a series of ligands. The metal complex of which have been widely studied. In the present study pyrazoline Schiff base were synthesized and they form a tri co-ordinated complexes. The ligand were derived from Schiff bases are known to stabilize metal complexes with oxidation state (II) should be easily accessible. On the basis of this we carried out the reaction of pyrazoline Schiff bases with starting complex [$CuCl_2$ $(PPh_3)_2$].

The Schiff bases used in this work were synthesized by general condensation method of pyrazoline and its derivatives with the appropriate ortho amino phenol and ortho amino thio phenol in 1:1 ratio Schiff base ligands are soluble in common organic solvents. They were treated with $CuCl_2$ $(PPh_3)_2$ in 1:1 molar ratio. Characterization has been studied by Infrared, UV spectroscopy & elemental analysis. As a part of application the new complexes were studied potentiometrically as ion selective electrode [ISE].

ELEMENTAL ANALYSIS

Elemental Analysis of the Schiff base and complexes were recorded at Sophisticated Test and Instrumentation Centre, Cochin. The theoretical value and experimental value are given in a table I. The comparison of theoretical value with the experimental confirms the molecular formula suggested for the above new complexes.

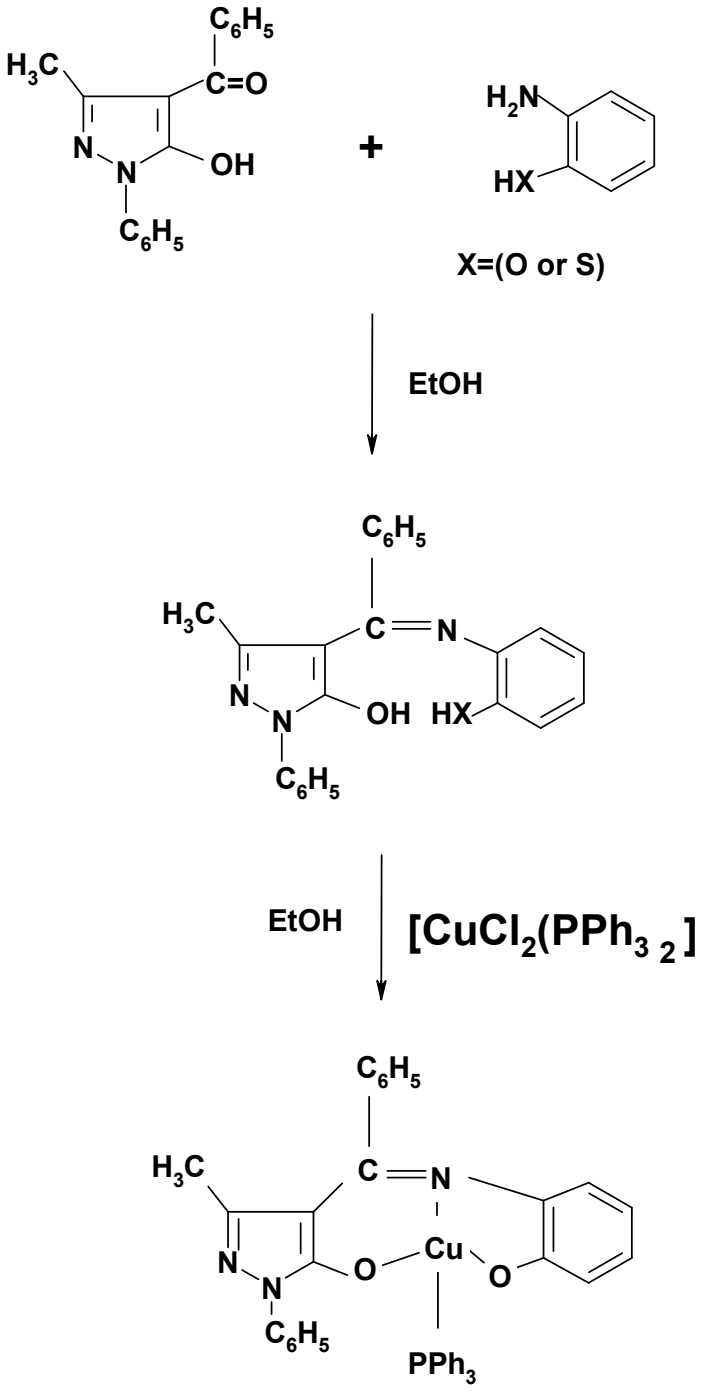

C6H5
H3C
C=O
N
N
OH
C6H5
+
H2N
HX
X=(O or S)
EtOH
C6H5
H3C
C
N
N
N
OH
HX
C6H5
EtOH
[CuCl2(PPh3 2]
C6H5
H3C
C
N
N
N
O
Cu
O
C6H5
PPh3

TABLE I-ELEMENTAL ANALYSIS OF SCHIFF BASE AND COMPLEXES

Sl. No	Sample	Theoretical value				Experimental value			
		C%	H%	N%	S%	C%	H%	N%	S%
1.	BP	73.38	5.03	10.07	-	73.01	4.96	9.99	-
2.	BPOAP	74.79	5.14	11.38	-	74.01	5.12	10.91	-
3.	BPOATP	71.6	4.9	10.8	8.3	70.80	4.01	9.86	7.85
4.	BPOAPCu	71.0	4.6	6.06	-	69.8	4.1	5.99	-
5.	BPOATPCu	69.49	4.5	5.9	4.51	68.89	3.91	5.10	3.95

