ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

GRADUATE PROJECT (CHEM. 774)

SYNTHESIS AND STRUCTURAL STUDIES ON METAL COMPLEXES DERIVED FROM THE REACTION BETWEEN NINHYDRIN AND EACH OF ASPARTIC ACID AND THREONINE SEPARATELY IN THE PRESENCE OF Co (II) AND Zn (II).

BY: WONDIMAGEGN KUMALA

JULY 2006

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A PROJECT PRESENTED TO THE SCHOOL OF GRADUATE STUDIES
ADDIS ABABA UNIVERSITY.

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY.

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LONG LIVE MY MOTHER!

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Wondimagegn Kumala.
July 2006

Table of Contents Page

List of Tables

List of Figures

List of Abbreviations and Symbols

DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
B.M	Bohr magneton
RP	Ruhemann's Purple
Asp. A	Aspartic Acid
Thr	Threonine
Char	Characteristic
Cal	Calculated
Max	Maximum
M.Pt.	Melting Point
Dec. T	Decomposition Temprature
Λ_m	Molar Conductance
ν	Stretching Frequancy
χ_g	Gram Susceptibility
χ_m	Molar Susceptibility
μ_{eff}	Effective magnetic moment
$\mu_{s.o.}$	Spin only magnetic moment
mM	Millimolar

ABSTRACT

SYNTHESIS AND STRUCTURAL STUDIES ON METAL COMPLEXES DERIVED FROM THE REACTION BETWEEN NINHYDRIN AND EACH OF ASPARTIC ACID AND THREONINE SEPARATELY IN THE PRESENCE OF Co (II) AND Zn (II).

By: Wondimagegn Kumala

Abstract: Co (II) and Zn (II) of Ruhemann`s Purple derived from ninhydrin and each of L- Aspartic acid and L-Threonine were successfully synthesized. The two complexes were distinctly colored and stable to atmospheric conditions. The complexes were characterized by elemental analysis, molar conductance and magnetic susceptibility; as well as infrared and electronic spectral studies. The Ruhemann`s Purple was shown to behave as a monobasic tridentate ONO donor. An octahedral geometry is proposed for the two complexes.

Key words: Co (II) & Zn (II) complexes, ninhydrin, Ruhemann`s
Purple, Aspartic acid, Threonine

1. Introduction

Amino acids are the basic structural building units of proteins. They form short polymer chains called peptides or polypeptides, which in turn form structures called proteins. [1]

They are organic molecules, which contain at least one carboxyl (COOH) and one amino ($-NH_2$) group. The variations, between the different amino acids, lie in the nature of their R groups (side chains). [2, 3] There are twenty amino acids that are normally present in the proteins of mammalian tissues. All possess in common a primary amino group, a substituent, a carboxyl moiety, and hydrogen atom attached to the α- carbon atom.

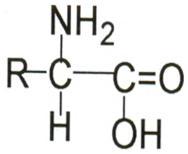


Fig.1. General Structure of α- Amino Acid

The amino acids, proline and hydroxyproline (that differs from proline by the presence of a hydroxyl (OH) group attached to the C (gamma) atom) , may be considered as α- amino acids whose respective amino group have become involved in the closure of a pyrrolidine ring. [4] They are amino acids that contain a secondary amino group and form tertiary peptide bonds. Proline, for example, is sometimes incorrectly called an imino acid.

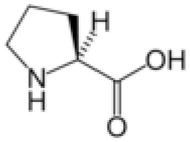
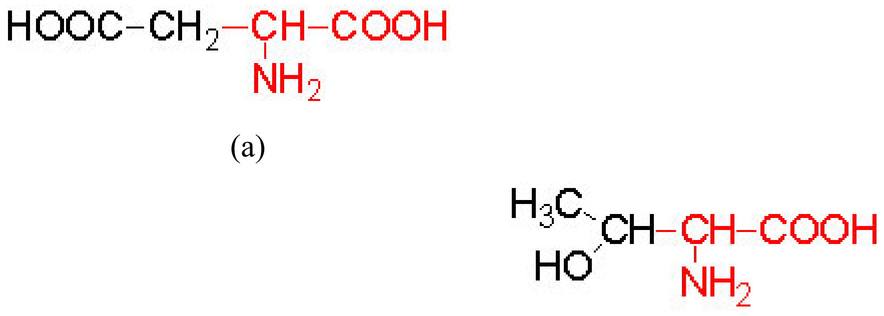


Fig. 2 The Structure of L-Proline Containing Secondary Amine Group.

A tetrahedral carbon atom with 4 distinct constituents is said to be chiral. The one amino acid not exhibiting chirality is glycine since its "R-group" is a hydrogen atom. Chirality describes the handedness of a molecule that is observable by the ability of a molecule to rotate the plane of polarized light either to the right (dextrorotatory) or to the left (laevorotatory).

All of the amino acids in proteins exhibit the same absolute steric configuration as L-glyceraldehydes. Therefore, they are all L-α-amino acids. D-amino acids are never found in proteins, although they exist in nature. D-amino acids are often found in polypeptide antibiotics.

The amino acids under present investigation being Aspartic acid (with acidic side chain) and Threonine (with polar side chain) , have the following structures:



(a)

(b)

Fig .3 Structures of Aspartic Acid (a) and Threonine (b)

The α-COOH and α-NH_2 groups in amino acids are capable of ionizing (as the acidic and basic R-groups of the amino acids). As a result of their ionizability the following ionic equilibrium reactions may be written:

$$R\text{-}COOH \text{ <--------> } R\text{-}COO^- + H^+$$

$$R\text{-}NH_3^+ \text{ <---------> } R\text{-}NH_2 + H^+$$

The equilibrium reactions, as written, demonstrate that amino acids contain at least two weakly acidic groups. However, the carboxyl group is a far stronger acid than the amino group. At physiological pH (around 7.4) the carboxyl group will be unprotonated and the amino group will be protonated. An amino acid with no ionizable R-group would be electrically neutral at this pH. This species is termed as a zwitterion.

The net charge (the algebraic sum of all the charged groups present) of any amino acid, peptide or protein, will depend upon the pH of the surrounding aqueous environment. As the pH of a solution of an amino acid or protein changes so too does the net charge. This phenomenon can be observed during the titration of any amino acid or protein. When the net charge of an amino acid or protein is zero the pH will be equivalent to the isoelectric point: pI. This is shown, for example in the titration of Alanine.

