ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH O,N,O AND O,O DONOR LIGANDS

BY: GIRMA SISAY

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF ADDIS ABABA
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Synthesis and characterization of some transition metal complexes with O,N,O and O,O donor ligands

By: Girma Sisay

Approved by the examining board	Signature
Dr. B. S. Shyamala Advisor	-----------------------------
Dr. Yonas Chebude Examiner	-----------------------------

Dedicated to:

All my family and Tuka Bethel Prayer team

Declaration

I hereby declare that this thesis entitled “Synthesis and characterization of some transition metal complexes with O,N,O and O,O donor ligands′′ is an authentic research work carried out by me under the guidance of Dr. B. S. Shyamala Donge. No part of this work shall be published in scientific journals or reported in the media without the knowledge and consent of my advisor.

Name of candidate	Signature
Girma Sisay	--------------------
Name of advisor	
Dr. B. S. Shyamala Donge	--------------------

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List of abbreviations and symbols

μ_{eff} – effective magnetic moment

BM – Bohr magneton

T – Temprature

^{0}C – degree Celsius

µS – micro Siemens

^{1}H NMR – proton nuclear magnetic resonance

^{13}C NMR– carbon -13 nuclear magnetic resonance

IR – infrared

UV-Vis – ultraviolet- visible

AAS – atomic absorption spectroscopy

nm – nanometers

4-AR – 4-acetyl resorcinol

3-AC – 3-aminocoumarin

DMF – dimetyl formamide

DMSO – dimetyl sulfoxide

THF – tetrahydrofuran

h – hour

min – minute

CT– charge transfer

M – Metal

L – Ligand

O_h – octahedral

T_d – tetrahedral

mL – milliliter

NB–nitrobenzene

s – singlet

d – doublet

m – multiplet

ppm – parts per million

Hz – Hertz

J – coupling constant

mp – melting point

g – gram

TLC– thin layer chromatography

Abstract

Novel Schiff base mixed ligand complexes of Cu(II) and Zn(II) were prepared from 3-AC and 4-AR by template synthesis. Also, new metal complexes of chromium(III), iron(III) and copper(II) ions were synthesized with 4-AR. All the complexes were characterized by elemental and metal ion analyses, IR and UV-Vis spectroscopy, magnetic susceptibility data and conductance measurements.

Analytical data of the mixed ligand complexes shows a M:L ratio of 1:2 and 1:1 for copper and zinc complexes, respectively. Based on these data, an octahedral geometry for Cu(II) complex and a tetrahedral geometry for the Zn(II) complex was proposed. In the Cu(II) complex, the mixed ligand acts as an O,N donor and in the Zn(II) complex, it acts as an O,N,O donor. Attempt to synthesize the mixed ligand complexes with Cr(III), Fe(III) and Ni(II) ions were not successful.

Complexation of chromium(III), iron(III) and copper(II) ions were carried out with 4-AR successfully. The ligand coordinates through the phenolic oxygen and the carbonyl oxygen atoms (i.e. the ligand behaves as O,O donor). An octahedral geometry for Cr(III) and Fe(III) complexes and a tetrahedral geometry for the Cu(II) complex was proposed. Attempt to synthesize the Ni(II) and Zn(II) complexes with 4-AR were not successful.

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Key words: Mixed ligand complexes, 3-aminocoumarin (3-AC), 4-acetylresorcinol (4-AR), Schiff base.

1. Introduction

1.1. Chemistry of Coumarins:

Coumarins, or benzo-α-pyrones, are a very large and important family of compounds. Their defining structure consists of fused pyrone and benzene rings, with the pyrone carbonyl group at position 2[1]. The study of coumarins began more than 200 years ago. Coumarins owe their class name to 'Coumarou', the vernacular name of the Tonka bean (*Dipteryx odorata Willd,* Fabaceae), from which coumarin was isolated in 1820. Coumarin is a widely occurring secondary metabolite that occurs naturally in several plant families and essential oils. It has been used in flavoring food and in cosmetic products as a fragrant[2-4]. The coumarin nucleus corresponds to benzo-α-pyrone (2*H*-1-benzopyran-2-one).

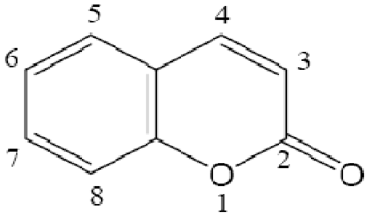


Fig. 1: Structure of Coumarin (2H-chromen-2-one)

Coumarins are widely distributed natural products isolated mainly from umbelliferae, rutaceae and leguminosae plants. As of now, more than 1000 natural coumarin derivatives have been described. Several compounds are isolated from micro-organisms or animals. The well known novobiocin (an antibiotic) and aflatoxin (a mycotoxin) are also coumarin derivatives. Interestingly, micro-organisms usually produce isocoumarin derivatives. Majority of coumarins isolated from plants contain an oxygen substituent at C-7. Some coumarins contain an isoprenoid side chain and some of these are condensed with another oxygen heterocycle (eg: furano coumarin)[5]. Many substituted coumarins and their derivatives have been developed synthetically, which are known to exhibit a wide spectrum of pharmacological activities, such as, antimicrobial, antifungal, anticoagulant, anti-inflammatory, antioxidant, analgesic etc[6-12]. In many instances, these properties were enhanced by incorporating suitable pharmacophores.

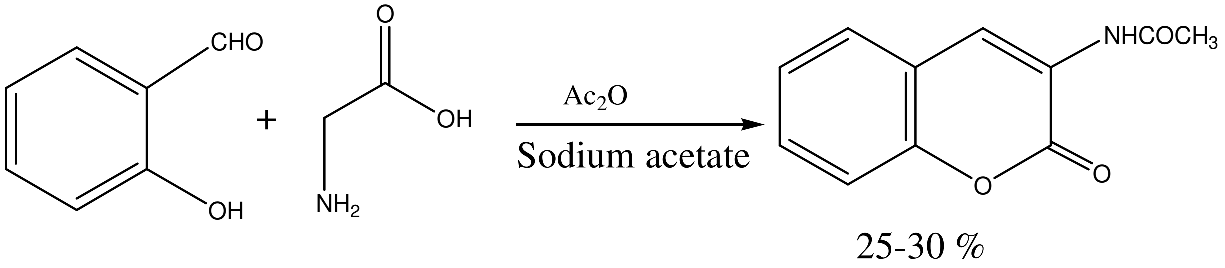
Spectral data of coumarins: Coumarin absorbs ultraviolet light at ~320 nm. The exact wavelength and the complete UV spectrum depend on the substituents present. In particular, by observing spectral changes in the presence of alkali and complexing agents, it is possible to obtain information on the hydroxylation pattern in the nucleus. IR spectra of coumarin exhibit strong absorption peak at 1729 cm^{-1} due to carbonyl group in addition to absorption peaks due to aromatic ring. In the ^1H NMR spectrum 3H and 4H give doublets at δ 6.3 and 7.8 respectively with J~10 Hz. Aromatic protons appear at δ 6.9 to 7.6. The distribution of the net electron charge at various atoms in the coumarin molecule shows variations.

Several methods used for the synthesis of coumarins include Pechmann, Perkin, Knoevenagel, Reformatsky, and Wittig reactions[13-15]. Among these, the Pechmann reaction is the most extensively applied method. It involves the condensation of phenols with β-ketonic esters in the presence of an acidic catalyst to give 4-substituted coumarins. Various catalysts employed for this reaction include sulfuric acid, phosphorus pentoxide, aluminium chloride and trifluoroacetic acid. In all cases, an excess of the catalyst is required (up to 10–12 equivalents in some cases), and their corrosive nature makes it difficult to handle them and often leads to the formation of several side products. Furthermore, the disposal of hazardous acid waste causes environmental problems. These difficulties have led to attempts in finding alternative, environmentally benign synthetic routes[16]. Various methods using Nafion-H, zeolite H-BEA, Amberlyst 15, montmorillonite clay, and microwave irradiation have been employed for Pechmann condensation[17]. However, most of these methods have disadvantages such as expensive reagents, long reaction time, low selectivity, use of large amounts of solid supports and difficulty in purification. An alternative approach is the use of ionic liquids as reaction media, which could offer a solution to solvent emission and catalyst recyclability problems. Ionic liquids possess advantages such as negligible vapor pressure, reasonable thermal stability, recyclability, and the ability to dissolve many organic and inorganic substrates[18].

1.1.1. 3-aminocoumarin

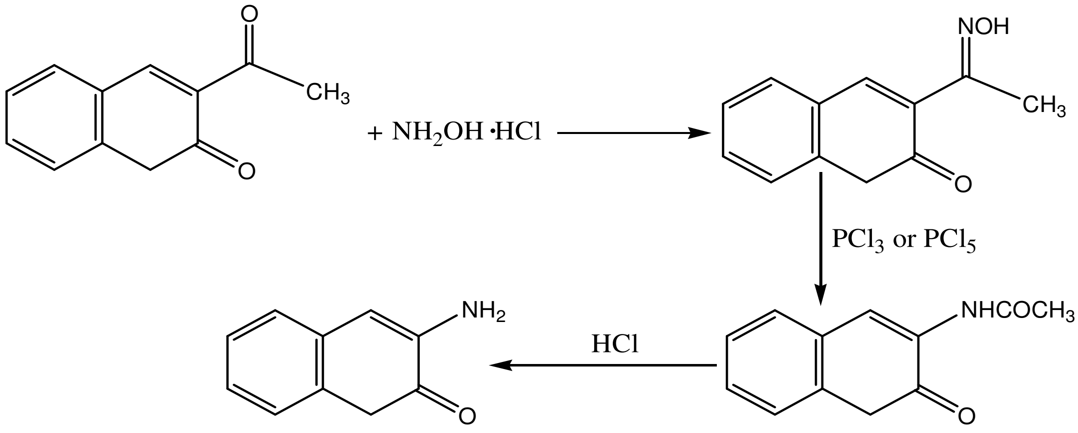
Aminocoumarins which contain an amino group bonded to the benzene nucleus are widely investigated, where as those containing amino group in α-pyrone ring have received great attention in recent years. From the group of aminocoumarins, 3-aminocoumarin and its derivatives are not well studied. The 3-aminocoumarin moiety can be recognized in the molecular structure of several natural antibiotics, such as novobiocin, chlorobiocin, coumermycin, etc. These antibiotics and their derivatives are in the research focus[19].

First synthesis of 3-aminocoumarin was reported by Linch in 1912. He tried two possible ways of preparing 3-aminocoumarin. One of the method, based on Perkin reaction involved condensation of salicylaldehyde with glycine[20].



Scheme 1: Synthesis of 3-acetylaminocoumarin from salicylaldehyde and glycine in presence of acetic anhydride and sodium acetate.

The maximum yield of 3-acetylaminocoumarin in this method was only 25-30%. Hence, the method was considered to be unsatisfactory. An alternate method involved the condensation of 3-acetylcoumarin with hydroxylamine hydrochloride. The oxime of this compound when treated with phosphrous trichloride and phosphorous pentachloride underwent Beckmann rearrangement to give 3-acetylamino coumarin in about 75% yield. The subsequent acid catalyzed hydrolysis of 3-acetylaminocoumarin gave 3-aminocoumarin in 65% yield.



Scheme 2: Modified method for synthesis of 3-aminocoumarin

1.2. Acetyl resorcinol

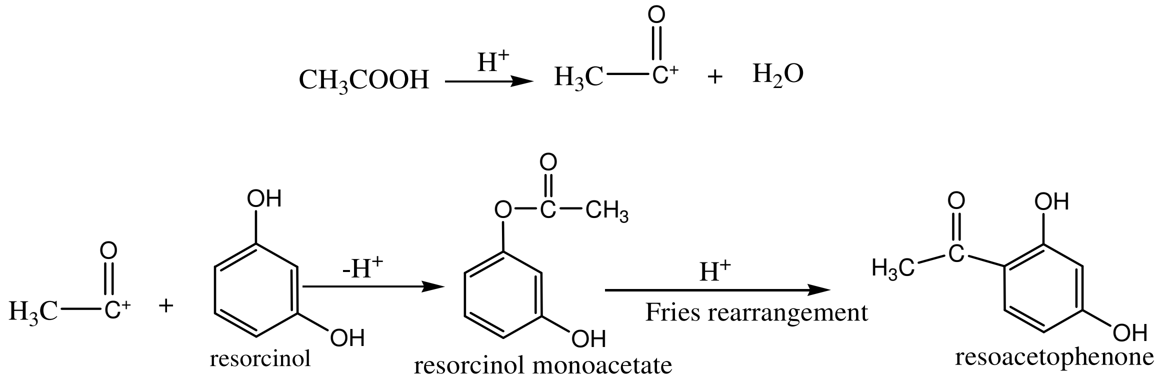
Resorcinol has been widely known as a versatile chemical compound utilized extensively in the development of advanced chemistry[22] to benefit living organisms. Resorcinol molecule has two hydroxyl groups in the aromatic ring structure, and they are located at meta-positions with respect to each other. The high reactivity of resorcinol is primarily associated with the location of these two hydroxyl groups in the benzene ring.

As far as the reactivity of resorcinol is concerned, the hydrogen atom adjacent to the hydroxyl groups, namely at carbon atoms 2, 4 and 6 are particularly reactive towards electrophilic substitution. All these three positions of the molecules are doubly activated by the two hydroxyl groups. Electrophilic substitution reaction such as alkylation, acylation, halogenation, nitration and sulfonation can occur predominantly. The 5-position of resorcinol is considered to be non-reactive and therefore under normal conditions electrophilic substitution may not take place at this position[22].

1.2.1. 4-acetyl resorcinol

Acylation of resorcinol is a very important reaction leading to the formation of 2,4-dihydroxy acetophenone also known as resoacetophenone(4-acetyl resorcinol) and 2,4-dihydroxy-5-acetyl acetophenone (reso-di-acetophenone). 4-acetyl resorcinol (4-AR) finds wide applications as an intermediate in the manufacture of pharmaceuticals, perfumes, fine chemicals and leukotriene antagonists[23]. It also used in spectrophotometric determination of iron and its application in sunscreen composition.