FTIR-SPECTRA

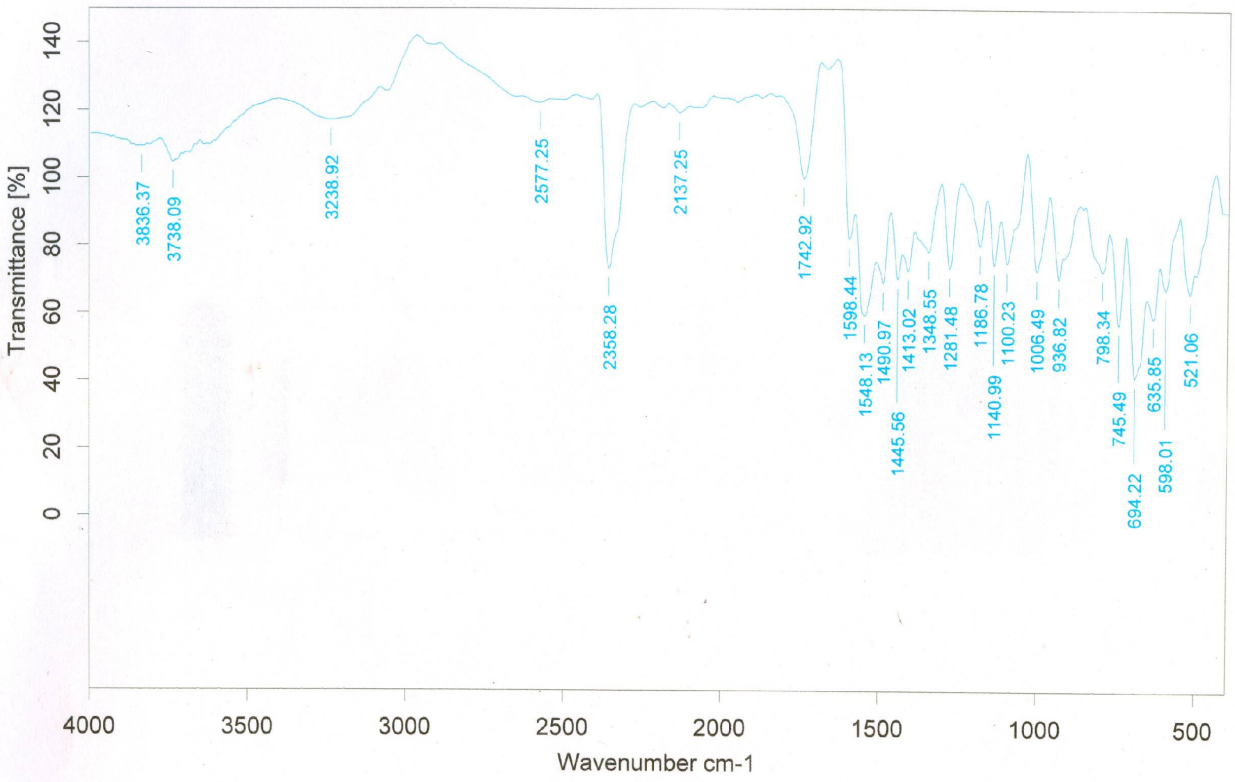
FTIR spectra were recorded in systronic pc based double beam spectrophotometer 2202 (4000-400cm^{-1}). The FTIR spectra of the Copper (II) Schiff base complexes have been compared with that of free Schiff base ligand and this comparison leads to the indication for the coordination site in the complexes. The characteristic IR absorption frequencies found for the free lignd will be slightly shifted if some donor atoms of the ligand attached to the metal ion in the complexes. Hence by examining the IR spectra of the complexes and that of the free Schiff ligand, it is possible to get information about the attachment of the ligand molecule to the metal ion in the complexes.