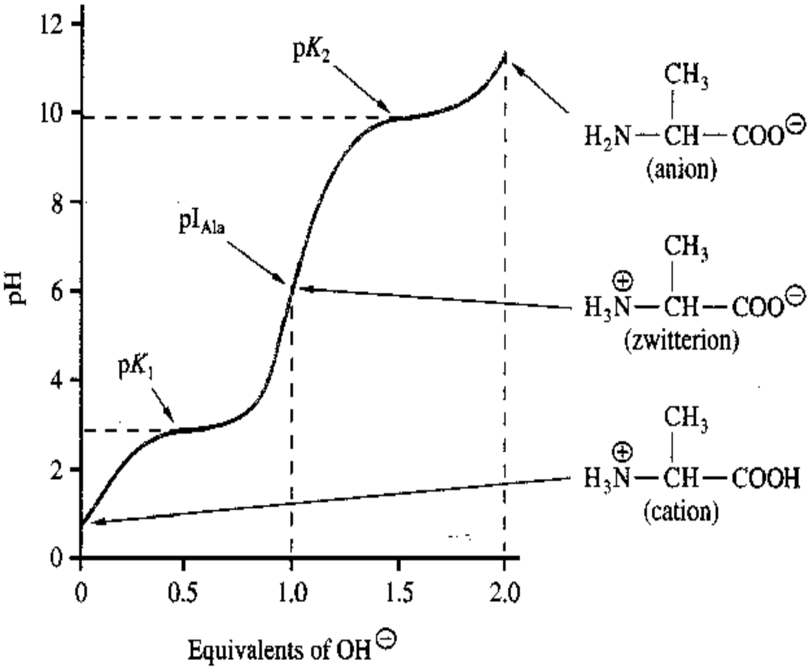


Fig.4 Titration Curve for Alanine.

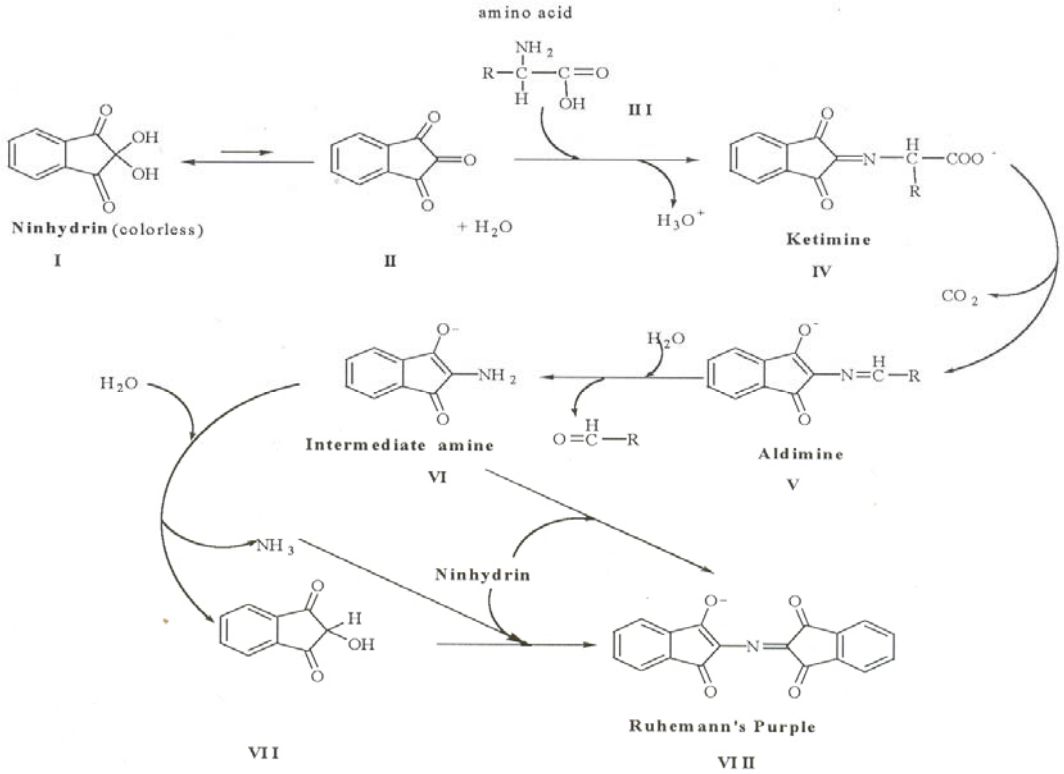
An important group of reaction of an amino acid is the condensation of the amino group with many carbonyl-bearing compounds. Condensation reactions of this type produce Ketimine or Aldimine Schiff bases depending on the type of the carbonyl compound. These Schiff bases have been very important as ligands to metals and due to their biochemical importance. [5] The reaction products of amino acids are in most cases colored or fluorescent compounds, which can be used in qualitative and quantitative analysis. [6]

Identification and quantification of constituent amino acids in a mixture is required in the biochemical investigation of proteins and peptides. The most extensively used method is the ninhydrin reaction, in which ninhydrin (2, 2-dihydroxy-1, 3-indandione or 1, 2, 3-triketohydrindene hydrate; I and II in scheme 1) reacts with amino acids to give a characteristically blue /purple, colored compound popularly known as Ruhemann`s Purple (in scheme 1, VIII) [6, 7]. It was by chance that Sigfried Ruhemann first observed this color reaction in 1911.[8,9] The λ_{max} of the blue compound (scheme 1, VIII) is 570 nm [7,10,11] and this forms the basis for the spectrophotometric quantitative determination of amino acids that can detect as little as one microgram quantity. [7, 12]

Several workers introduced modifications to the method [7], the most noticeable ones being those by Moore, Stein et .al [13, 14] and Doi et. al. [15]

The mechanism however, was not well understood until very recently and this gave rise for a series of theories as reviewed by Mc Caldin as shown in Scheme 1. [16-18]

It has a condensation step that leads to a Schiff base formation followed by decarboxylation, hydrolysis and finally further condensation with another ninhydrin molecule to give the final product, Ruhemann`s purple. [16-18] The kinetic aspects have been well studied by Friedman and Siegel.[10]



Scheme 1 The Reaction of Ninhydrin with α-Amino Acids.

The Ketimine IV (Schiff base) is a potential ligand, that can act as a tridentate forming two stable five membered rings on complexation. If the side group of the amino acid is not considered for the present discussion the Schiff base can have metal binding sites as shown in fig 1.

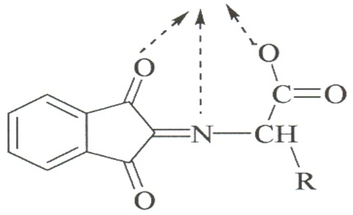


Fig.5. Possible metal binding centers of a Schiff base derived from Ninhydrin and α-Amino Acid.

In support of this, a fairly recent study on the coordination of the Schiff base derived from ninhydrin and glycine to some metal ions showed that if a metal ion is present before the reaction commences, the reaction does not always proceed to the final product, but stops at the first step, the metal ion forming a highly stable complex with the Schiff base. [19]

The intense blue product called Ruhemann`s Purple is generally characteristic of those amino acids having α - amino groups. However, proline, which is secondary amine, yield yellow product and asparagine, which has a free amide group, reacts with ninhydrin to produce a characteristic brown product.