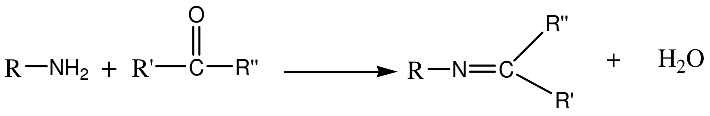
4-acetyl resorcinol (resoacetophenone) is synthesized by Friedel–Crafts acylation of resorcinol. The acylating agents such as acetic anhydride and acetyl chloride have several disadvantages. Acetic anhydride gives acetic acid as a co-product whereas acetyl chloride leads to HCl generation. Acetic anhydride is a restricted chemical due to its potential use in narcotics and not readily available in many countries. It would be attractive from a green chemistry viewpoint to use acetic acid as the acylating agent with a solid acid. The preparation of 4-acetyl resorcinol by Fries rearrangement of phenolic esters, and acylation with carboxylic acid has been studied with such catalysts as zinc chloride, Amberlyst-15, zeolites, and HCl, BF_3 etherate, BF_3 complex, HBr and $HClO_4$[23].



Scheme 3: Mechanism for the synthesis of 4-acetyl resorcinol (resoacetophenone)

1.3. O and N donors – Schiff bases

The condensation of primary amines with aldehydes and ketones give imines. Imines that contain an aryl group bound to the nitrogen or to the carbon atom are called Schiff bases, since their synthesis was first reported by Schiff[24, 25].



$$R{-}NH_2 + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'' \longrightarrow R{-}N{=}C(R'')(R') + H_2O$$

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of transition metal elements. In the area of bioinorganic chemistry, interest in Schiff base complexes has been centered on the role of such complexes in providing synthetic models for metal-containing sites in metallo-proteins and enzymes[26].

The effective role of Schiff base ligands is well documented in biological, pharmacological, clinical and analytical applications. Schiff bases are capable of forming coordinate bonds with many of metal ions through either/both azomethine nitrogen and phenolic oxygen. A large number of Schiff bases and their complexes are of significant interest and attention because of their biological activity including anti-tumor, antibacterial, fungicidal, anti-carcinogenic and catalytic activity[27, 28]. Schiff bases are generally bi-, tri- or polydentate ligands capable of forming very stable complexes with transition metals. Some are used as liquid crystals.

The pharmacological activity of Schiff bases (containing O,N and O,N,O donor atoms) of 3-amino coumarin derived by condensation with salicylaldehyde, acetylacetone and ortho-nitrobenzaldehyde and their metal complexes are reported by Shyamala *et al.*[29(a,b,c)].

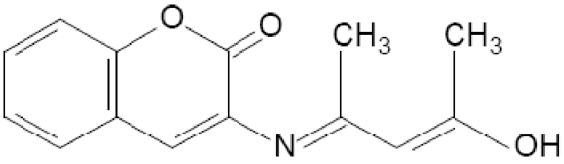
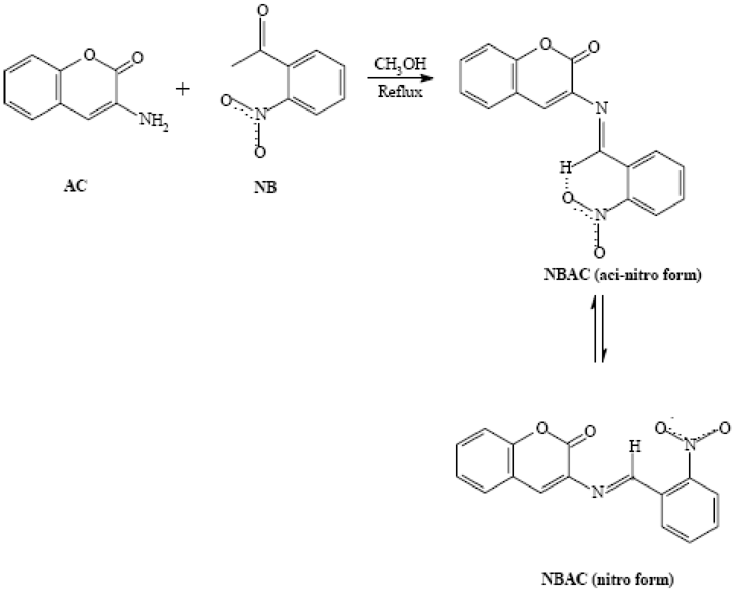


Fig. 2: Proposed structure of the ligand N-acetylacetonyl-3-aminocoumarin



Scheme 4: Synthesis Schiff base from 2-nitobenzaldehyde and 3-aminocoumarin

The O,N,N,O donor Schiff bases of 4-acetyl resorcinol with orthophenylene diamine and sulphanilamide have been reported by Venkatesh P. This study shows better activity of the Cu^{2+} and Zn^{2+} metal complexes of sulphanilamide Schiff base which might be due to its pharmacophore sulphanilamide and its potency is further enhanced by the metal coordination[30].

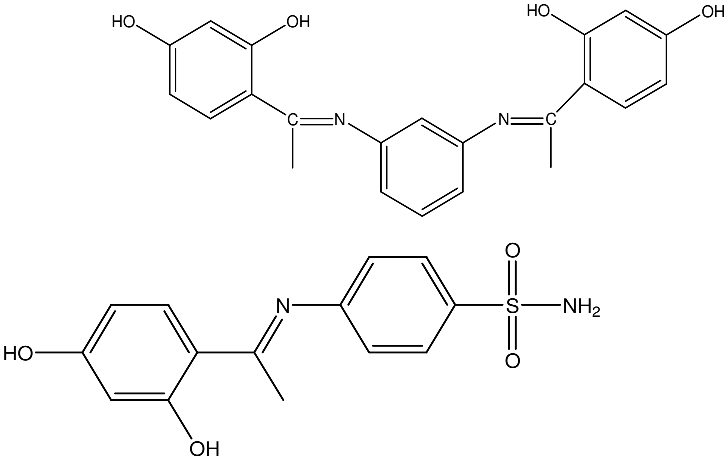


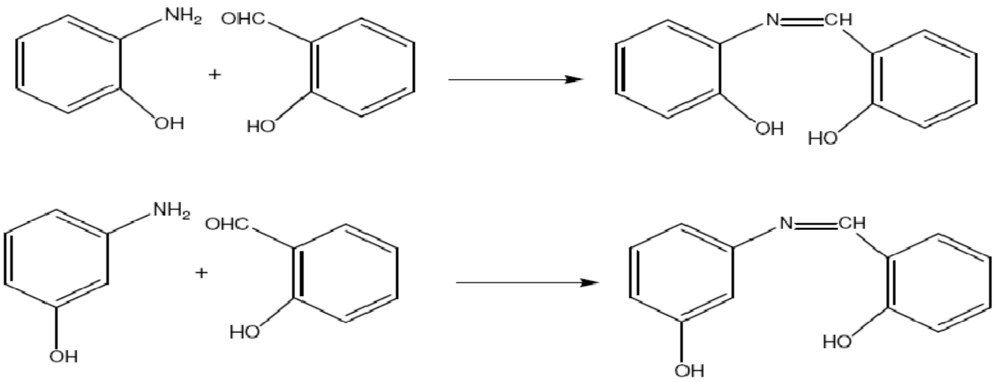
Fig. 3: Schiff bases derived from 4-acetyl resorcinol with orthophenylene diamine and sulphanilamide

1.4. Transition Metal complexes

Most of the 3d transition metal ions exhibit vital roles in biological systems. They are called metalloproteins. Metal ions, which are centers for enzymatic activity, determine the geometry of active sites and act as biological redox facilitators. As a consequence of their partially filled d orbitals, transition metals exhibit variable oxidation states and a rich variety of coordination geometries and ligand spheres[31].

Schiff bases complexes with most transition metal ions serve as models for biologically important species. Polynuclear complexes derived from multidentate ligands have documented interesting structural features. Literature survey reveals that a number of O,O, O,N,N and O,N,O donor sequences resulted in the formation of polynuclear metal chelates. A class of ligands with more than one independent chelating sequence substituted on a single phenyl function exemplifies bis-chelating ligands to bind two metal ions simultaneously and form polynuclear complexes[32].

Structure and activity studies of mixed ligand transition metal complexes of Cu^{+2}, Ni^{+2} and Co^{+2} ions with Schiff base ligands derived from the condensation of o-hydroxy benzaldehyde with amino phenols and nitrogen donor amine bases was reported by Saidul Islam *et al.*[33].



Scheme 5: O,N,O tridentate Schiff bases

Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. Metal ions bound to biologically active compounds may enhance their activities[34].

1.5. Chemistry of some transition metal ions

1.5.1. The chemistry of chromium(III)

Chromium(III) is an essential trace metal that is involved in the regulation of carbohydrate and lipid metabolism and insufficient dietary intake of it is associated with increased susceptibility to diabetes and cardiovascular diseases. While the role of Cr(III) in normal glucose metabolism is well recognized, its use as a therapeutic agent in diabetes is controversial because of conflicting human clinical data. The organic forms of Cr(III) such as chromium(III) picolinate or chromium niacinate are better absorbed than inorganic forms such as chromium(III) chloride.

From the Tanabe-Sugano diagram(electronic spectrum) for d^3 O_h chromium three spin allowed transition are expected which can be assigned as $^4T_2g \leftarrow {}^4A_2g$ (ν_1), $^4T_1g \leftarrow {}^4A_2g$ (ν_2) and $^4T_1g \leftarrow {}^4A_{2g}$ (ν_3). The magnetic properties of the octahedral Cr(III) complexes are uncomplicated. All such complexes must have three unpaired electrons irrespective of the strength of the ligand field, and this has been confirmed for all known mononuclear complexes. More sophisticated theory further predicts that the magnetic moment should be very close to, but slightly below, the spin only value of 3.88 BM[35, 36].

1.5.2. The Chemistry of Iron(III)

Iron is an important constituent in living systems. It is an active center in molecules which are responsible for oxygen transport and electron transport. It is found in metallo-enzymes such as oxidases, reductases, dehydrogenases, deoxygenases and dehydrases.

Iron(III)) in high spin state exhibits charge transfer bands in the near-uv region with strong low energy shoulders in the visible region that obscure the very weak, spin forbidden d-d bands. In the high spin complexes the magnetic moments are always very close to spin only value of 5.9 BM because the ground state has no orbital angular momentum and there is no effective mechanism for introducing any by coupling with excited state. The low spin complexes usually have considerable orbital contribution to their magnetic moment value of ~2.3 BM at room temperature[37].

1.5.3. The Chemistry of Copper (II)

Copper(II) forms stable complexes with nitrogen and oxygen donor ligands. Cu(II) complexes of nitrogen ligands are generally more stable than Cu(I) complexes. The most common coordination number of Cu(II) are 4, 5 and 6 but regular geometry are rare, and the distinction between square-planar and distorted octahedral coordination is not easily made. Mixed O and N donor ligands such as Schiff bases are of interest in that they provide examples of square-planar coordination and square-pyramidal coordination by dimerization[38, 39]. It has a biological role in sustaining life. Copper has antimicrobial property. Copper in trace quantities is required by all living organisms to maintain proper cellular functions.

A great majority of Cu(II) compounds are blue or green in color because of a single broad absorption band in the region of 600-900nm which is due to spin allowed transition ${}^2T_{2g} \leftarrow {}^2E_g$. Considerable distortion in octahedral symmetry is observed in Cu(II) complexes. The magnetic moment of mononuclear Cu(II) complexes are generally in the range of 1.75-2.20 BM, regardless of stereochemistry and independent of temprature except at extremely low temprature[37].

1.5.4. The Chemistry of Zinc(II)

Zinc has a specific role in bioinorganic processes because of the unique properties of the coordination compounds of the zinc (II) ions.

i) Zinc (II) can easily be 4-, 5-, or 6-coordinated, without a marked preference for six-coordination. The electronic configuration of zinc (II) is $3d^{10}$. In coordination compounds, there is no ligand-field stabilization energy, and the coordination number is determined by a balance between bonding energies and repulsion among the ligands. Tetrahedral four-coordinate complexes have shorter metal-donor distances than five- coordinate complexes, and the latter have shorter ones than six-coordinate complexes, whereas the ligand repulsion increases in the same order. Thus zinc (II) forms four coordinated tetrahedral complexes.

ii) As a catalyst, zinc in enzymes is exposed to solvents, which is most often, water. A coordinated water molecule exchanges rapidly, because ligands in zinc complexes are kinetically labile. This, again, can be accounted for by lack of preference for a given coordination number by the zinc ion. Zinc (II) is an ion of borderline hardness and displays high affinity for N and O donor atoms as well as for sulfur[40].

1.6. General objective:

Since coumarin moiety, O,N donating ligands and metal ions influence and enhance biological activity, the present investigation attempts at synthesizing metal complexes with O,O donor (4-acetyl resorcinol) and O,N,O donor ligands (derived from Schiff base of 3-amino coumarin and 4-acetyl resorcinol) with the aim to obtain more potent biologically active compounds and their metal complexes.

1.7. Specific objectives:

- Synthesis of metal complexes of Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with mixed ligand Schiff base derived from 3-aminocoumarin and 4-acetyl resorcinol by template method.
- Synthesis and characterization of transition metal (Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) complexes with 4-acetylresorcinol (4-AR).

2. Experimental

2.1. Instrumentation

IR spectra were recorded using Perkin-Elmer FT-IR spectrophotometer in the range of 4000-450cm^{-1}. ^{1}H and ^{13}C NMR was recorded in $CDCl_3$ by using Bruker Ultra- shield NMR (400 and 100.6 MHz for ^{1}H and ^{13}C, respectively). The magnetic susceptibility of the complexes was measured using MSB-AUTO, Sherwood magnetic balance. Elemental analysis of CHN was done by using Exter Analytical CE 440 elemental analyzer. Molar conductivities of the complexes were recorded at room temperature using HANNA Instrument EC 214 conductivity meter. The metal estimation was done using BUCKER Scientific 210 VGB atomic absorption spectrophotometer. The electronic spectrum of Zn complex was recorded in the UV and visible region (200-900 nm) by Cary 5E UV-VIS NIR spectrophotometer and for other complexes it was carried out in the range of 200-900 nm by SPECTRONIC GENESY^{TM} 2PC UV-Visible spectrophotometer. Melting or decomposition point was determined by Stuart SMP3 digital melting point apparatus.