TABLE FOR FTIR SPECTRUM

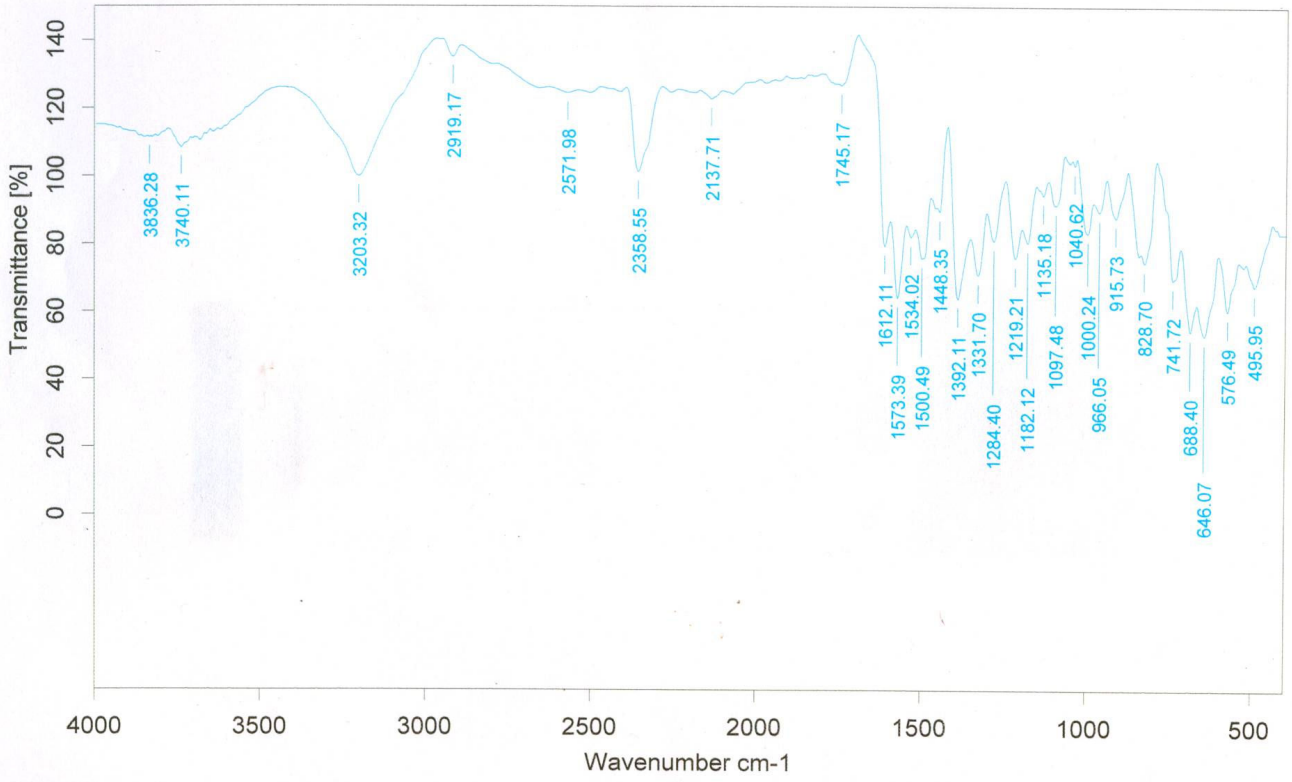
υ (cm^{-1})	BP (cm^{-1})	BPOAP (cm^{-1})	BPOATP (cm^{-1})	BPOAPCu (cm^{-1})	BPOATPCu (cm^{-1})
O-H	3238.92υ	3203.32	3347.30	3196.88	-
S-H	-	-	2586.33	-	-
N-N	1140.99	1135.18	1057.19	1062.63	1018.93
C=N	1598.44	1612.11	1601.78	1612.71	1643.07
C-N	1348.55	1182.12	1364.38	1185.81	-
C=O	1742.92	1745.17	1745.62	1743.66	-
C-O	1186.78	1135.18	1133.24	-	1139.11
C-H	-	-	3059.42	3050.93	3052.38
C-S	-	-	745.61	-	735.78
N-H	2358.28	2358.55	2357.92	2357.33	2359.74
C-C	-	1500.49	-	-	-

The absorption OH band at 3238.92cm^{-1} in 1-phenyl-3-methyl 4-benzoyl pyrazoline -5-one this band range is further increased in BPOATP (3347.30cm^{-1}) and reduced in BPOAP (3203.32 cm^{-1}) Schiff base ligand. The absence of OH band in Schiff base complexes confirms that 'O' from 'OH' gets coordinated to the Cu atom.

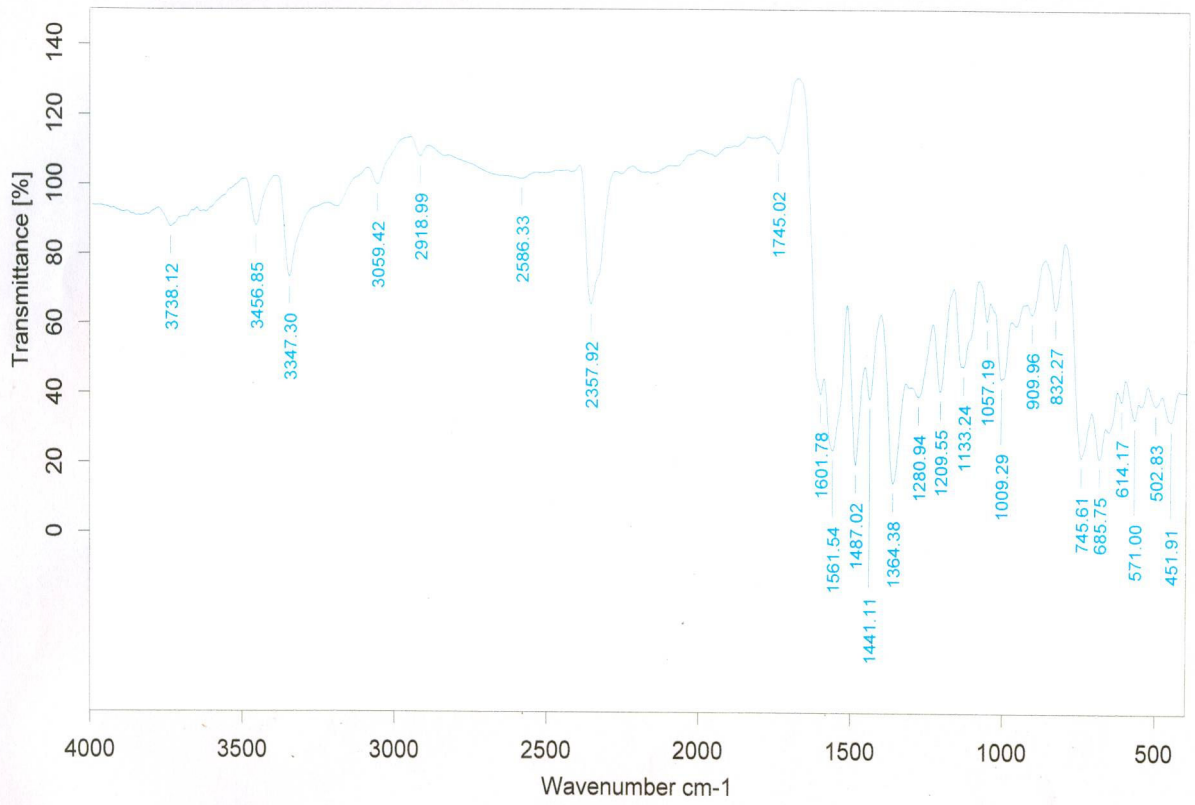
Band absorbed at 2586.33cm^{-1} in the spectra of Schiff base ligand which is characteristic of S-H band in Schiff base ligand(BPOATP).Very sharp band at 1742.92cm^{-1}, 1745.17cm^{-1},and 1745.62$cm^{-1}$was assigned due to C=O in BP Schiff base ligand (BPOAP & BPOATP) but it is missing in Schiff base ligand complex (BPOATPCu). The C-O absorption band occurs at 1135.18cm^{-1}, 1133.24cm^{-1} in Schiff base ligand and it is missing in (BPOAPCu) complex.