Since the discovery of ninhydrin reaction, extensive efforts have been made to apply manual and automated ninhydrin reactions as well as ninhydrin spray reagents to the detection, isolation, and analysis of numerous compounds of interest across a broad spectrum of disciplines. These include agricultural, biochemical, clinical, environmental, food, forensic, microbiological, medical, nutritional, plant, and protein sciences.

The Ninhydrin reaction has also been used in the determination of nitrogen content of amine containing samples [20] and forensic science to study fingerprints. [21] The chemical reactions involved are complex and, as a result, the development conditions need to be controlled if optimum results are to be obtained. The method is very effective for the development of fingerprints on porous surface such as paper. However, some paper surfaces (certain bank notes, for example) react strongly with the reagent and its use is limited in such cases.

Amino acids are stable compounds that, due to an affinity for cellulose, do not tend to migrate through a dry paper substrate with time. The amino acid content of the eccrine secretion also appears to remain relatively constant. As a result, very old latent prints can be developed with ninhydrin on documents stored under favorable conditions. The development of 30-year -old prints has been recorded.

1.1 The Chemistry of Co (II) & Zn (II) Ions

The coordination chemistry of transition metal ions is considered in this work: Co (II) and Zn (II) will be presented in terms of their d^n configuration.

1.1.1 **Cobalt (II) complexes**

Cobalt (II) with a d^7 configuration is known in four coordinate (tetrahedral) and six coordinate (octahedral) stereochemistry. The electronic spectra of tetrahedral cobalt (II) complexes are more intense than those of the octahedral ones. [22]

In octahedral Co (II) complexes, $^4T_{1g}$ and $^2A_{1g}$ are the spin free and spin paired ground states, respectively. For high spin octahedral geometry, a band near 8000-10000cm^{-1} can be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ transitions. A multiple band observed a round 20000cm^{-1}is attributed to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transition.

The electronic spectrum of high spin octahedral complexes usually shows three spin allowed transitions corresponding to $^4T_{1g} \rightarrow {}^4T_{2g}$ (6200-11300cm^{-1}), $^4T_{1g} \rightarrow {}^4T_{1g}$(P) (a multiple band near 20000 cm^{-1}) and $^4T_{1g} \rightarrow {}^4A_{2g}$ (P) (1200-16000cm^{-1}, frequently not observed).[23,24]

Tetrahedral Co (II) complexes are high spin with the $^4A_2$ ground state and three spin allowed transitions with much greater intensities than octahedral case are expected corresponding to $^4A_2 \rightarrow {}^4T_1$ (F) (4600-7780 cm^{-1}) $^4A_2 \rightarrow T_1$ (P) (13250-16300 cm^{-1}) and $^4A_2 \rightarrow {}^4T_2$.

Square planar Co (II) complexes are unusual and can be distinguished from tetrahedral complexes since they exhibit a narrow band near 8500cm^{-1}and a stronger band near 20000 cm$^{-1.}$

1.1.2 **Zinc (II) Complexes**

Zn (II) ion forms numerous complexes of various stereochemical types in which tetrahedral complexes are predominant. Square planar geometry is less common. Monomer and polymeric Zn (II) complexes have been reported. These complexes are diamagnetic and do not possess any d-d transitions due to d^{10} configuration.

2. Objectives and Scope of the Present Investigation

It was aimed to synthesize Co (II) & Zn (II) complexes derived from the reaction between ninhydrin and each of Aspartic acid and Threonine.

It was also aimed to study the structure of Co (II) and Zn (II) complexes derived from the reaction between ninhydrin and each of Aspartic Acid and Threonine.

3. Experimental

3.1. Chemicals

Most chemicals used in the investigation were AnalaR grade. The two salts used were $CoCl_2.6H_2O$ (Riedel-de Haen) and $ZnCl_2$ (BDH). Other chemicals used include ninhydrin (Pharmacos), Aspartic acid, Threonine (Aldrich), HNO_3, $AgNO_3$. Absolute ethanol (Fluka) was used as a solvent throughout the investigation. Solvents like DMSO, DMF, acetonitrile, ethyl acetate, cyclohexane, petroleum ether, acetone, chloroform, benzene, and distilled water were used.

3.2. Instrumentation

Electronic Spectra of the compounds were recorded using SPECTRONIC GENESYS 2PC UV-Vis Spectrometer with a 1 cm cell in DMSO at room temperature. Melting points /decomposition temperatures of the products were determined on Electro thermal IA 9200, Digital Melting Point Apparatus. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR Spectrometer in the range 4000 - 400 cm^{-1} in KBr medium. Molar conductivities of the complexes in DMF were recorded at room temperature with freshly prepared 1 mM solutions using a JENWAY 4330 Conductivity and PH meter. Metal contents of the complexes were determined using a Flame Atomic Absorption Spectrometer (BUCK MODEL SCIENTIFIC 210 VGP). Magnetic Susceptibility measurements of the complexes in the solid state were carried out on a MSB-AUTO (Sherwood Scientific). Elemental analysis of the complexes was done by Exter Analytical CE 440 EA Elemental Analyzer. Chloride from the samples was determined as AgCl by the sodium fusion method using standard methods. [25, 26] The purity of the complexes was also tested by thin layer chromatography.

3.3. Synthesis

3.3.1. Synthesis of Co (II) & Zn (II) complexes derived from the reaction b/n Ninhydrin & Each of Aspartic acid & Threonine.

The complexes of Co (II) and Zn (II) were synthesized using a general procedure. The ligand was prepared in the reaction mixture in the presence of the metal ion. 0.01 mole (1.7814gm) of ninhydrin was dissolved in the minimum possible amount of ethanol (about 20 ml) and 0.01 mole of a metal salt was added to the resulting solution which was stirred until all of it dissolved. The resulting solution was refluxed for half an hour, followed by addition of 0.01 mole of the amino acid to the hot mixture and refluxed further for two hours. The resulting colored precipitate was then filtered off in hot conditions through a Whatman # 50 filter paper by suction, washed with ethanol, and then with a 50:50 mixture of ethanol and petroleum ether (50–80 ^{o}C). The product was then dried in open air and stored in a desiccator.

3.3.2. Studies on the Coordination Property of Ruhemann`s Purple

The coordination of Ruhemann`s Purple with the metal ions was studied for the comparison purpose. A 1:2 mixture of the amino acid and ninhydrin (0.0025 and 0.005 moles) were dissolved in the minimum possible amount of ethanol (about 40 ml) and left over night. A metal salt (0.0025 moles) was then added and refluxed for more than two hours. The resulting solid was filtered in hot condition, washed first with ethanol and then with a 50:50 mixture of ethanol and petroleum ether (50-80 ^{o}C). The product was then dried in open air, dried and characterized.