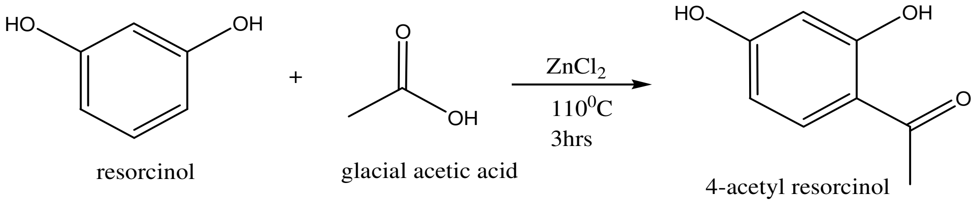
2.2. Chemicals and reagents

The chemicals and reagents that were used in this investigation are: Anhydrous $ZnCl_2$, acetic anhydride, resorcinol, acetic acid, glycine, salicylaldehyde, $NaHCO_3$, $CrCl_3{}^{\cdot}6H_2O$, $FeCl_3$, $NiCl_2{}^{\cdot}6H_2O$, $CuCl_2{}^{\cdot}2H_2O$, $ZnCl_2$, conc. HCl, piperidine, solvents such as ethanol, methanol, chloroform, dimetylsulfoxide (DMSO), dimetylformamide (DMF), acetonitrile, acetone, dichloromethane, tetrahydrofuran (THF) and water. All the chemicals utilized in this work were of AnalaR grade. Methanol and ethanol were distilled for further purification.

2.3. Synthesis

2.3.1. Synthesis of 4-acetyl resorcinol (2,4-dihydroxy-acetophenone)[41] (4-AR)

Anhydrous zinc chloride (16.5 g) was dissolved in 15.8 mL glacial acetic acid. Resorcinol (11.0 g) was added and the mixture was heated at 110°C for 3 h. The resulting solution was cooled to room temperature and then poured over crushed ice. The product was filtered and washed with 30% HCl to remove excess zinc chloride. The product was recrystallized from methanol, dried and weighed. Yield: 8.8 g (80%), m.p: 144^0C.



Scheme 6: Synthesis of 4-acetylresorcinol

2.3.2. Synthesis of 3-aminocoumarin (3-AC)[42]

3-aminocoumarin can be prepared in three steps. These are: i) acylation of glycine to form acetylglycine, ii) synthesis of 3-acetylaminocoumarin by reacting acetylglycine, salicylaldehyde & piperidine in acetic anhydride, iii) hydrolysis of 3-acetylaminocoumarin to form 3-aminocoumarin.

a. Preparation of acetylglycine

Acetylglycine was synthesized by adding acetic anhydride (14.5 g, 0.14 mol) to a solution of glycine (5.0 g, 0.06 mol) in water (75 mL). The reaction mixture was stirred for 20 min. at room temperature, and cooled in a refrigerator overnight. Acetylglycine which separated as white crystals was filtered, washed with cold water and dried at 100^0C. Yield: 4.2 g (84%), m.p: 206-208^0C.

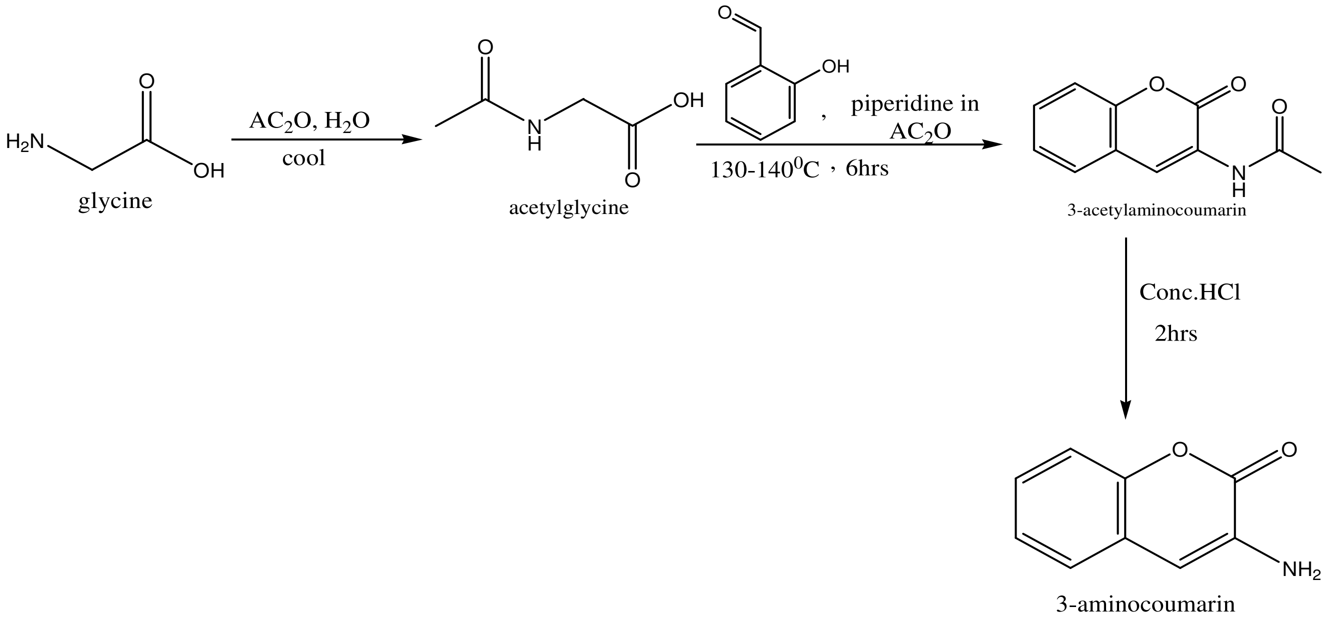
b. Synthesis of 3-Acetylaminocoumarin

3-Acetylaminocoumarin was prepared by heating a mixture of acetylglycine (5.0 g, 0.043 mol), salicylaldehyde (12.2 g, 0.1 mol) and a drop of piperidine in acetic anhydride (5 mL, 0.049 mol) at 130-140^oC for 6 h. The reaction mixture was cooled, diluted with 10 ml of water, and further refluxed for 30 min. The gummy mass thus obtained after removal of water under reduced pressure was repeatedly washed with ether to remove adhering traces of piperidine and acetylglycine. The crude product when crystallized from ethanol furnished the product as a crystalline solid. Yield: 2 g (40%), m.p: 200-203^0C.

c. Hydrolysis of 3-Acetylaminocoumarin

3-Aminocoumarin was prepared by treating a solution of 3-acetylaminocoumarin (5 g, 0.024 mol) in hot ethanol (25 mL) with concentrated hydrochloric acid (5 mL) and the resulting mixture was refluxed for 2 h. The reaction mixture was cooled diluted with water, neutralized with aqueous saturated sodium bicarbonate and kept overnight. The solid thus separated was filtered. Further purification by crystallization from ethanol gave the product, a creamish crystalline solid, Yield: 3.5 g (70%), m.p: 127^0C. It was characterized by ^{1}H NMR.

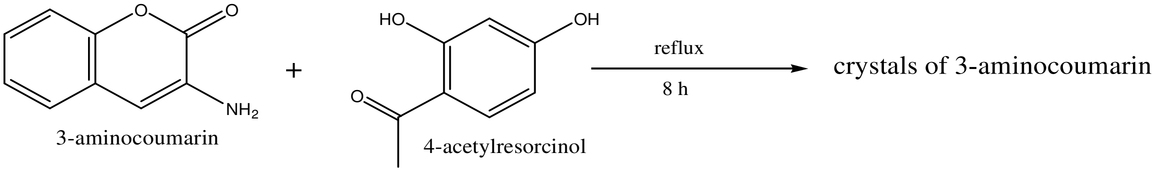
^{1}H NMR: 4.3 ppm (s, NH_2), 6.76 ppm (s, CH), 7.20-7.40 ppm (m, CH). These results are concurrent with the reported data.



Scheme 7: Synthesis of 3-aminocoumarin

2.3.3. Synthesis of Schiff base ligand

The preparation of the ligand was attempted by the following method. The 3-aminocoumarin (0.50 g, 0.0031 mol) was dissolved in methanol (20 mL) and heated for few minute. Then, resoacetophenone (0.47 g, 0.0031 mol) was added to the hot alcoholic solution of 3-aminocoumarin. The mixture was refluxed over water bath for more than 8 h. The solution was cooled overnight and needle like crystals were obtained. TLC, melting point and NMR spectroscopy data of the product revealed that it was 3-aminocoumarin, and the Schiff base condensation did not take place. So, an alternate template method synthesis was carried out.



Scheme 8: failed reaction for the synthesis of Schiff base ligand

2.3.4. Synthesis of metal complexes

a. **Template synthesis**: The metal complexes were synthesized by template method. To a solution of 4-acetylresorcinol (5.62 g, 0.037 mol) in hot methanol (20 mL), solution of metal ion (0.02 mol each) was added. The resulting mixture was refluxed on a water bath for about half an hour. After 30 min. of refluxing, 3-aminocoumarin (6 g, 0.037 mol) was added. The pH of solution was adjusted to 7 with alcoholic ammonia solution (1:1) and refluxed further for about 8-18 h over water bath. The solid obtained was filtered, washed with methanol, and air dried. Yield: 2.64 g (42%) and 2.3 g (46.2%) for Cu(II) and Zn(II), respectively.

b. **Synthesis of 4-acetyl resorcinol complexes**: 5 g (0.033 mol) of 4-acetyl resorcinol was dissolved in 20 mL methanol and heated for few minutes. To this hot solution, 0.011 mol of Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} (2.92, 1.78, 3.9, 2.8 and 2.23 g, respectively) in 20 mL methanol was added. The pH of the solution was adjusted to 7 by alcoholic KOH (10%, v/v). The resulting mixture was refluxed over water bath for 4-8 h. The obtained solid product was filtered, washed with methanol and dried. Yield: 1.28 g (56%), 1.42 g (80%) and 2 g (52%) for Cr^{3+}, Fe^{3+} and Cu^{2+}, respectively.

3. Result and discussion

Mixed ligand complexes of zinc(II) and copper(II) resulted by template synthesis. Cr(III), Fe(III) and Ni(II) ions did not yield such complexes. Similarly, 4-acetyl resorcinol formed complexes with Cr(III), Fe(III) and Cu(II). Attempts to synthesize Ni(II) and Zn(II) complexes of 4-acetyl resorcinol were not successful.

All metal complexes obtained were colored and stable to air and moisture at room temprature. Except Zn(II) complex, all are soluble in common organic solvents such as DMF, DMSO, and acetonitrile and sparingly soluble in acetone, chloroform, methanol, dioxane and water. However, the zinc complex is soluble only in DMF and acetonitrile and sparingly soluble in other solvents. The observed molar conductance values (17.32 – 60.10 S cm^2 mol^{-1} in Table 1) of the complexes in 10^{-3} M DMF solution suggests the non-electrolytic nature of these complexes. The complexes do not show sharp melting points. They decompose at temperatures above 300^0C (Table 1).

The analytical data reveals M:L ratio of 1:1 and 1:2 for Zn(II) and Cu(II) mixed ligand complexes respectively (Table 1). In case of transition metal complexes of 4-acetyl resorcinol, the ratio of M:L was 1:1, 1:2 and 1:3 for Fe(III), Cu(II) and Cr(III) complexes respectively. The data has good agreement with the suggested structure of the complexes.

Table 1: Elemental analysis and some physical characteristics of ligands and complexes

Compounds Empirical formula	Molecular Weight (g/mol)	color	m.p/ dec. pt (^{0}C)	Yield (%)	Found (calculated) %				Conductivity (S cm^2 mol^{-1})
					C	H	N	M	
3-aminocoumarin $C_9H_7NO_2$	161	creamish	131	70	(67.07)	(4.35)	(8.70)		-
4-acetyl resorcinol $C_8H_8O_3$	152	orange	144	80	63.46 (63.53)	4.81 (4.46)	-		-
Zn(L)Cl $ZnC_{17}H_{12}NO_4Cl$	394.9	yellow	> 303	46.2	52.33 (52.65)	3.46 (3.05)	3.42 (3.55)	16.56 (16.97)	17.32
$Cu(L)_2(NH_3)H_2O$ $CuC_{34}H_{29}NO_9$	687	Dark brown	> 300	42	58.47 (59.38)	2.40 (4.22)	6.16 (6.11)	9.02 (9.24)	60.10
$Cu(L')_2$ $CuC_{16}H_{14}O_6$	365.5	green	> 314	52	52.18 (52.53)	5.90 (6.57)	-	29.60 (29.40)	43.40
$Cr(L')_3$ $CrC_{24}H_{21}O_9$	505	brown	> 300	56	56.69 (57.03)	4.39 (4.16)	-	11.09 (11.88)	45.45
$Fe(L')(H_2O)_2Cl_2$ $FeC_8H_{11}O_7Cl_2$	314	red	> 300	80	32.53 (30.48)	3.54 (3.49)	-	18.18 (17.83)	14.47

L = $C_{17}H_{12}NO_4$, L' = $C_8H_7O_3$

Infrared spectra

The characteristic infrared frequencies of ligand and metal complexes are listed in Table 2 and 3. The IR spectrum of 3-aminocoumarin shows a doublet at 3428 cm^{-1} and 3313 cm^{-1} assignable to asymmetric and symmetric ν_{NH2} respectively. The strong band located at 1706 cm^{-1} was assigned to $\nu_{C=O}$ of coumarin moiety. Lowering of this peak from the expected value of 1729 cm^{-1} for unsubstituted coumarin may be due to conjugation between C=O and the NH_2 group at C3[19]. Slight broadening of the $\nu_{N\text{-}H}$ can also be accounted to this H-bonding. The peak at 1589 cm^{-1} is due to rocking frequency of $\delta_{N\text{-}H}$ and $\delta_{C\text{-}H}$. the weak band located at 1407 cm^{-1} is assigned to $\nu_{C\text{-}N}$. Infrared spectrum of the 4-acetyl resorcinol shows two broad bands at 3573 cm^{-1} and at 3301cm^{-1} that may be attributed to H-bonded two phenolic OH stretching frequencies ($\nu_{O\text{-}H}$) [43]. In addition there are three strong bands at 1631 cm^{-1}, 1607 cm^{-1} and 1206 cm^{-1}, which are assigned to the $\nu_{C=O}$, $\nu_{C=C}$ and $\nu_{C\text{-}O}$, respectively.