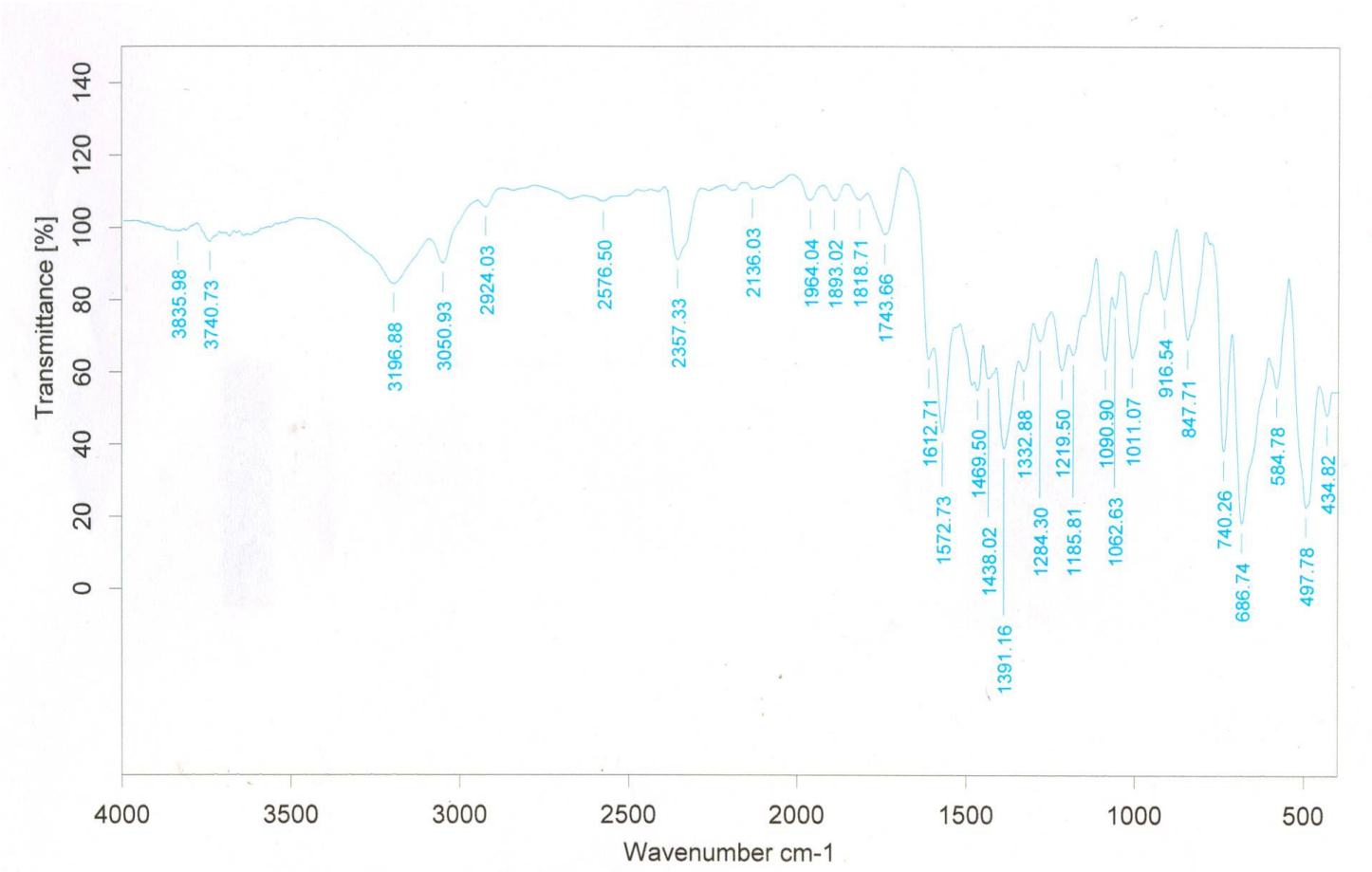
Date of Measurement: 02/02/2009	Sample Name: 2G MG BP
Filename: SKS.69	Resolution :4