4. **Results and Discussion**

4.1. **General**

Ninhydrin and Aspartic acid (or Threonine) form a deep blue purple compound known as Ruhemann`s Purple which maximally absorbs at 416 and 570 nm within 20 minutes of mixing. [10] The metal complexes isolated from both amino acids (Aspartic acid and Threonine) are distinctly colored, stable to atmospheric condition and are soluble in common solvents like DMSO, DMF (giving blue solution) ethanol, methanol, acetone (giving light red color solution) and insoluble in solvents like petroleum ether, and benzene.

The solvent ethanol and 1:1:1 molar ratio of ninhydrin, metal ion and amino acid is suitable for optimum yield. These were adopted throughout the synthetic work.

A preliminary survey with several different mixtures of metal ions, ninhydrin and amino acid showed that in the presence of some Co (II) and Zn (II) ions Ruhemann`s Purple is formed. Both the procedures gave the same color (appearance), the same decomposition temperatures, the same characteristic electronic spectra, as shown in table I and characteristic IR frequencies, etc.

The complexes were subjected to chloride analysis by sodium fusion test and precipitation as AgCl. [25, 26] The result indicates the absence of chloride in the complexes. The Co (II) and Zn (II) complexes neither melt nor decompose up to 370 ^{o}C. Ruhemann's Purple synthesized by mixing amino acid and ninhydrin coordinate with Co (II) and Zn (II) ions. Their comparison with the general procedure is given in table I.

Table I. Physical properties of the two complexes obtained from the general procedure and Ruhemann`s Purple of both amino acids.

	General Procedure				Ruhemann`s Purple Procedure			
	Zn (II)		Co (II)		Zn (II)		Co (II)	
	ASP.A	Thr.	ASP.A.	Thr	ASP.A.	Thr.	ASP.A.	Thr.
Color	Dark Brown	Dark Brown	Brick Red	Brick Red	Dark Brown	Dark Brown	Brick Red	Brick Red
Appea-rance	Powder	Powder	Powder	Powder	Powder	Powder	Powder	Powder
% yield	63	61	59	56	62	60	57	55
Char. UV-Vis λmax (nm)	420,601	420.601	420.605	420.605	420,601	420,.601	420,605	420,605

4.2 **Analytical Studies**

4.2.1 Elemental Analysis

The analytical data of the complexes are given in table II. The data shows a metal to ligand ration of 1:2 in Co (II) and Zn (II) complexes of Ruhemann`s Purple.

The metal, analyses of the two complexes are in good agreement with the proposed composition. They match with an octahedral geometry.

4.2.2 Conductivity Data of the metal complexes

The molar conductance values of the Zn (II) and Co (II) complexes of Ruhemann`s purple are given in table II.

The molar conductance (Λ_m) values were recorded from conductivity measurements using the solvent DMF. The molar conductance values of the products obtained from the complexes are very small, in the range of 25-30 $\Omega^{-1}cm^2 mol^{-1}$. This shows that they are non - electrolytes .[27]

Table II. Analytical and Molar conductance data for Co (II) and
Zn (II) complexes of Ruhemann`s purple complexes.

Complex	%H		%N		%C		%Metal		Λ_m DMF $\Omega^{-1}cm^2 mol^{-1}$
	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	
$ZnRP_2$	2.39	( )	4.18	( )	64.53	( )	9.78	9.69	29
$CoRP_2$	2.41	( )	4.22	( )	65.17	( )	8.89	8.70	30

In DMF Λ_m b/n 0-65 $\longrightarrow$ non -electrolytes
b/n 65-90 $\longrightarrow$ 1:1 electrolyte

4.3 Electronic Spectral Studies

The electronic spectral studies of the Ruhemann`s purple complexes of Co (II) and Zn (II) were run by dissolving them using DMSO in the visible region (400-800 nm). The electronic spectrum of the complexes of Co (II) and Zn (II) show nearly common bands around 23800 cm^{-1} and 16525 cm^{-1} , which are the characteristic band of the exocyclic azomethine chromophore in the coordination, which in the free state absorbs at 24691.36 cm^{-1} and 17543.36 cm^{-1} in Ruhemann`s purple as shown in table III.

Table III. Electronic Spectral data of Ruhemann`s purple complexes of Co (II) and Zn (II); and free Ruhemann`s purple

Compound	Non-Ligand Electronic spectral bands (cm^{-1})	Assignment
Ruhemann`s Purple	24691.36, 17543.36	Bands of uncoordinated azomethine group
$ZnRP_2$	23,809.52, 16638.94	Bands of the coordinated azomethine group
$CoRP_2$	23866.35,16528.93	Bands of the coordinated azomethine group

4.4 Magnetic Susceptibility

The magnetic moment of Ruhemann`s purple complex of Co (II) was done at 22°c (295°k) giving gram susceptibility (χ_g) to be 9.825×10^{-6}

A 1:2 metal to Ruhemann`s purple ratio of Co (II) complex has a molecular weight of 662.9 gm/mol. Effective magnetic moment of this complex is found to be 3.91 BM using the general relation:

$$\chi_m = \chi_g M_m$$

$$\mu_{eff} = 2.824 \{\chi_m T (k)\}^{1/2}$$

where χ_g is the measured gram susceptibility.

χ_m is molar susceptibility.

T is temperature in Kelvin at which the value was recorded.

μ_{eff} is the magnetic moment in Bohr Magneton.

From effective magnetic moment value obtained, the number of unpaired electrons was calculated by using the relation

$$\mu_{s.o} = \{n(n+1)\}^{1/2}$$

where n is number of unpaired electrons. For n= 3, $\mu_{s.o} =$ 3.46. Both the calculated and found values indicate the presence of tree unpaired of electrons, which agrees with high spin octahedral geometry of the Co (II) complex.

Ruhemann`s purple complex of Zn (II) has a magnetic moment of zero indicating a diamagnetic nature of the complex.

4.5. Infrared Spectral Studies

From the data shown in table IV the sharp NH stretching band of the free amino acids at 3200-3000 cm^{-1} and the OH stretching frequency of ninhydrin are not observed indicating the derivatization of these groups.

Ninhydrin shows three bands in the carbonyl stretching region: 1768, 1754 and 1720 cm^{-1} .[29] The bands at 1754 and 1720 cm^{-1} are characteristics of its 1,3 –dicarbonyl functional group [30] and the 1768 cm^{-1} band is characteristic of the intermediate carbonyl in the tricarbonyl species , which is in equilibrium with the dihydroxy species .

The complexes of Co (II) and Zn (II) show a new, strong band sharp peak in the region of 1530-1505 cm^{-1}, which is a characteristic to the coordinated azomethine group.