In Cu(II) complex, a strong broad band centered at 3450 cm^{-1} and 3330 cm^{-1} can be assigned to $\nu_{O\text{-}H}$ of coordinated water molecule and phenol, respectively. The $\nu_{N\text{-}H}$ for coordinated ammonia molecule is obscured by this broad band. Zn(II) complex shows a medium broad band in the region 3500-3300 cm^{-1} which is assigned to $\nu_{O\text{-}H}$ stretching frequency. The broad nature of the band suggests presence of intra or/and intermolecular H-bonding. The band at 3301cm^{-1} observed due to $\nu_{O\text{-}H}$ in 4-AR disappeared in both copper and zinc complexes indicating deprotonation of OH and coordination between metal ion and oxygen of phenol. The Zn(II) and Cu(II) complexes exhibit bands at 1669 cm^{-1} and 1746 cm^{-1} respectively which are assigned to $\nu_{C=O}$ moiety of the coumarin[44]. This carbonyl stretching is located at higher frequency in Cu(II) complex indicating its non participation in coordination to the metal ion[45]. It also accounts for the disappearance of H-bonding between C=O and NH_2 that shifts $\nu_{N\text{-}H}$ of 3-AC to lower frequency in comparison to unsubstituted coumarin. The band located at 1631cm^{-1} which was assigned to acetyl carbonyl group of 4-acetyl resorcinol also disappeared in both the mixed ligand complexes. This confirms that the condensation reaction has taken place and Schiff base has formed. The band observed as a shoulder at 1630 cm^{-1} in Cu(II) complex can be assigned to the bending mode of NH_3 of ammonia[47]. New bands at 1606 cm^{-1} in Zn(II) complex and at 1610 cm^{-1} in Cu(II) complex are assigned to $\nu_{C=N}$ stretch. The azomethine stretching frequency in free Schiff bases are normally observed around 1630-1620 cm^{-1} [48]. This band is seen shifted to lower frequency indicating the involvement of azomethine nitrogen in coordination to metal[46]. It is also deducible that mixed ligand Schiff base complex has formed. The phenolic $\nu_{C\text{-}O}$ stretching is seen to have shifted to higher frequency by 17-27 cm^{-1} in both the complexes showing coordination of the metal to the ligand through oxygen of phenol.

A medium band around 1031 cm^{-1} in Zn(II) complex and 1050 cm^{-1} in Cu(II) complex is characteristic of $\nu_{O\text{-}C\text{-}O}$ corresponding to cyclic grouping of 3-aminocoumarin. Some new bands identified in the zinc complexes at 490 cm^{-1} have been assigned to stretching frequency of metal chlorine bonds ($\nu_{M\text{-}Cl}$). New bands at 593 and 622 cm^{-1} in Zn(II) complex and at 451 and 476 cm^{-1} in Cu(II) complex are assigned to $\nu_{M\text{-}N}$ and $\nu_{M\text{-}O}$, respectively[47].

Table 2: Important IR absorption frequencies (in cm^{-1}) of 3-AC, 4-AR and mixed ligand Schiff base complexes

No.	Compound	ν(N-H)	ν(O-H) phenolic	ν(C=O)	ν(C=N)	ν(C-O)	ν(M-O)	ν(M-N)	ν(M-Cl)
1	3-AC	3428 (asy) 3313(sym)	-	1705 s	-	1170 ν(C-O-C)	-	-	
2	4-AR	-	3573 w, br, 3301 s, br	1631sh		1206 s			
3	Zn(L)Cl	-	3353 m, br	1669 sh (coumarin)	1606 s	1243 w	622 w	593 m	490 w
4	$Cu(L)_2(NH_3)H_2O$	Obscured by broad band	3450 s, br (H_2O) 3330 s, br	1746 s (coumarin)	1610 s	1223 s	476 m	451m	-

s= strong, br = broad, m = medium, w = weak, sh = shoulder, asy= asymmetric, sym= symmetric

A medium broad band was observed for each complex of 4-acetyl resorcinol in the range of 3500-3200 cm^{-1}. This is assignable to ν_{O-H} of phenol. This band obscures the stretching frequency of the coordinated water in the iron complex which is normally observed in the same region. The $\nu_{C=O}$ for acetyl carbonyl shows downward shift to lower frequency in all complexes by 38-18 cm^{-1} indicating coordination of carbonyl oxygen of acetyl group to the metal ion. On the other hand, phenolic (ν_{C-O}) stretching frequency shows a shift to higher frequency by 54- 36 cm^{-1} in all complexes revealing the formation of M-O bonds via deprotonation. The new non ligand bands observed in the region 723-469 cm^{-1} are assigned to ν_{M-O} indicating M-O bond formation. In iron complex, an additional non ligand band seen at 448 cm^{-1} is assigned to $\nu_{M-Cl.}$

Table 3: Important IR frequencies of 4-AR and its metal complexes

compounds	ν(O-H) (intermolecular H-bonded)	ν(O-H) (intramolecular H-bonded)	ν(C=O)	ν(C-O)	ν(M-O)	ν(M-Cl)
4-AR	3573 w, br	3301s, br	1631sh	1206 s	-	-
Cr(L')$_3$	3226 m, br	-	1603 s	1242 s	662- 448 w	-
FeL'(H$_2$O)$_2$Cl$_2$	3375 m, br	-	1593 m	1296 m	723- 618 w	515 w
Cu(L')$_2$	3350 m, br	-	1613 m	1244 s	621-469 m	-

Electronic spectra and magnetic moments

In both 3-aminocoumarin and 4-acetylresorcinol, absorption bands observed at 323 nm and 318 nm, respectively that are assignable to n→π* transition of carbonyl group. Similarly, the $\pi \rightarrow \pi^*$ transition band of benzene ring was observed at 242 nm for 3-aminocoumarin and at 230 nm and 270 nm for 4-acetylresorcinol.

Copper(II) complex of mixed ligand Schiff base shows a broad absorption band at 460 nm (21739 cm^{-1}) which can be assigned to d-d transition corresponding to $^2T_{2g} \leftarrow {}^2E_g$. A weak band was observed around 390 nm which is characteristic of charge transfer transition.

As expected for a d^{10} electronic configuration, the electronic spectrum of zinc(II) mixed ligand complex does not show any d-d transition. The observed bands are due to the ligand and charge transfer transitions. The bands at 325 nm (30769 cm^{-1}) and 286 nm (34965 cm^{-1}) are assigned to n→π* transition of azomethine[48] and to $\pi \rightarrow \pi^*$ transition of benzene ring, respectively. The other band located at 473 nm (21,142 cm^{-1}), is assigned to charge transfer transition. The yellow color of the complex may be conjured as having arisen from this absorption in the visible region[49].

Chromium complex of 4-acetylresorcinol shows absorption bands at 230 nm, 250 nm, 294 nm, 384 nm and 564 nm. The first three bands are assigned to $\pi \rightarrow \pi^*$ transition of benzene ring, n→π* of carbonyl group and charge transfer transition, respectively. The bands at 384 nm (26,041 cm^{-1}) and 564 nm (17,730cm^{-1}) are assigned to the d-d transition corresponding to $^4T_{1g}$ (F) ← $^4A_{2g}$ and $^4T_{2g} \leftarrow {}^4A_{2g}$, respectively[36]. Iron(III), deduced as a high spin(d^5) complex based on its magnetic susceptibility, shows a very broad band around 500 nm (20,000cm^{-1}) which can be assigned to spin forbidden d-d transition as well as charge transfer transitions. Copper(II) complex of 4-acetylresorcinol shows intense band at 457 cm^{-1} (21,881 cm-1), which indicates d-d transition corresponding to $^2E \leftarrow {}^2T_2$. The greater intensity of this band supports tetrahedral geometry of this complex[50]. The magnetic moment of complexes is listed in Table 4.

Except zinc complex, the obtained complexes are paramagnetic in nature. The observed magnetic moment for copper mixed ligand was 2.05 BM. This experimental value agrees with expected magnetic moment's value for one unpaired electron (1.75-2.2 BM) in octahedral geometry. The observed magnetic moment value is significantly larger than the spin only value showing the orbital contribution to the magnetic moment. Zn(II) mixed ligand is a diamagnetic complex and has zero magnetic moment. Cu(II) complex of 4-AR has a magnetic moment of 1.69 BM as expected for a spin only value for one unpaired electron (1.73 BM). Fe(III) complex has a magnetic moment of 5.34 BM revealing high spin d^5 nature of Fe^{3+} in the complex. The data has good agreement with expected value for five unpaired electrons in octahedral geometry (5.6 - 6.1 BM). The Cr(III) complex shows a magnetic moment of 3.92 BM, corresponding to three unpaired electrons. It is close to the excepted value for O_h geometry (3.84–3.90 BM)[37, 51, 52].

Table 4: Electronic spectra and magnetic moment data

compounds	Transitions (nm)			$\mu_{eff\ (BM)}$
	d-d / CT	π→π* / benzene	n→π* / carb. /azom.	
3-AC		242	270 (carb.)	-
4-AR	318	230	323 (carb.)	-
Zn(L)Cl	473 (CT)	-	325 (azom.)	diamagnetic
$Cu(L)_2(NH_3)H_2O$	460, 390			2.05
$Cu(L')_2$	457			1.69
$Cr(L')_3$	564, 384			3.92
$Fe(L')(H_2O)_2Cl_2$	500			5.34

carb. = carbonyl, azom. = azomethine

4. Conclusion

From the results obtained for copper(II) and zinc(II) mixed ligand complexes, it is clear that Schiff base of mixed ligands has formed through the template method of synthesis. The ligand acts as bidentate O,N donor in Cu(II) complex, coordinating to the metal through oxygen of phenol and azomethine nitrogen of Schiff base of the mixed ligand and as a tridentate O,N,O donor in Zn(II) complex, coordinating to the metal through oxygen of phenol, azomethine nitrogen and carbonyl oxygen of coumarin. Based on elemental and metal ion analyses, IR, and electronic spectral data, magnetic susceptibility and conductance data, an octahedral geometry for the Cu(II) complex and a tetrahedral geometry for Zn(II) complex was suggested. The proposed structures are given in Fig. 4.

Extension of this work can be carried out to synthesize a single crystal and thereby crystal structures can be determined. Also biological activity of these complexes can be evaluated as the complexes contain the biologically active coumarin moiety. Additional data as thermal analysis, x-ray crystallography and ESR spectral study (for Cu^{2+} complex) may also be conducted.

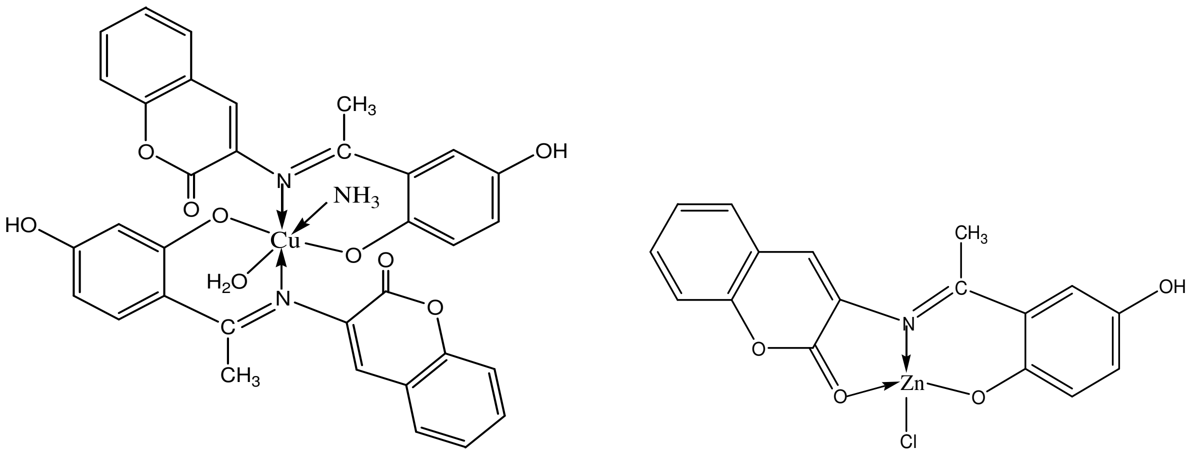


Fig. 4: Suggested structure of Cu^{2+} and Zn^{2+} mixed ligand Schiff base complexes

Based on the elemental and metal ion analyses, IR and electronic spectral data, magnetic moments and conductance data, an octahedral geometry is suggested for chromium(III) and iron(III) complexes and a tetrahedral geometry is suggested for copper(II) complex of 4-acetyl resorcinol. It is proposed that the ligand acts as a bidentate O,O donor, coordinating to the metal ion through oxygen of phenol and oxygen of acetyl carbonyl group. The structures are depicted in Fig. 5.

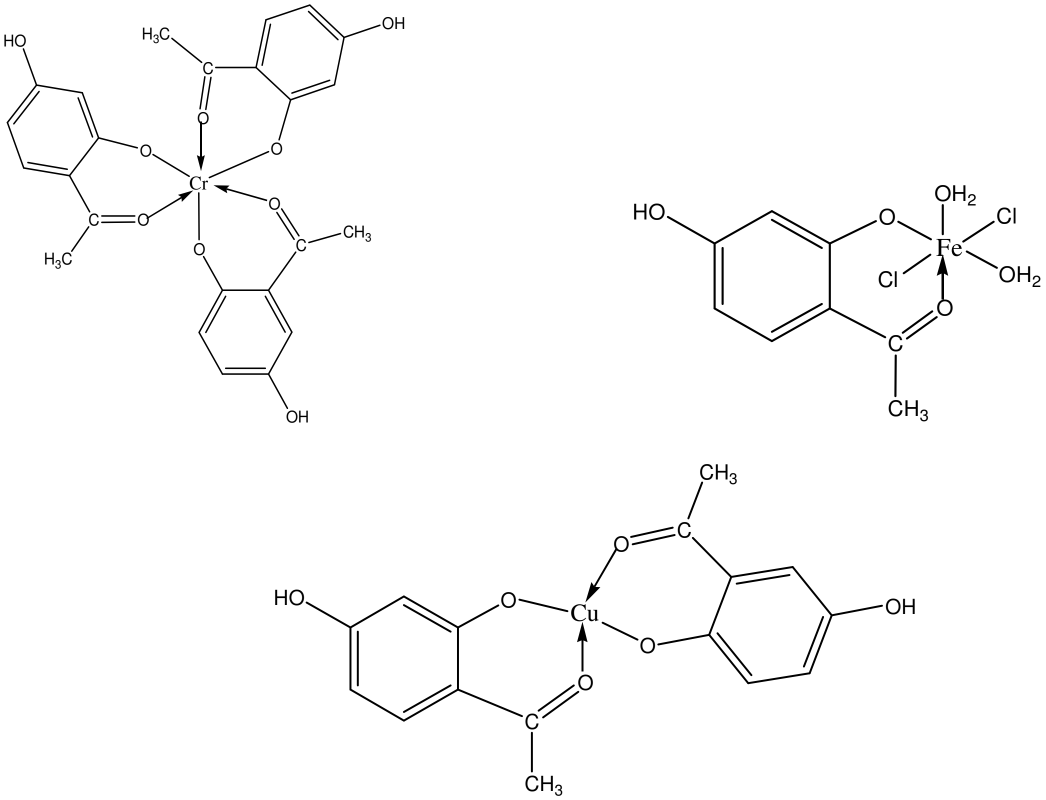


Fig. 5: Suggested structure for Cr^{3+}, Fe^{3+} and Cu^{2+} complexes of 4-acetyl resorcinol

Thermal analysis, x-ray crystallography and study of their biological activity can add further evidence to this work.