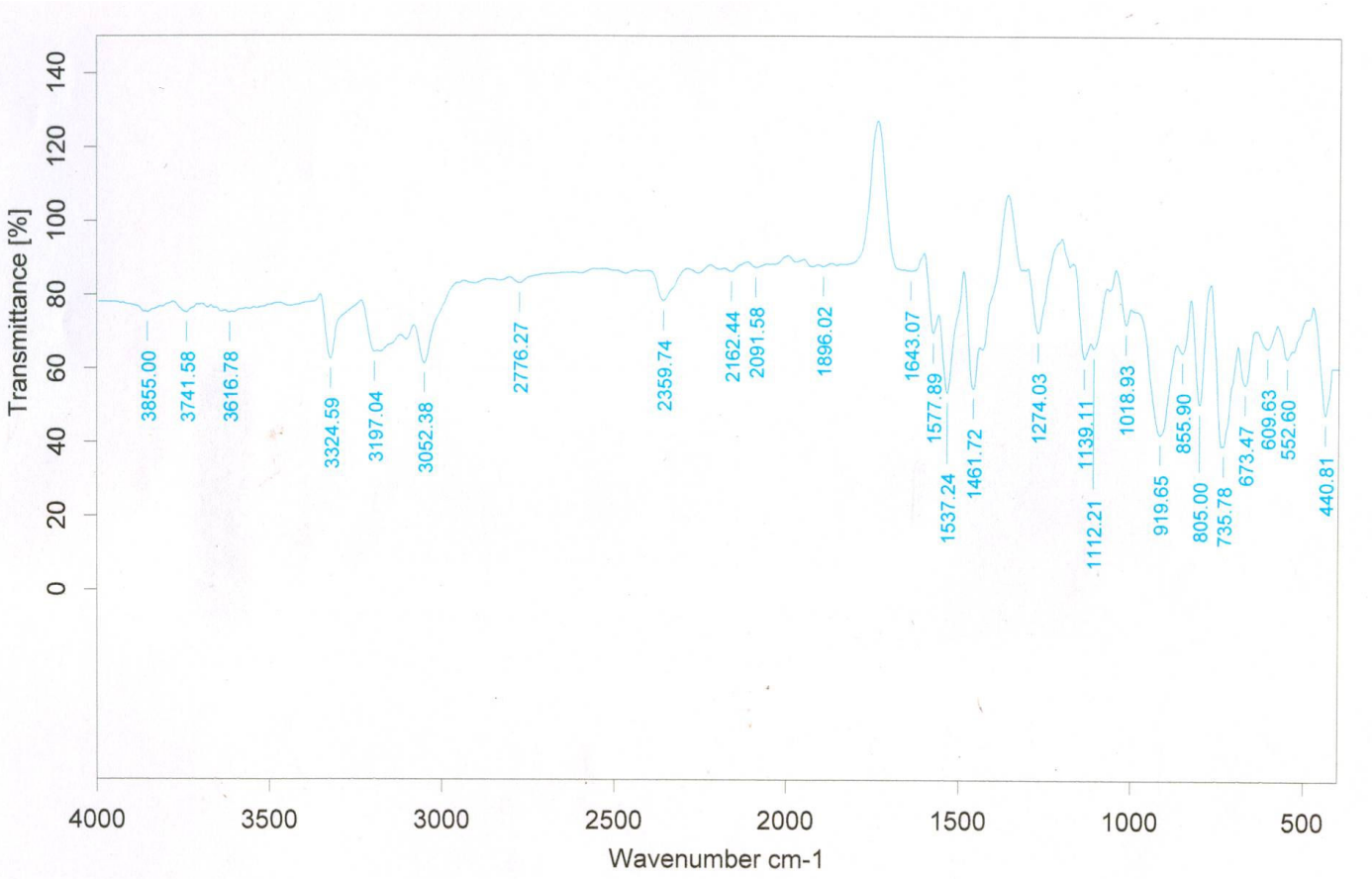
Date of Measurement: 02/02/2009	Sample Name: 2GS MG BPOAP
Filename: SKS.66	Resolution :4



Date of Measurement: 02/02/2009	Sample Name: 2GA MG BPOATP
Filename: SKS.67	Resolution :4



Date of Measurement: 02/02/2009	Sample Name: 2GS1 MG BPOgPCU
Filename: SKS.61	Resolution :4



Date of Measurement: 02/02/2009	Sample Name: 2GA1 MG
Filename: SKS.58	Resolution :4

Absorption band at 1500.49 cm^{-1} indicates the presence of C-C band in BPOAP clearly confirms that the benzoyl pyrazoline which is in keto- enol tautomerism is completely converted into enol form. The sharp absorption band at 1186.78cm^{-1}, 1135.18cm^{-1}, 1133.24cm^{-1}, 1 and 1139.11cm^{-1} was assigned due to C-O in BP, Schiff base ligand (BPOAP & BPOATP) and Schiff base complexes (BPOATPCu) 3059.42cm^{-1} ,3052.38cm^{-1} and 3050.93cm^{-1} are assigned due to the characteristic of C-H in BPOATP, BPOATPCu and BPOAPCu. The C-S band appears in the range of 800-600cm^{-1}. The N-H band shown in Schiff base ligand and complexes indicates that the amino group present in compounds. C=N band value shifts from lower to higher value, indicates the nitrogen from C=N group gets coordinated to the metal atom (Cu) through the lone pair of electron.

UV-SPECTRA

Double beams ultra violet spectroscopy were recorded from systronic double beam uv spectro photometer. The UV spectra of the nickel (II) Schiff base complexes have been compared with that of free Schiff base ligand. The electronic spectra of Schiff base ligands and their complexes have been recorded in chloroform and ethanol. The spectrao data adre given in below table 3 and representative spectra are displayed in figure.