The frequencies for the carbonyl groups in ninhydrin are shifted from 1754 cm^{-1} and 1720cm^{-1} to 1730-1710cm^{-1} and 1712-1702 cm^{-1} in the complexes. This indicates the involvement of one of the two carbonyl groups of ninhydrin in coordination with metal ion.

The C=N stretching frequency of the free aromatic azomethine groups occur between 1640-1620 cm^{-1} (1637 cm^{-1} in Ruhemann's purple) but with complexes it occurs at 1540-

1500cm^{-1} . A negative shift of about 100cm^{-1} is a strong evidence of the coordination of the azomethine group via nitrogen. [31] This is one indication for the condensation reactions that occurred between the amine group of the amino acid and the carbonyl group of the ninhydrin, and further the absence of peaks due to such groups from the starting material infers that condensation reaction has taken place.

Generally the infrared spectra data shows that the Ruhmann's purple is coordinated via oxygen and nitrogen, in the complexes of Zn (II) and Co (II).The carbonyl stretching frequency of uncoordinated Ruhemann's purple occurs near 1739cm^{-1} .[32] A negative shift to lower frequency in the complex indicates the coordination of the carbonyl group to metal ions.

The complexes show weak bands in the region 1740-1710cm^{-1}.These are the bands of the uncoordinated carbonyl groups in the complexes. The complexes show M-N and M-O bands in the region 750-200 cm^{-1}.

Other supporting bands include an M-O-C stretching vibration that appears in the region 1245-1200 cm^{-1} .

Each of the Co (II) and Zn (II) complexes has identical IR Spectras, which is a good indication for the formation of Ruhemann's Purple. Had it been a Schiff base, for each of the amino acids their IR Spectras would have been different and there would be a strong band at 2500-3000cm^{-1} forexample, in IR of Co (II) complex, which is not seen. Medium bands in Co (II) complexes at 3311.15cm^{-1} and 3510.32cm^{-1} might be due to common impurities in each of the amino acids.

In IR of Zn (II) complexes the very weak band at 3448.05cm^{-1} is due to moisture in KBr.

Compound	**νOH/NH**	**νC=0 Free**	**νC=0 Cord.**	**νC=C Aromatic**	**νC=N**	**ν_aCOO$^-$**	**ν_sCOO-**	**νM-O-C**	**Other non-ligand bonds ν (M-N, M-O..)**
Ninhydrin	3200- 3000(b,s)	1768(s) 1754(s) 1720(s)	-	1590(s)	-	-	-	-	-
Threonine	3000- 2500	-	-	-	-	1610(s)	1405(s)	-	-
RP	-	1739(s)	-	1581(m)	1637(m)	-	-	-	-
ZnRP$_2$	-	1720(w) 1702 (w)	1635(vs)	1593(s)	1505(vs)	-	-	1209(vs)	656(w) 525(m)
CoRP$_2$	-	1705 1678(w)	1648(s)	1605(m)	1509	-	-	1217	731(s) 520

Table IV. Infrared Spectral data of the Zn (II) and Co (II) complexes of Ruhemann's Purple and starting materials * (KBr pellets).

Intensities in parenthesis-b-broad, vs-very strong, s-strong,
m-medium, w-weak, a-asymmetric, s-symmetric,
Assignment based on K.Nakomato [33] , ν –stretching vibration

5. Conclusion

Both α-L-Aspartic Acid and α-L-Threonine form Ruhemann's Purple complexes for each of Co (II) and Zn (II) ions. This is confirmed specially from IR and electronic spectral studies.

Generally based on the elemental analysis, conductance, magnetic susceptibility and Infrared and electronic spectral data the following structure is proposed for the reaction of ninhydrin with each of L-Aspartic Acid and L-Threonine in the presence Co (II) or Zn (II) ions.

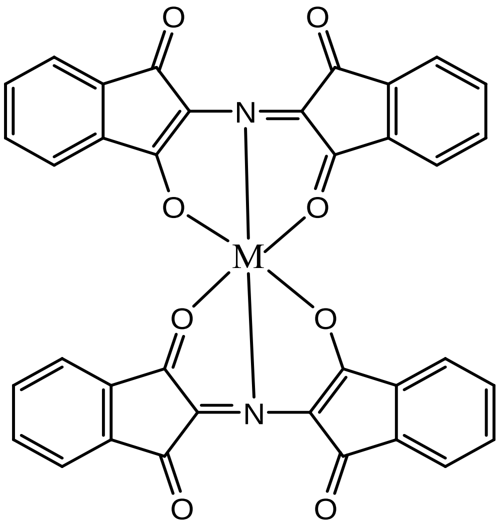


Fig 7 . Proposed structure for of the Ruhemann's Purple Complexes of Co (II) and Zn (II)