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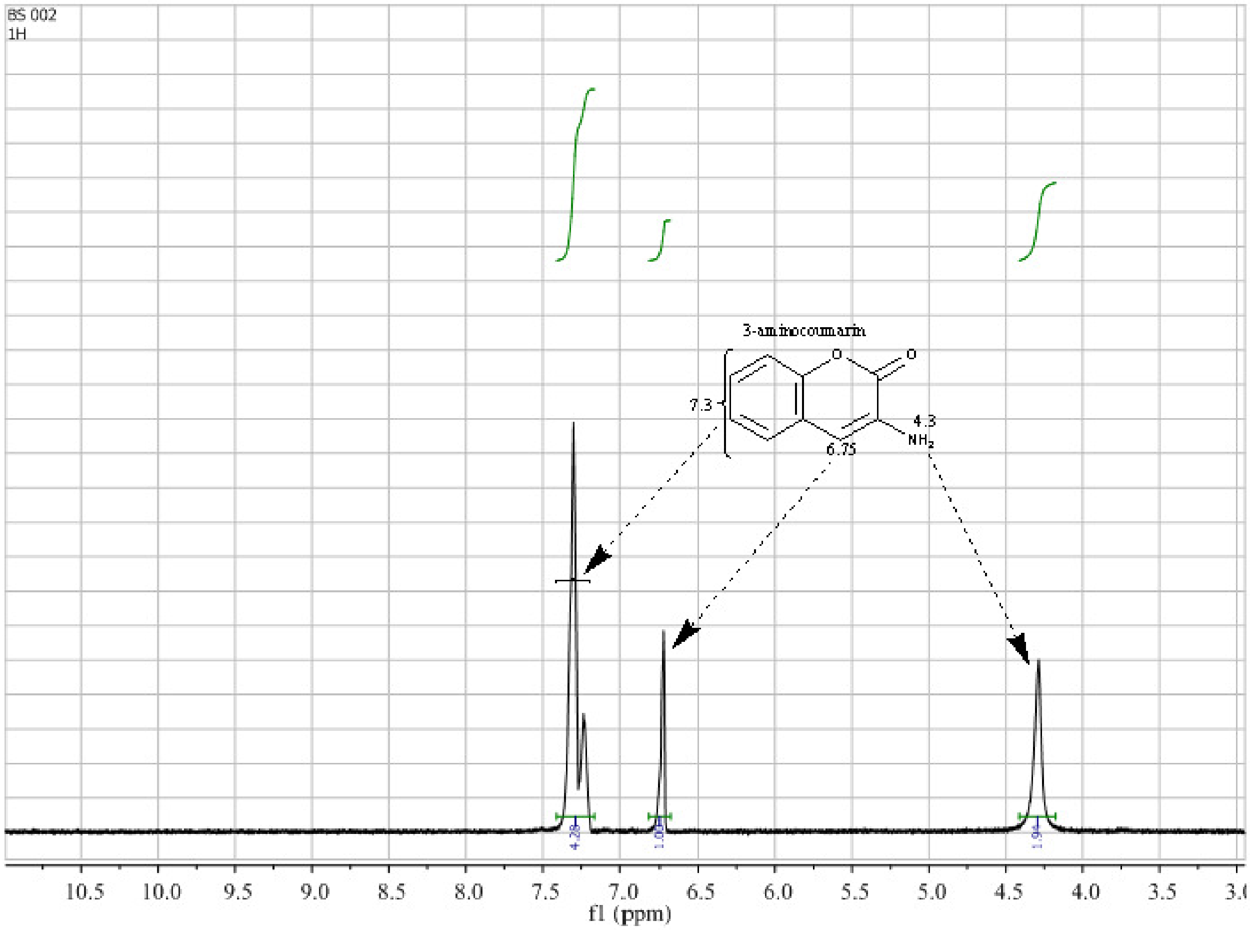
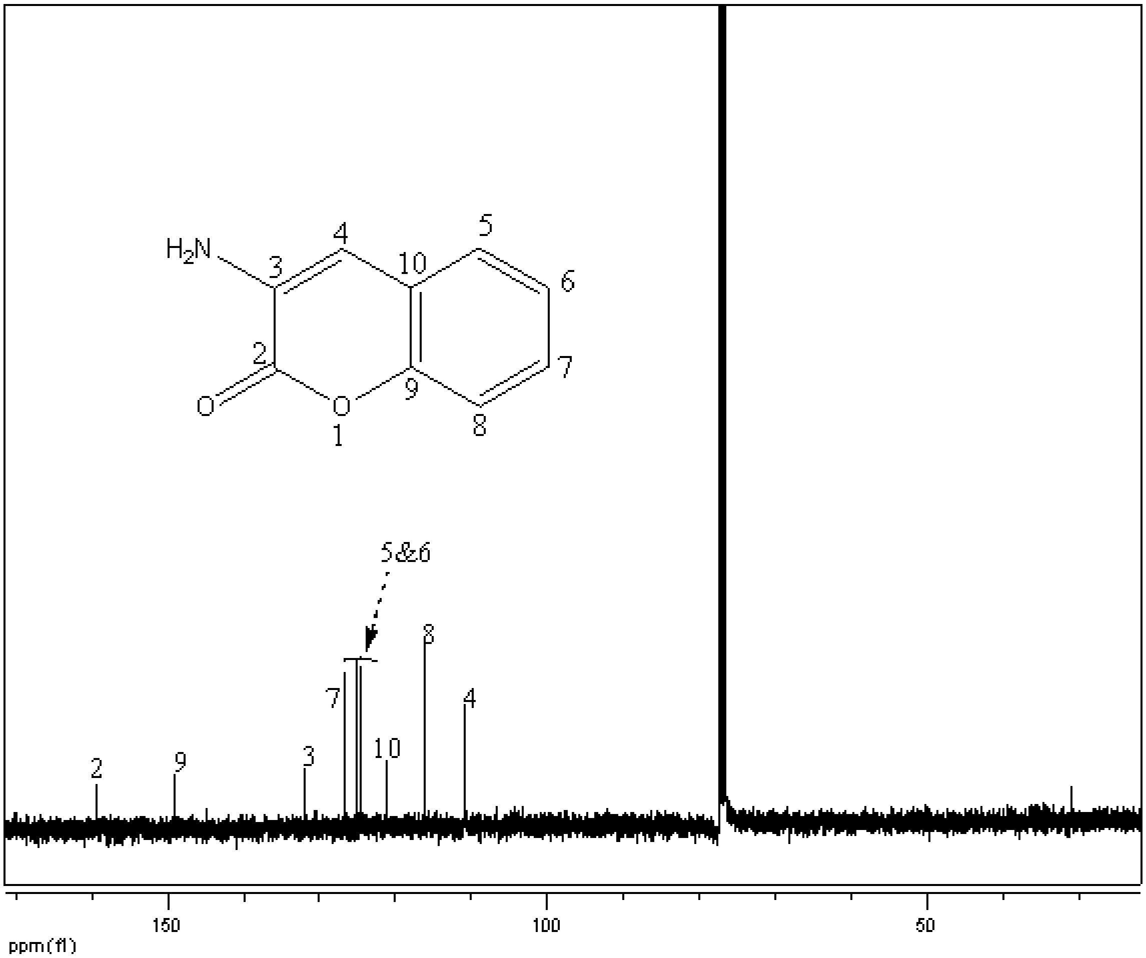
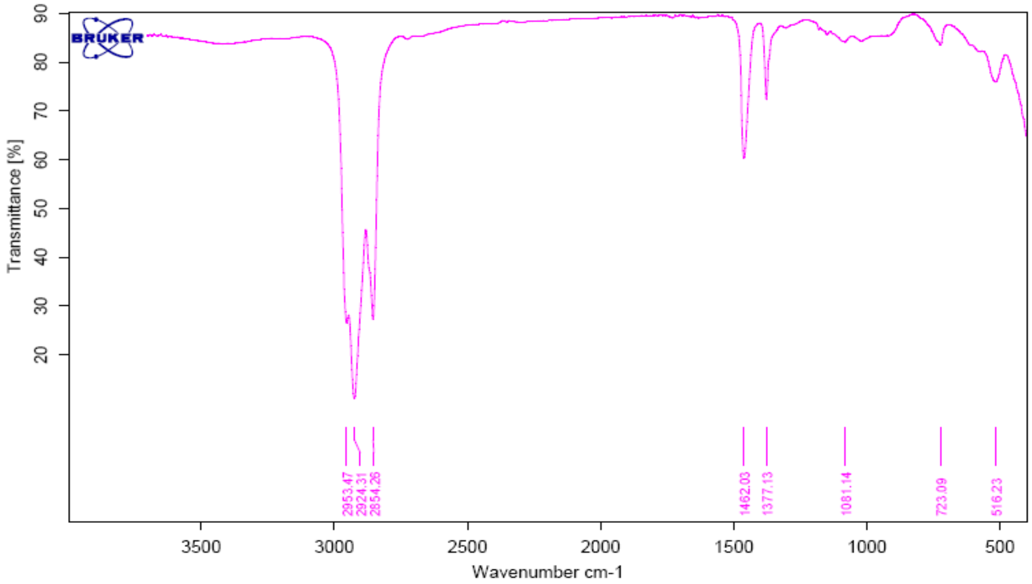


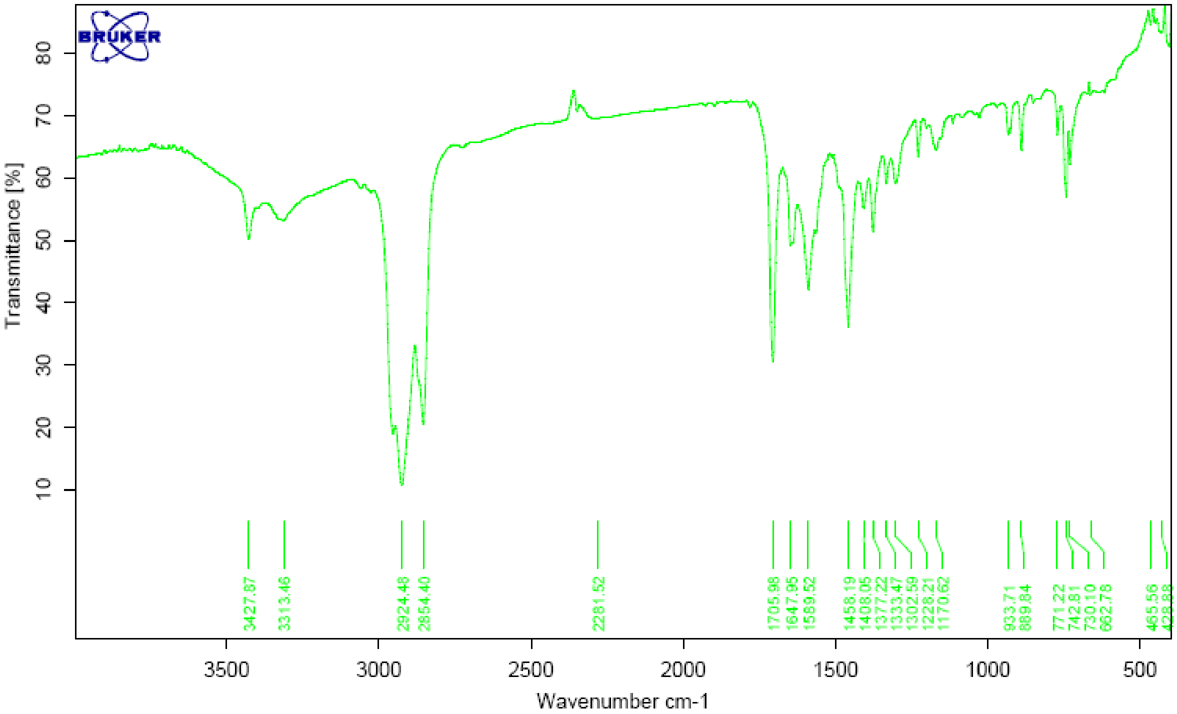
Appendix 1: 1H NMR spectra of 3-aminocoumarin



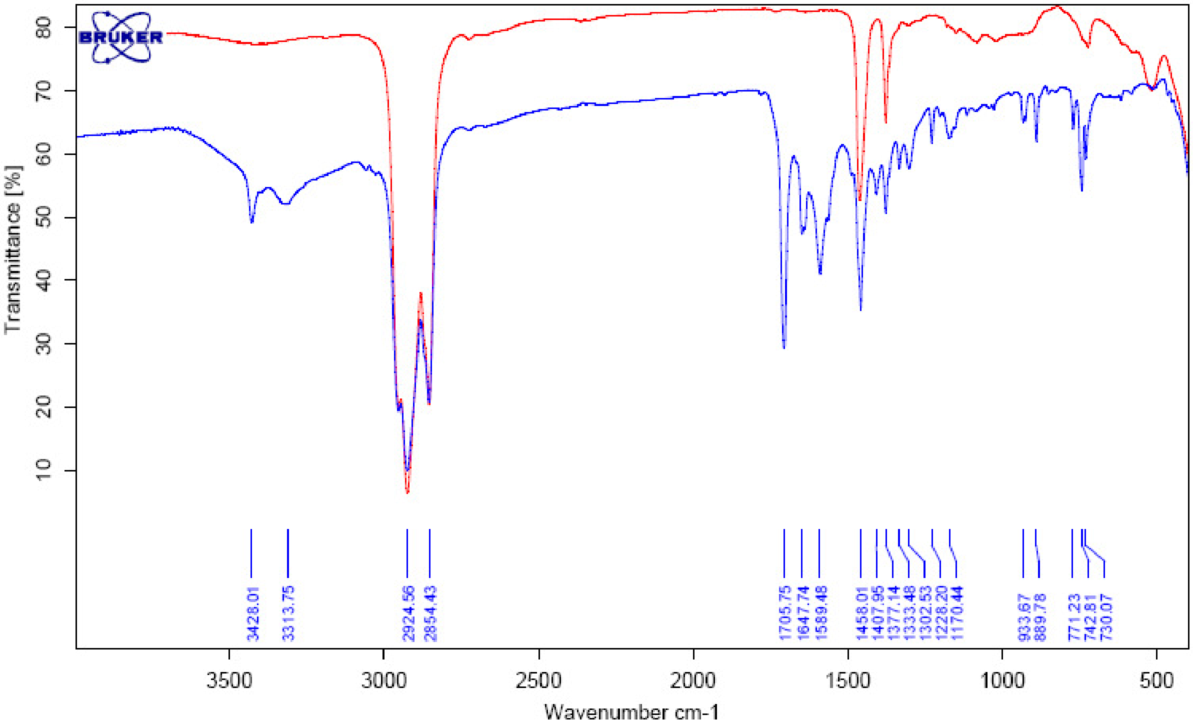
Appendix 2: ^{13}C NMR spectra of 3-aminocoumarin