Table-3 UV-spectroscopy of free Schiff base ligand and the complexes

Complexes	Amax (nm)	Assignment
BP	260.8 320.0 345.6	Quartz ultraviolet region
BPOAP	320.0 345.0 360.0	Quartz ultraviolet region Quartz ultraviolet region Visible region
BPOATP	316.8 369.6 404.8	Quartz ultraviolet region Quartz ultraviolet region Visible region
BPOAPCu	299.2 369.6 393.6	Quartz ultraviolet region Quartz ultraviolet region Visible region
BPOATPCu	264.4 312.0 355.2	Quartz ultraviolet region

The electronic spectra of Schiff base ligands and their complexes have been recorded in chloroform and ethanol. The spectral data are given in table 3 and representative spectra are displayed in figure.

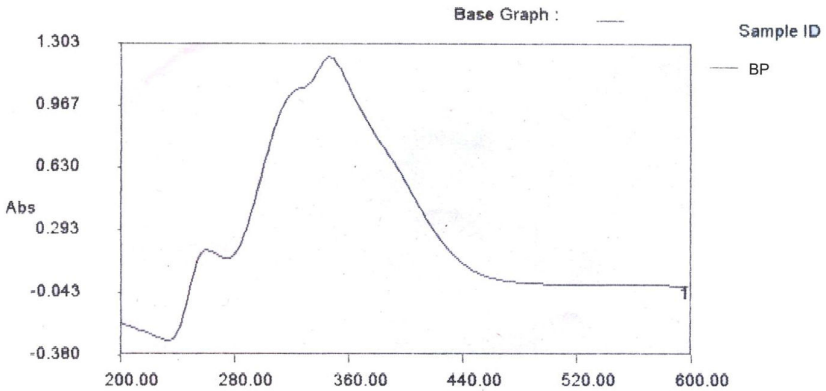
SYSTRONICS

DOUBLE BEAM UV-VIS Spectrophotometer: 2202

Date : 18/04/09 Time : 11:36:00

Name of the Company/Laboratory: Chemistry, SRMV CAS, CBE-20,TN

Mode of Operation: Scan Mode B.W.: 2.0 nm



Peak Pick		Pick Point	
345.6	1.227	320.0	1.039
260.8	0.184		

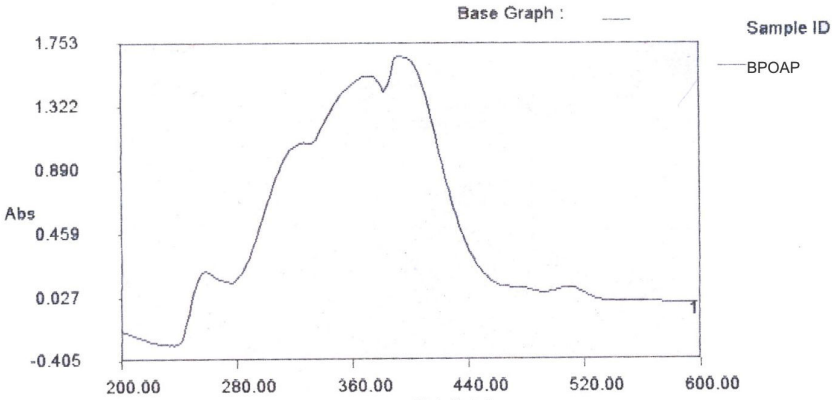
SYSTRONICS

DOUBLE BEAM UV-VIS Spectrophotometer: 2202

Date : 18/04/09 Time : 11:51:51

Name of the Company/Laboratory: Chemistry, SRMV CAS, CBE-20,TN

Mode of Operation: Scan Mode B.W.: 2.0 nm



Peak Pick

393.6 1.655

369.6 1.528

326.4 1.077

257.6 0.202

507.2 0.098

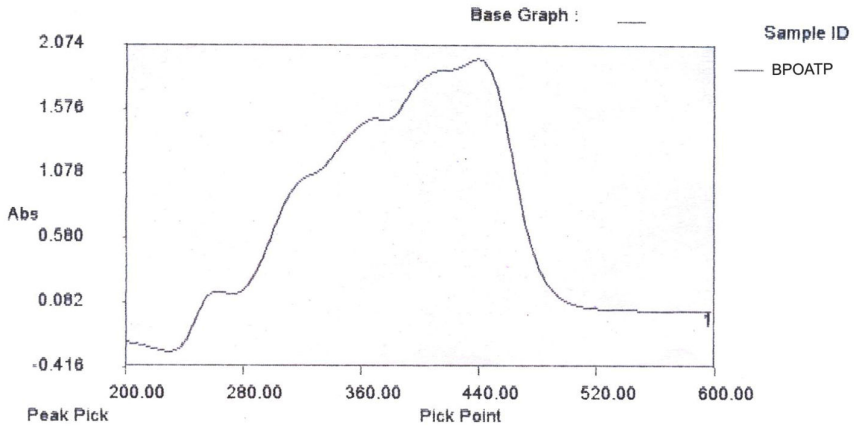
SYSTRONICS

DOUBLE BEAM UV-VIS Spectrophotometer: 2202

Date : 18/04/09 Time : 11:47:38

Name of the Company/Laboratory: Chemistry, SRMV CAS, CBE-20,TN

Mode of Operation: Scan Mode B.W.: 2.0 nm



Peak Pick		Pick Point	
438.4	1.962	316.8	1.001
369.6	1.503	404.8	1.841
262.4	0.164		