6. References

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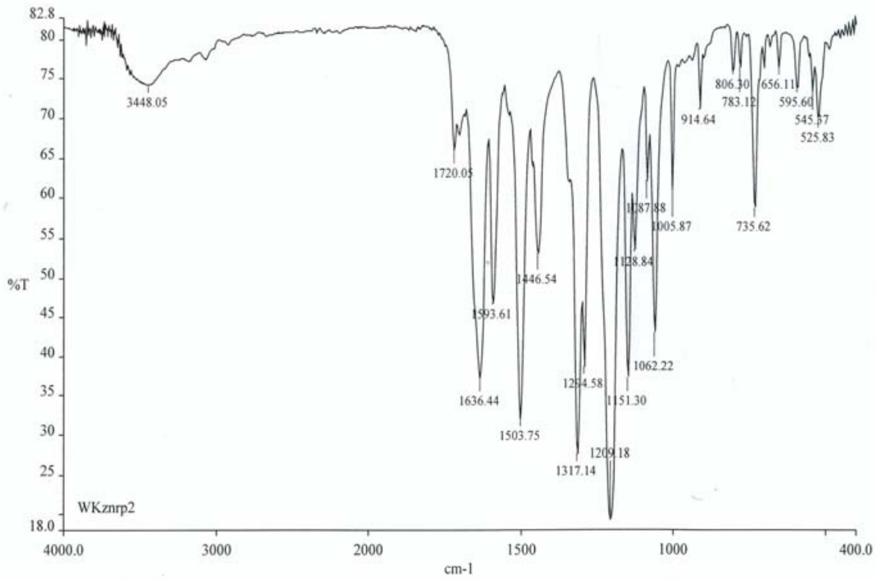
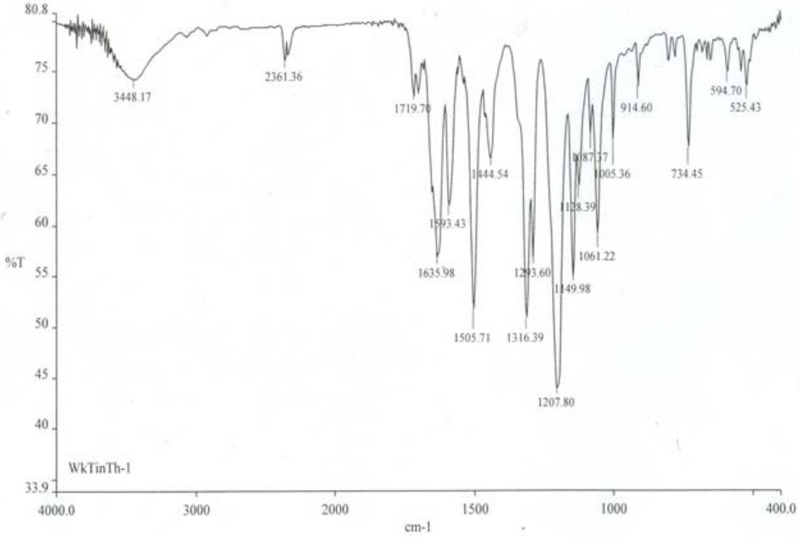
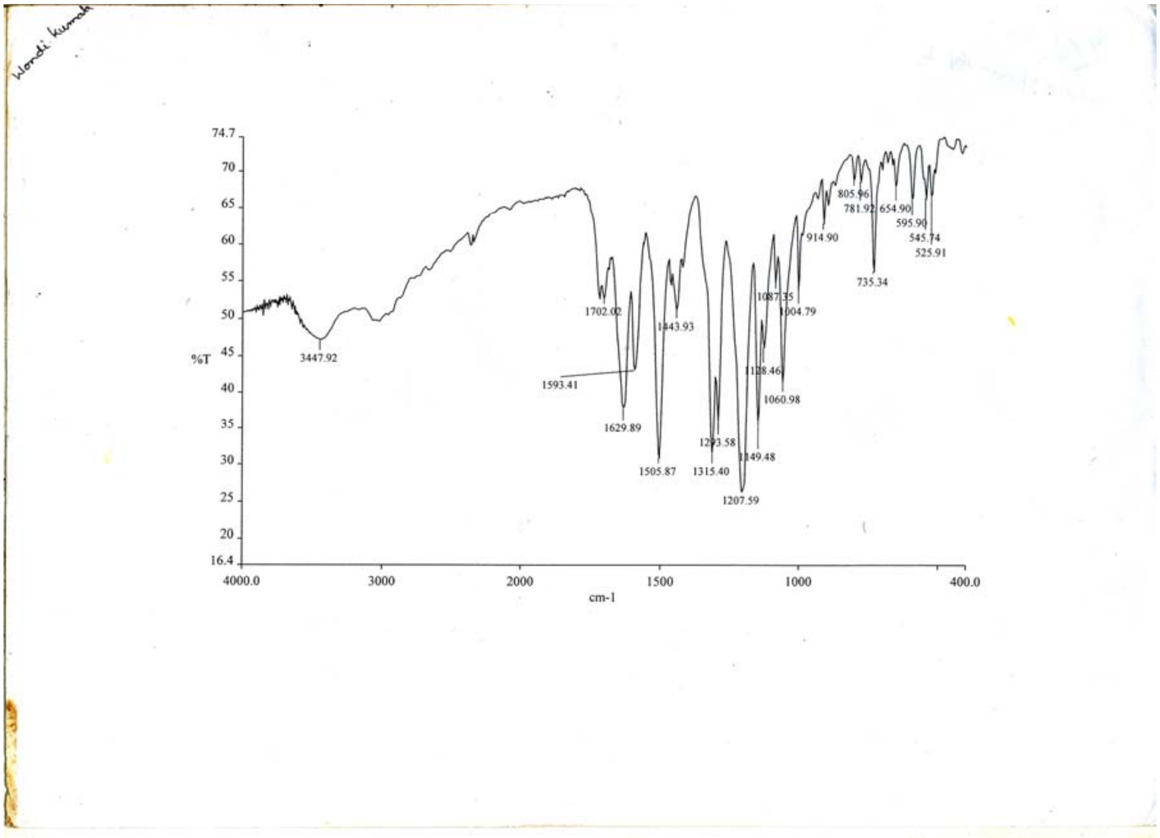
APPENDICES



IR of Zn (II) Complex of RP



IR of Zn (II) Complex of Ninhydrin & Threonine



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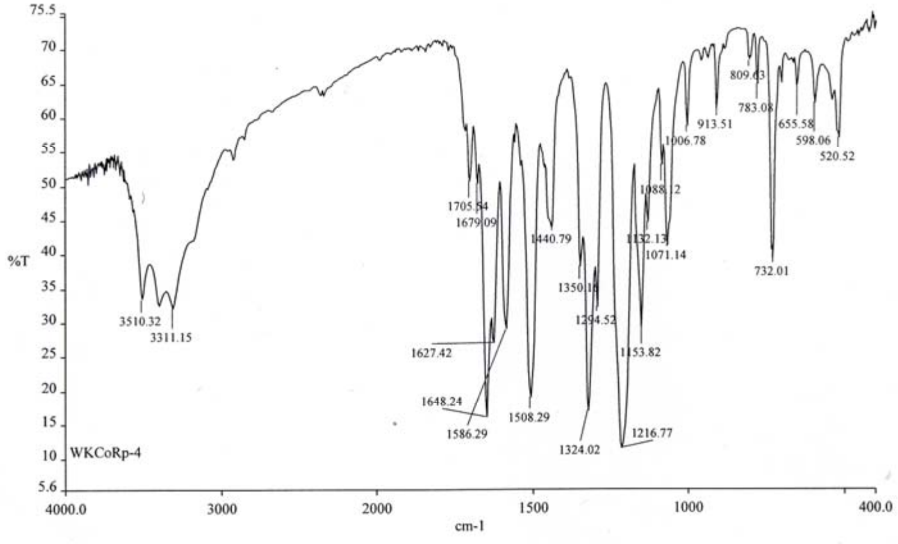