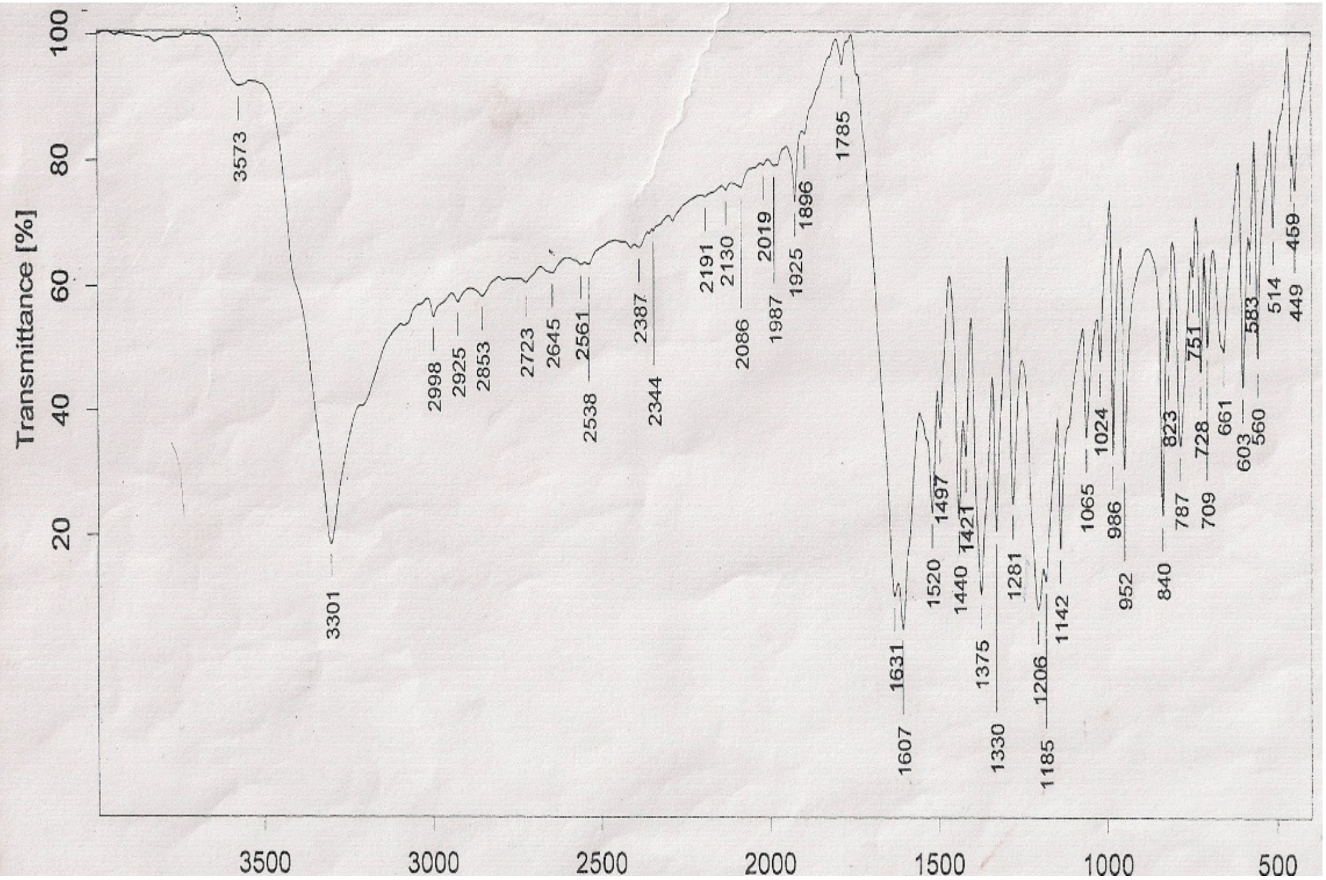
Appendix 3: IR spectrum of nujol



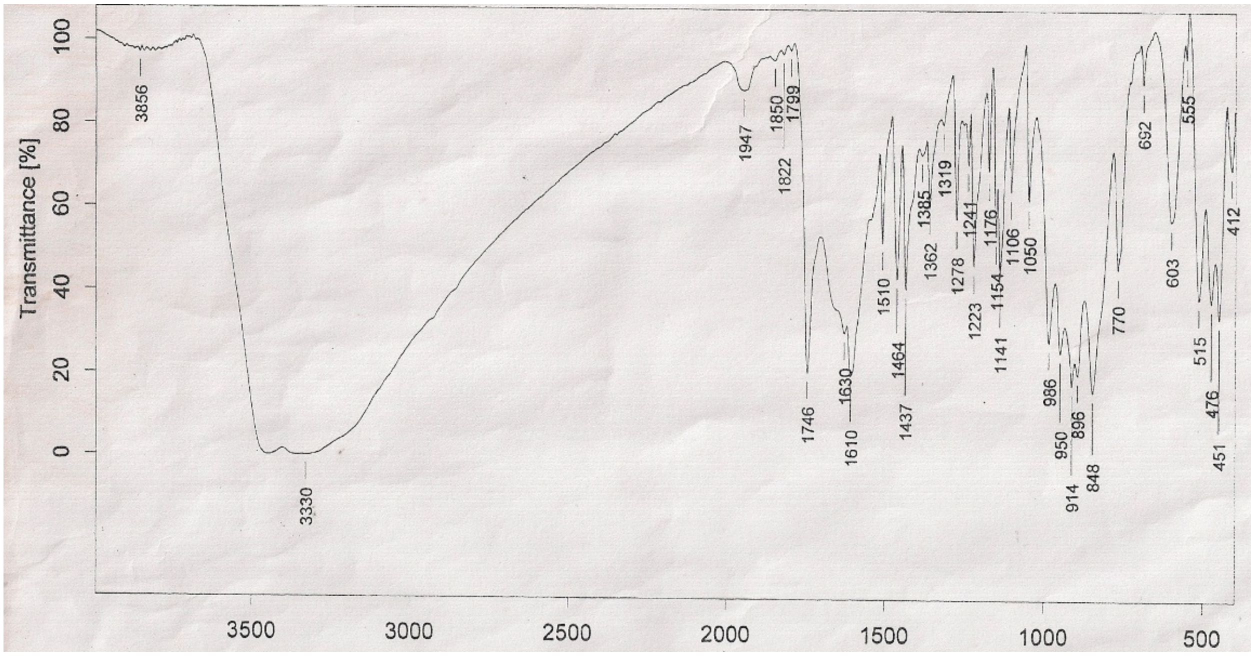
Appendix 4: IR spectrum of 3-aminocoumarin



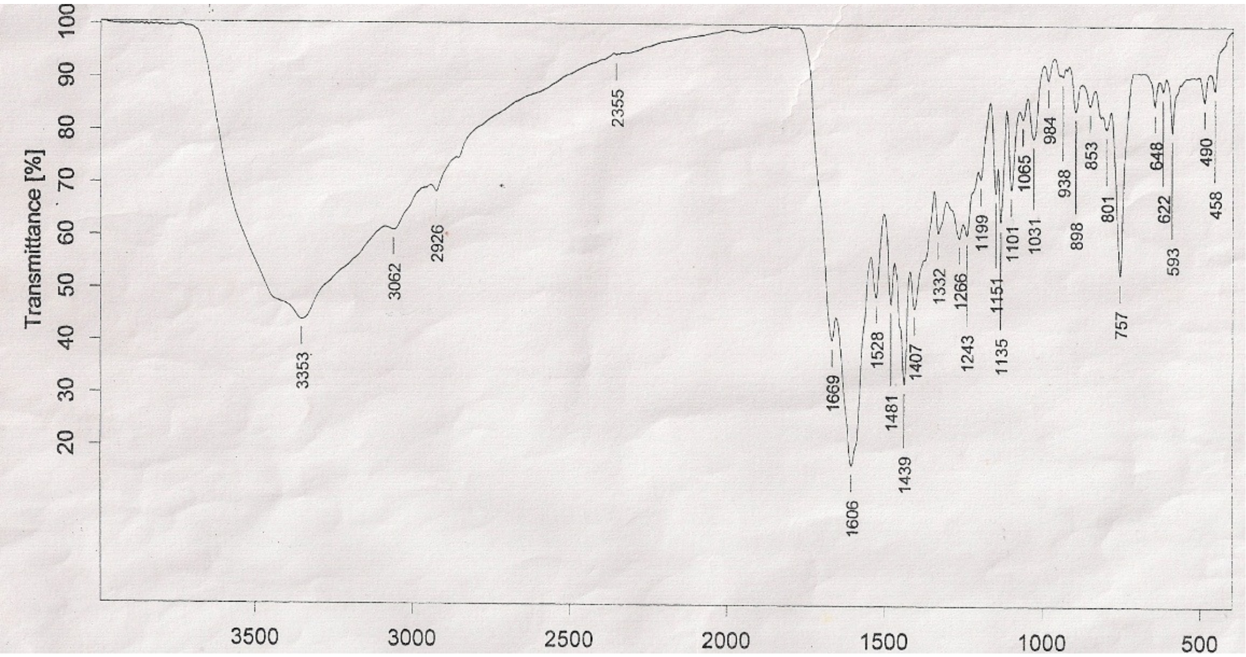
Appendix 5: IR spectrum of Nujol and 3-aminocoumarin



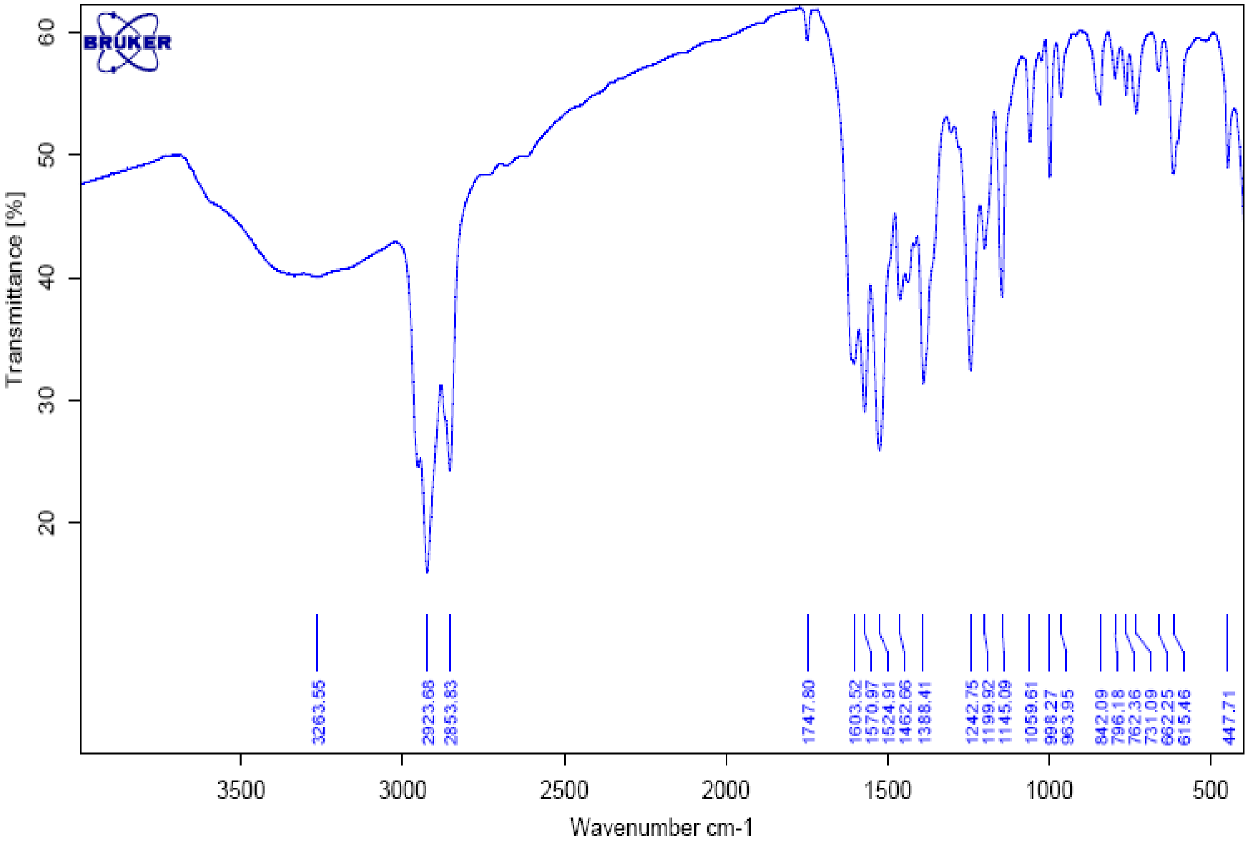
Appendix 6: IR spectrum of 4-acetyl resorcinol