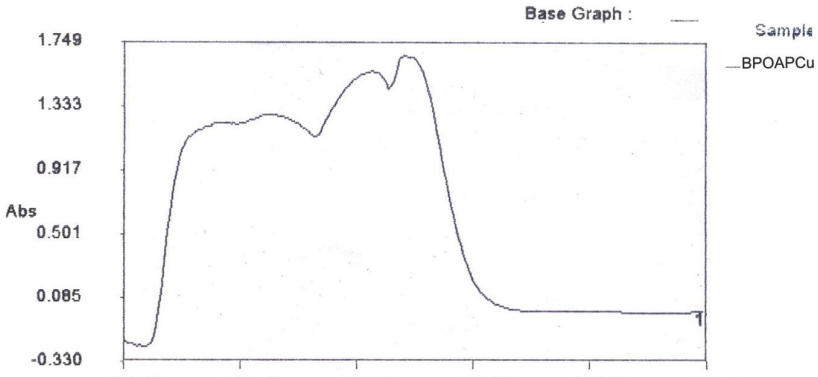
SYSTRONICS

DOUBLE BEAM UV-VIS Spectrophotometer: 2202 DOUBLE BEAM UV-VIS Spectror

Date : 18/04/09 Date : 18/04/09 Time : 12:2

Name of the Company/Laboratory: Chemistry, SRMV CAS, CBE-20,TN

Mode of Operation: Scan Mode B.W.: 2.0 n



Peak Pick	
393.6	1.654
369.6	1.556
299.2	1.282
251.2	1.174

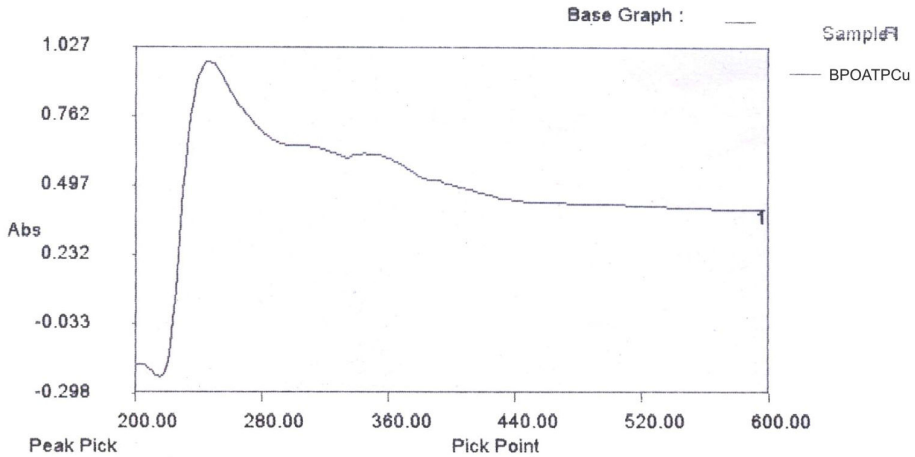
SYSTRONICS

DOUBLE BEAM UV-VIS Spectrophotometer: 2[illegible]DOUBLE BEAM UV-VIS Spectroph

Date : 18/04/09 Date : 18/04/09 Time : 12:40:4

Name of the Company/Laboratory: Chemistry, SRMV CAS, CBE-20,TN

Mode of Operation: Scan Mode **B.W.: 2.0 nm**



Peak Pick

246.4 0.967

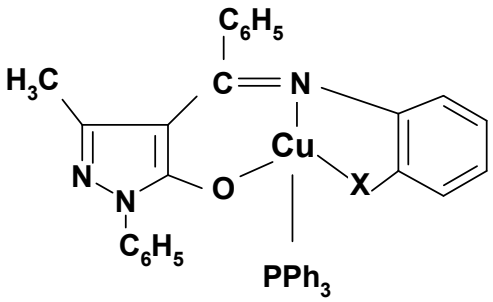
Pick Point

312.0 0.645

355.2 0.610

The electronic spectra of BP shows 3 bands (320nm, 345nm, 360nm) which occurs near quartz ultra violet region. Schiff base ligand imine is in extended conjugation with a pyrazoline ring system. Hence the near ultra violet region in BP is shifted to visible region in the case of Schiff base ligand and complexes.

The UV spectra of BPOAPCu complex shows B bamd ($\pi - \pi^*$) at 251.2 nm. It also shows bands in quartz and visible region. In BPOATPCu complex shows three bands (264.4 nm, 312 nm, 355 nm) which are assigned to quartz ultraviolet region. Based on the analytical and spectral data the following tetrahedral structure has been tentatively proposed for all the Schiff base complexes.



where X = O or S

POTENTIOMETRIC STUDIES

A digital potentiometer (Equiptronics Model EQ 602) was used for the potential measurements at 32 ± 0.1^0C

ELECTRODE RESPONSE:

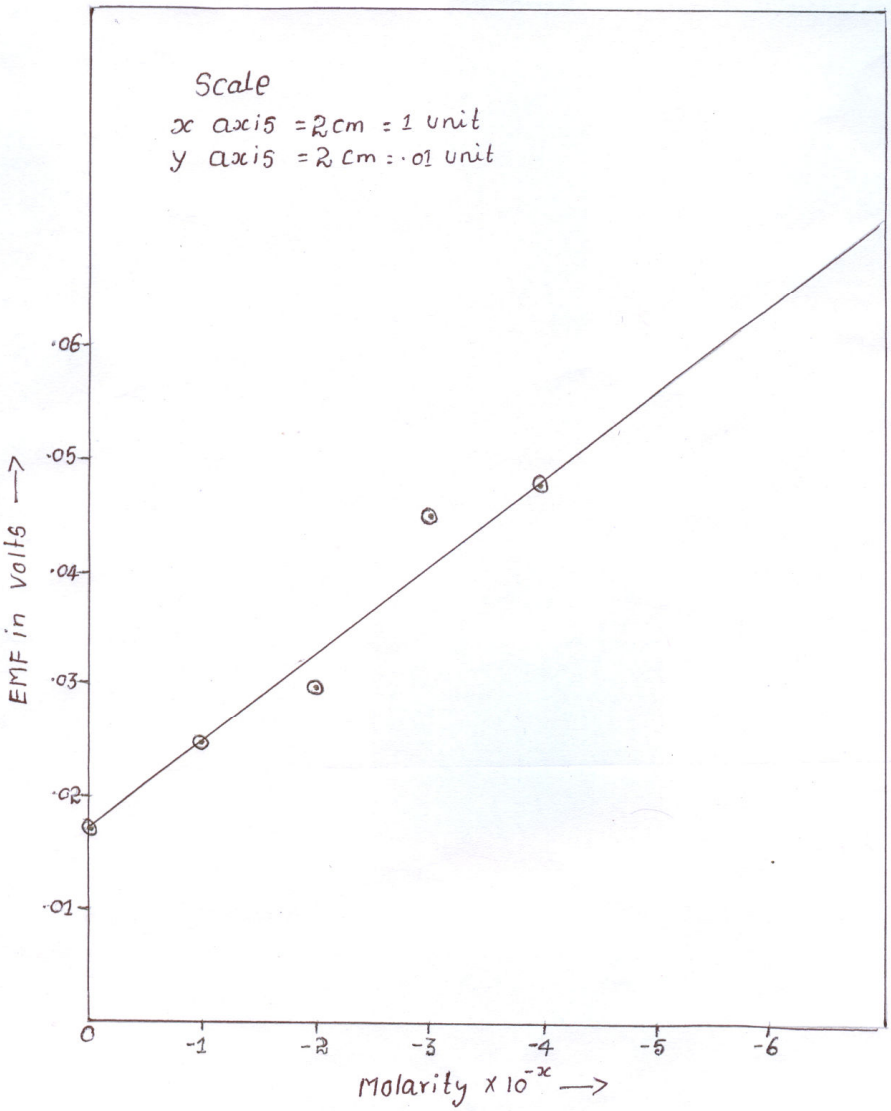
The electrode was first conditioned in 1M solution of Cu^{2+} ion till it attained stable equilibrium after which it was used for the determination of characteristic study of the electrode. The electrode potential for a series of standard solution of Cu^{2+} ion was measured. The electrode gives response to Cu^{2+} ion concentration in the range of 1×10^{-4} to1M (Table. I). This Cu^{2+} ISE reveals Nerstian slopes.

TABLE -1-ELECTRODE RESPONSE

Conc. of $CuSO_4$ solution (M)	**EMF(V)**
1M	0.015
1×10^{-1}M	0.018
1×10^{-2}M	0.020
1×10^{-3}M	0.026
1×10^{-4}M	0.027

Standard electrode potential of this electrode (E^0) determined by extrapolation method was found to be 0.027 V. The Nerstian slope value was found to be 30 MV/decade. To find out the response time, the electrode was dipped in 1M solution of Cu^{2+} and suddenly the concentration of the solution was changed to 0.1M. The variation in potential was noted at every second till constant potential was obtained at 5 seconds and remains constant. (Graph -1).

[Graph-1]


Scale
x axis = 2 cm = 1 unit
y axis = 2 cm = .01 unit
.06
.05
.04
.03
.02
.01
EMF in volts →
0
-1
-2
-3
-4
-5
-6
Molarity x 10^-x →

EFFECT OF pH AND EFFECT OF MEDIUM:-

To study the effect of pH a standard solution containing 1M Cu^{2+} ions were prepared in which series of buffer solution was added. It was found that the potential remains unchanged with in the range of 4, which is found to be the working pH of the electrode.

To study the effect of medium, a standard solution containing 1M Cu^{2+} ion in a series of 25%, 50%, 75% propanol was added. It was found that the potential remains unaffected with in 25% propanol medium.

SELECTIVITY:-

Selectivity is one of the most important characteristic of the electrode, which defines the nature of the device and extent to which it may be employed in the determination of a particular ion in the presence of other interfering ions. The selectivity is measured in terms of the potentiometric selectivity K , it measures the response of the sensor towards the primary ion in the presence of secondary ion present in sample solution. The selectivity coefficient has been determined by using fixed interference method (FIM) based on semi empirical Nicolski –Eisenmen equation. In this method the concentration of primary ion Cu^{2+} is varied where as the concentration of secondary interfering ions kept constant in the test solution which is 1×10^{-1}M concentration of interfering ion in present case. The potentiometric selectivity coefficient data of sensors for varies interfering ions (Cations & Anions) given in Table 2&3

TABLE -2- INTERFERENCE BY CATIONS

CATIONS	EMF(V)
Ni^{2+}	0.015
Mg^{2+}	0.013
Zn^{2+}	0.017

TABLE -3- INTERFERENCE BY ANIONS

ANIONS	EMF(V)
SO_4^{2-}	0.015

V. SUMMARY

1-phenyl-3-methyl-pyrazolin-5-one is converted in to its benzoyl derivative. The benzoyl pyrozoline on treatment with o-Amino phenol and o-Amino thio phenol is converted into corresponding new tridentate Schiff base ligands. These Schiff base ligands are then treated with starting Cu complex to synthesize new complexes. The structure of the new Schiff base ligand and the complexes were proposed on the basis of analytical and spectral data. In the present study, the [$Cu(PPh_3)$(BPOAP)] complex based membrane have been prepared along with the potentiometric performance of these sensors, effect of pH, effect of medium, response time and selectivity efficient with respect to different interfering ions have been studied.

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