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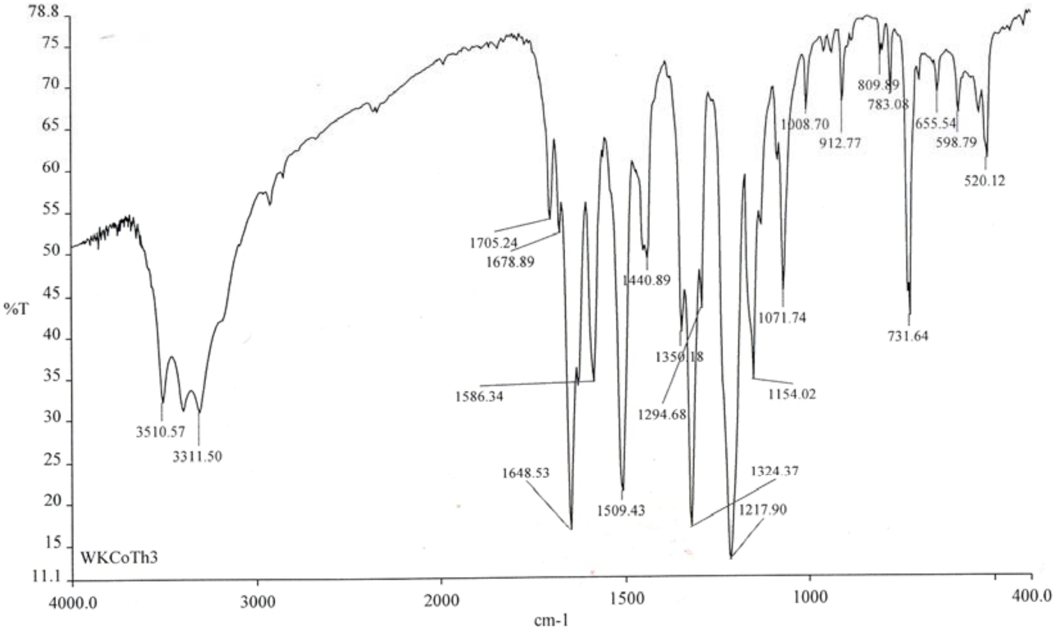

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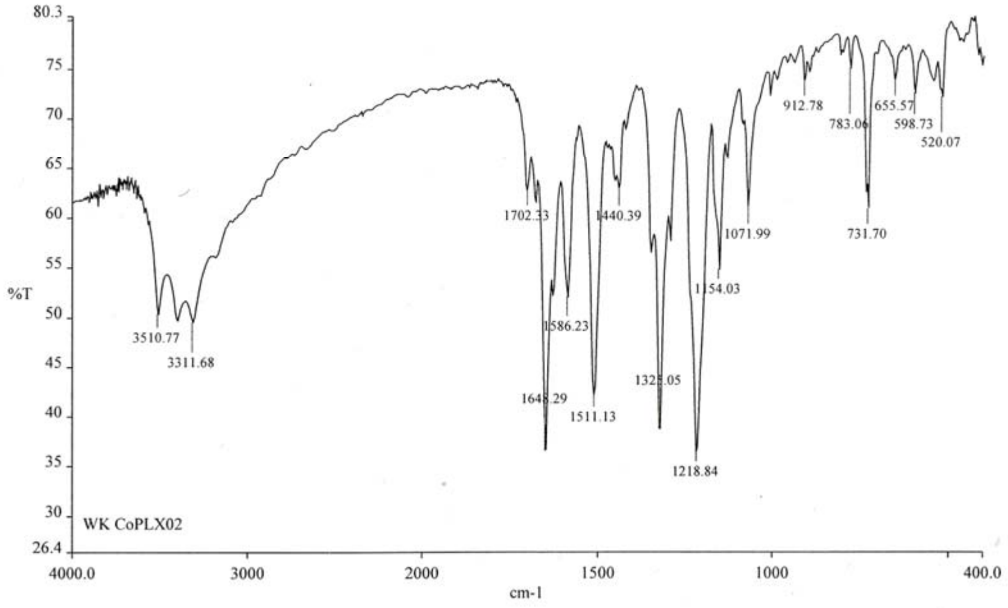
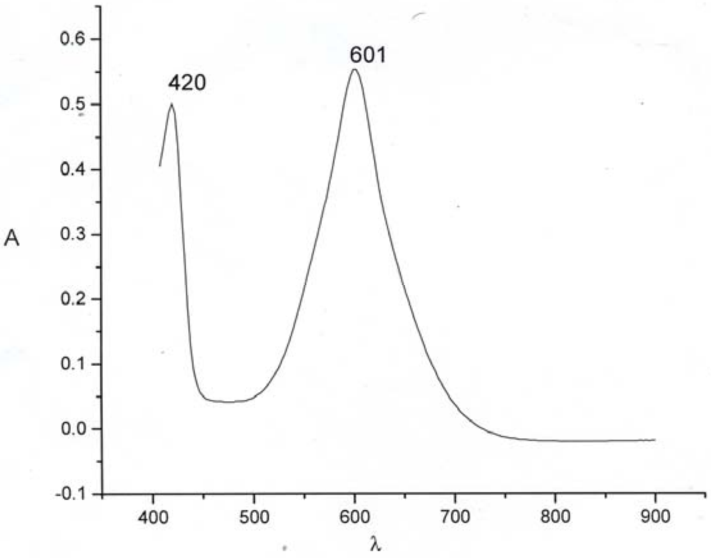


IR of Co (II) Complex of Ninhdrin & Aspartic Acid bare,



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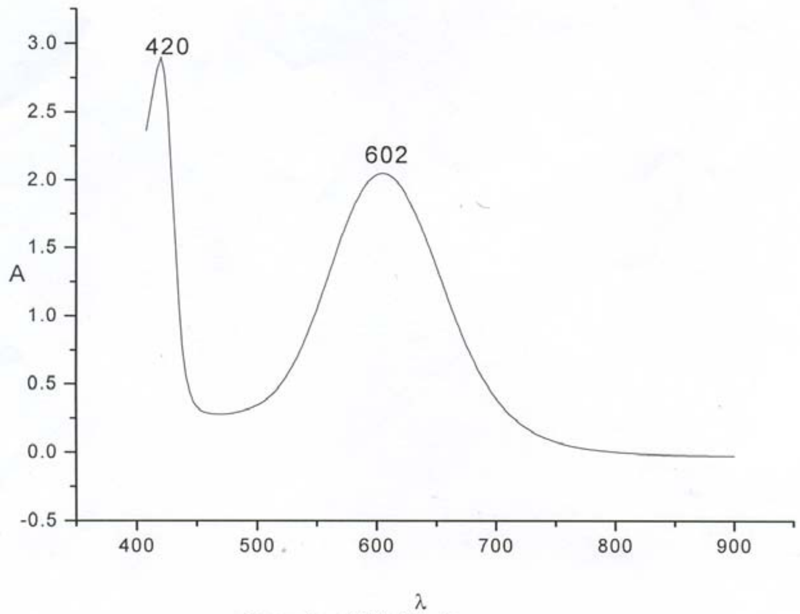