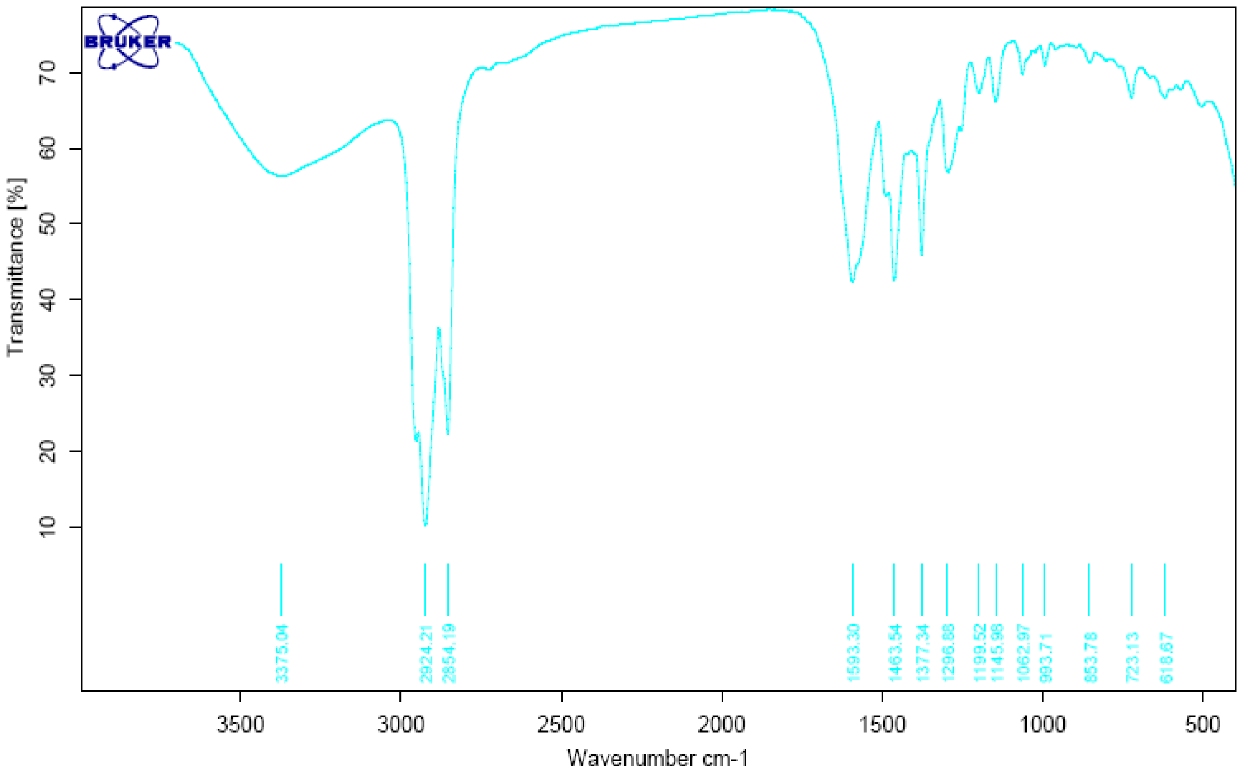
Appendix 7: IR spectrum of Cu^{2+} mixed ligand Schiff base complex



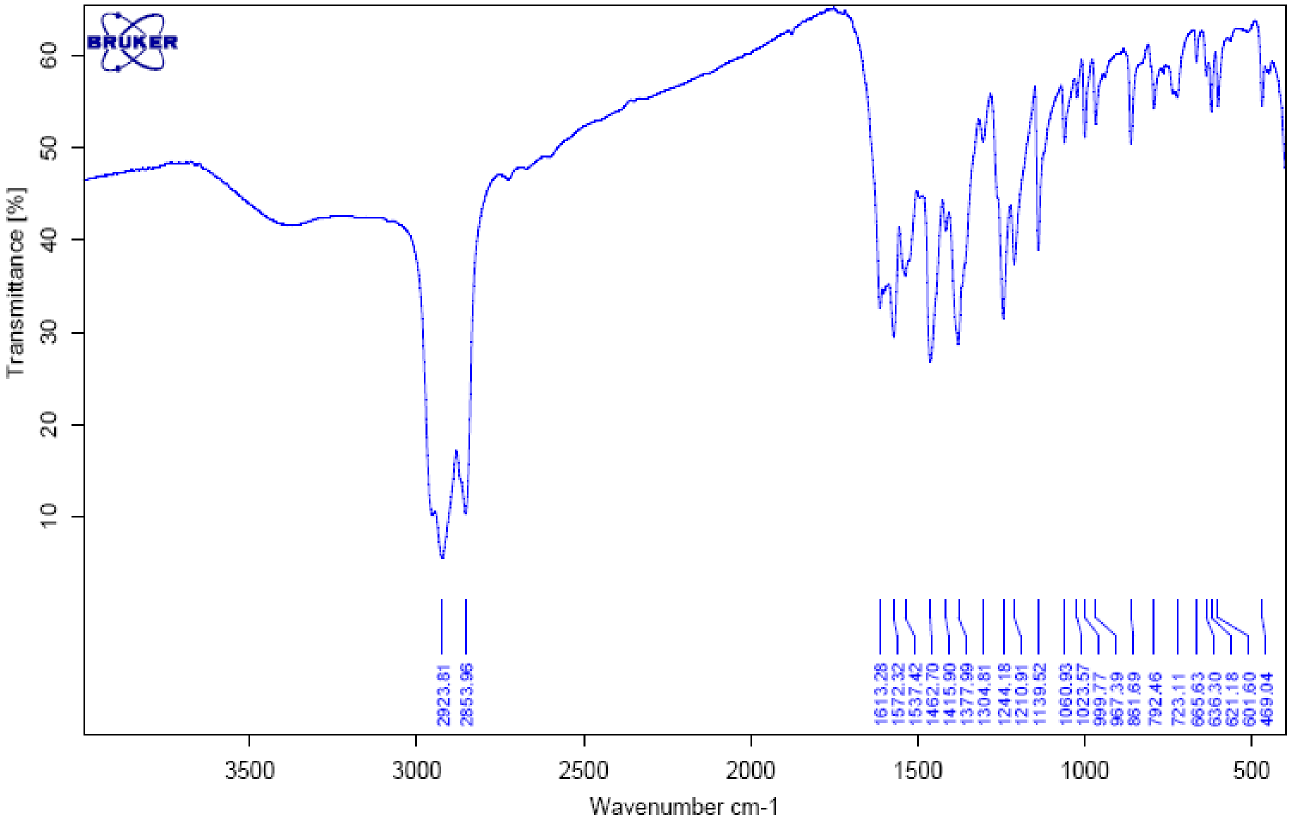
Appendix 8: IR spectrum of Zn^{2+} mixed ligand Schiff base complex



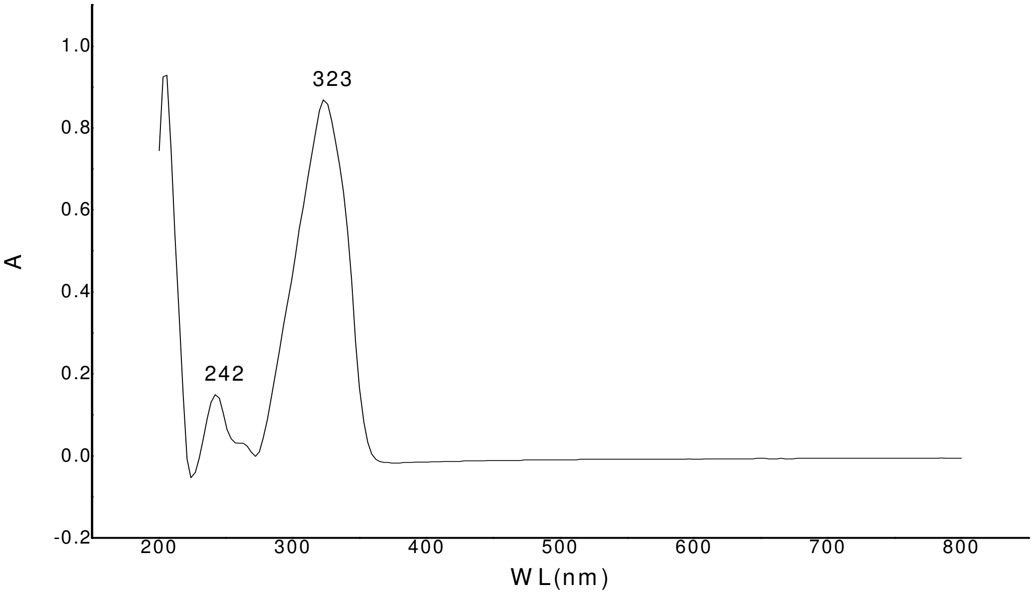
Appendix 9: IR spectrum Cr^{3+} complex of 4-acetylresorcinol



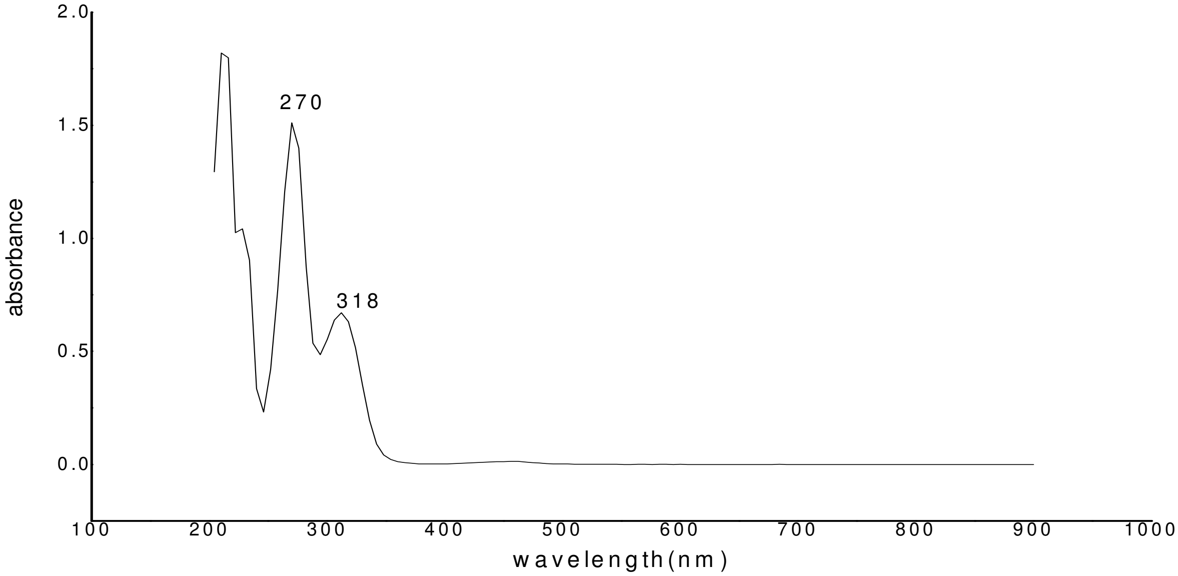
Appendix 10: IR spectrum Fe^{3+} complex of 4-acetylresorcinol



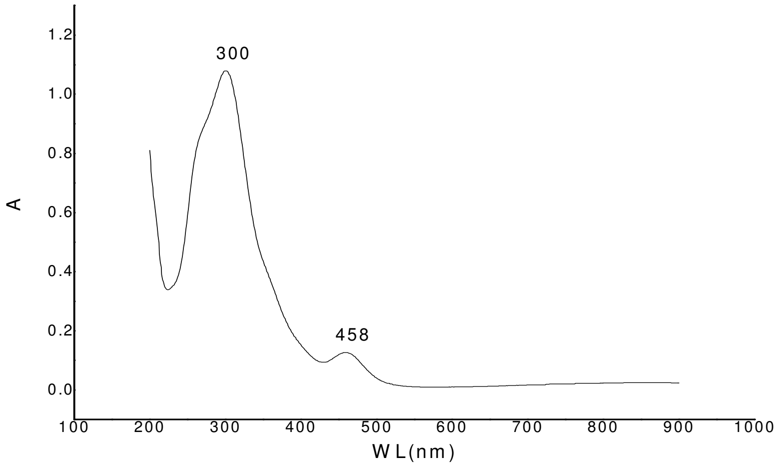
Appendix 11: IR spectrum Cu^{2+} complex of 4-acetylresorcinol

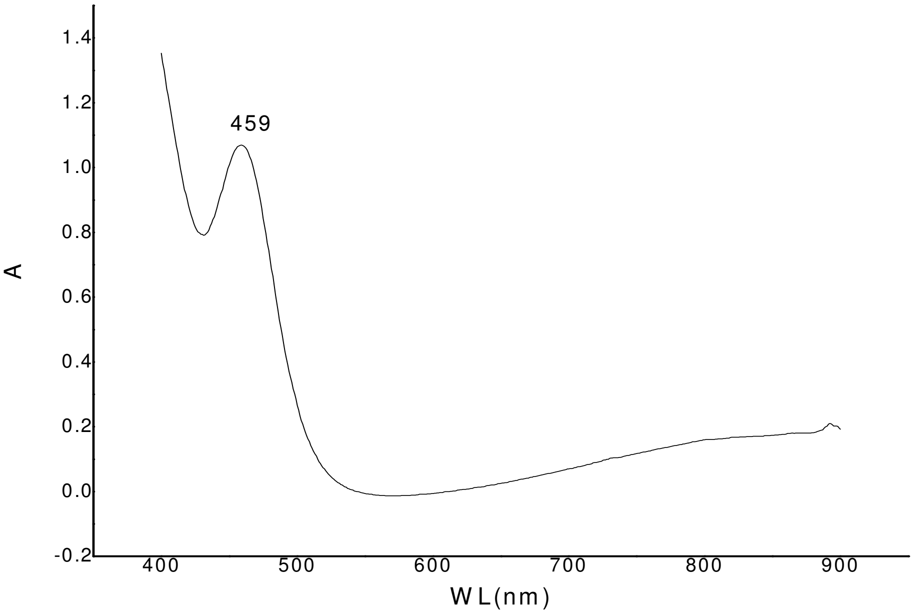


Appendix 12: UV-Vis spectrum of 3-aminocoumarin

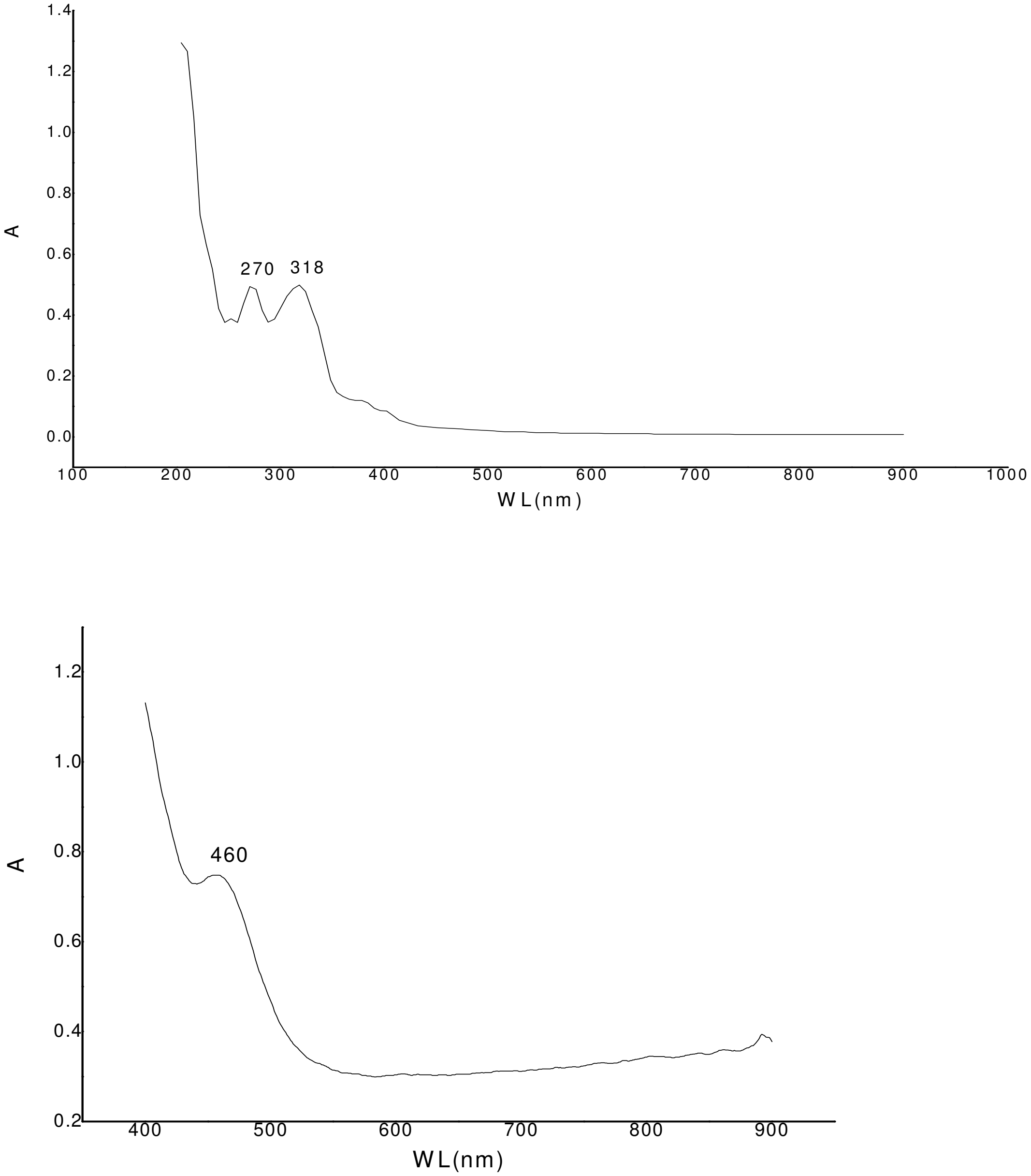


Appendix 13: UV-Vis spectrum of 4-acetylresorcinol

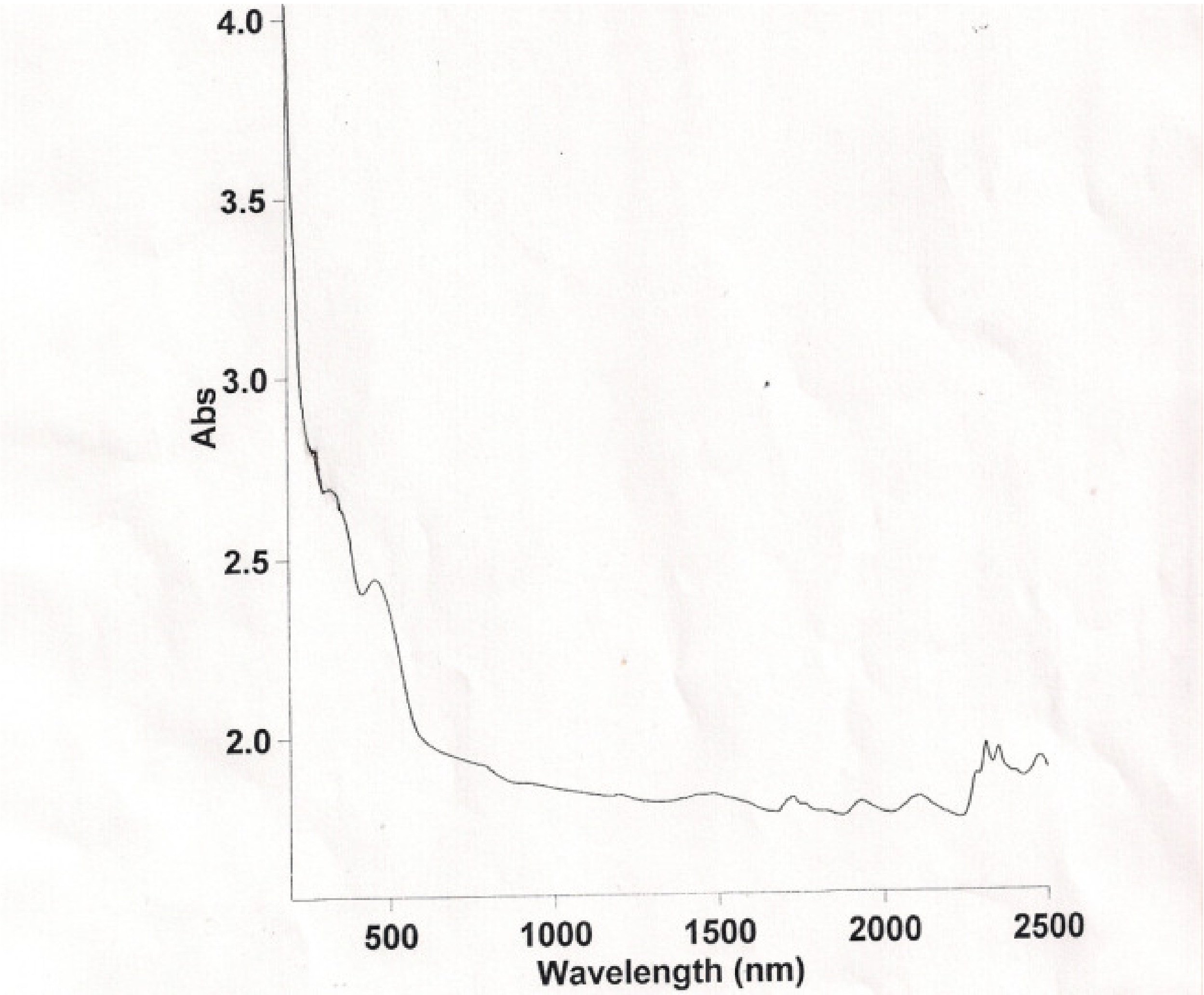




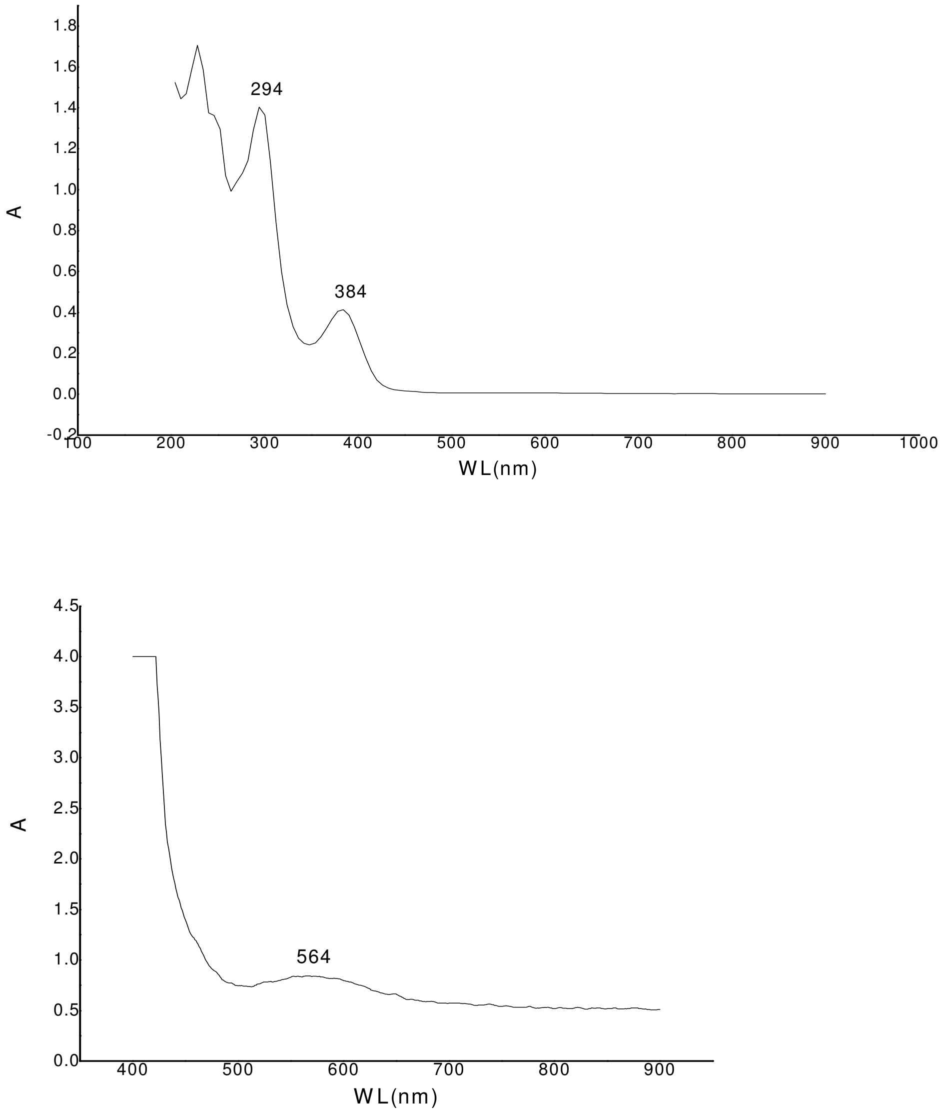
Appendix 14: UV-Vis spectrum of Cu^{2+}metal ion



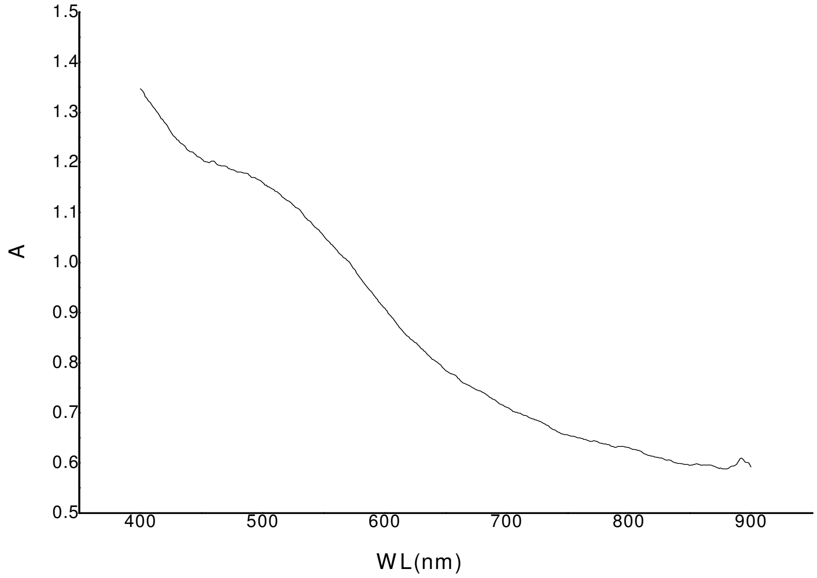
Appendix 15: UV-Vis spectrum of Cu^{2+} mixed ligand Schiff base complex



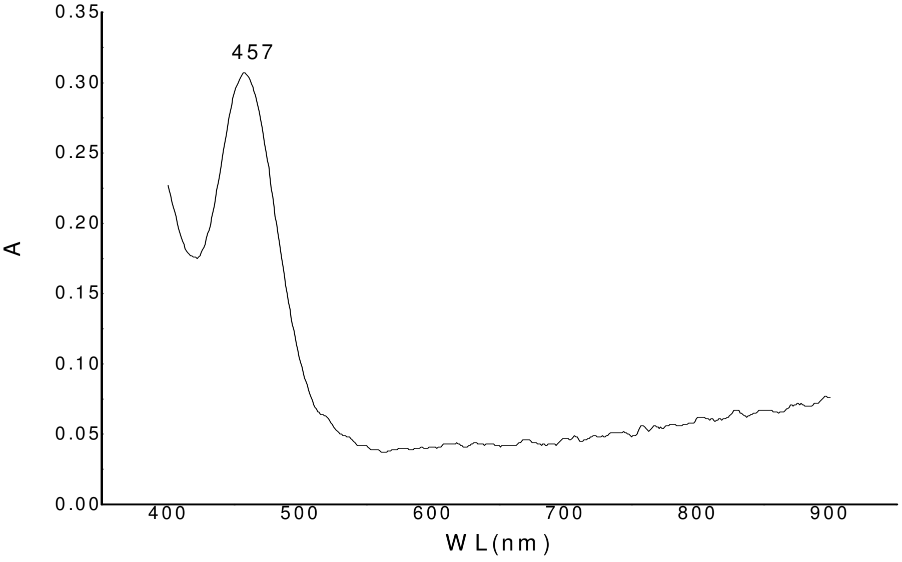
Appendix 16: UV-Vis spectrum of Zn^{2+} mixed ligand Schiff base complex



Appendix 17: UV-Vis spectrum Cr^{3+} complex of 4-acetylresorcinol



Appendix 18: Visible spectrum Fe^{3+} complex of 4-acetylresorcinol



Appendix 19: Visible spectrum Cu^{2+} complex of 4-acetylresorcinol