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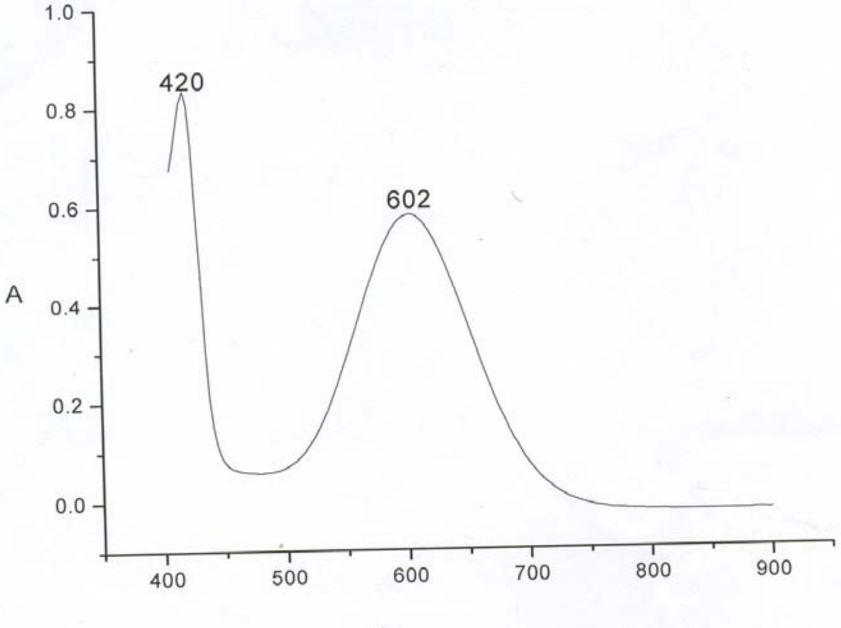
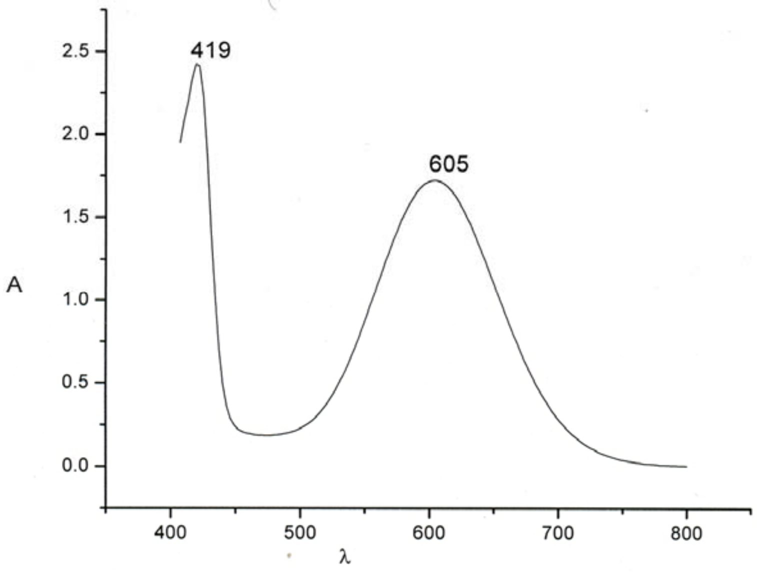
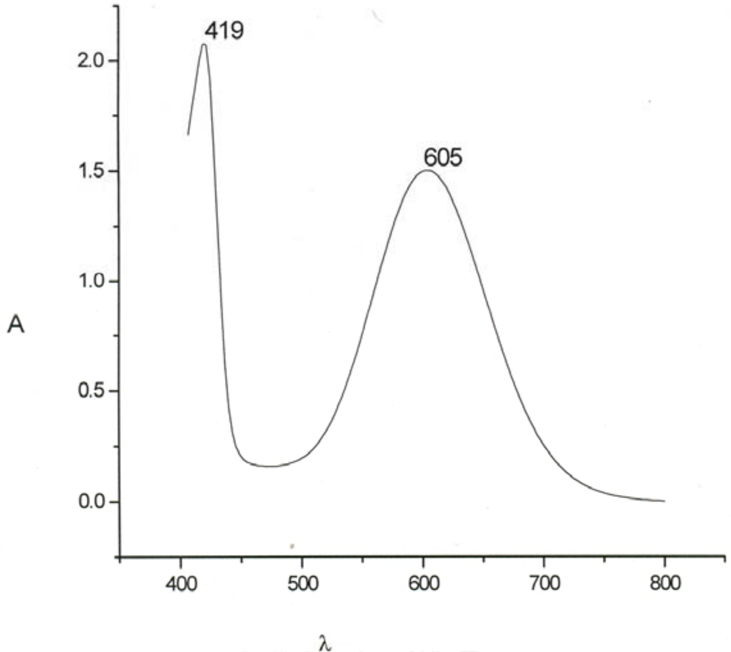


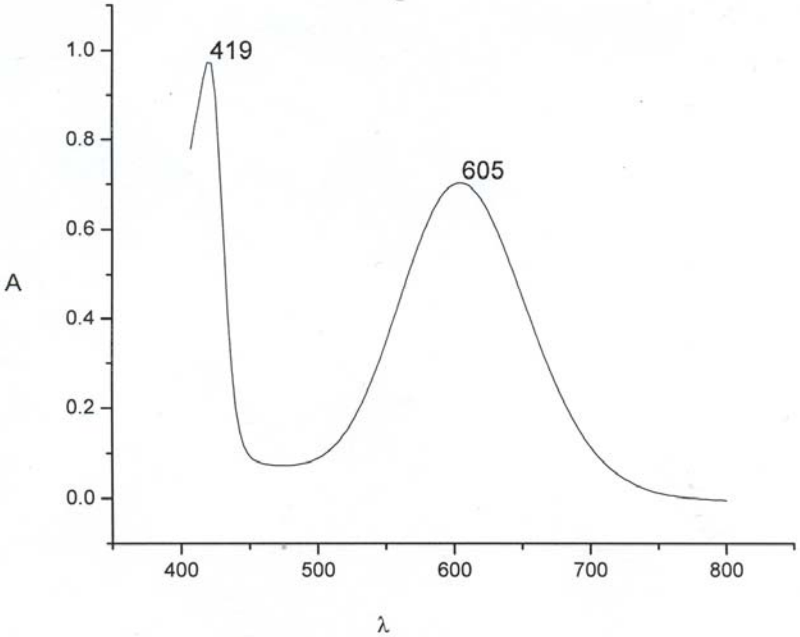
Zn cplx of NinAsp-1



Co(II) complex of RP



Co(II) Complex of Nin-Thr



Co(II) Complex of Nin-Asp

DECLARATION

This project is my original work; it has not been presented in this and any other University. All sources of materials used in this work have been duly acknowledged.

Name: WONDIMAGEGN KUMALA FUTASSA

Signature: ___________________

This project work has been submitted for the examination with my approval as the University advisor.

____

Dr. Yonas Chebude

And

____

Prof. V. J. T. Raju

Place and date of submission:

Office of Research and Graduate Program

Department of Chemistry

July, 2006