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METAL COMPLEXES OF A NEW-N-HETROCYCLIC LIGAND - STRUCTURAL STUDIES

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by

Yosef Alemayehu

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Table of contents

Page

DEDICATION……………………………………………………………… i

ACKNOWLEDGEMENT…………………………………………………...ii

LIST OF TABELES…………………………………………………………iii

LIST OF ABBRIVATION…………………………………………………..iv

LIST OF FIGURES………………………………………………………….....v

ABSTRACT…………………………………………………………………vi

1. Introduction ……………………………………………………………1

    1.1 Chemistry of Nickel (II) and Copper (II)……………………………....8

    1.2 Literature survey…………………………………………………………11

2. Objectives and scope of the present investigation……………………………..18

3. Experimental………………………………………………………………...20

    3.1 Chemicals and Solvents……………………………………………..20

    3.2 Instruments and Experimental conditions…………………………...20

    3.3 Synthesis……………………………………………………………..21

        3.3.1 Preparation of quinoxaline-2,3-dione……………………….21

        3.3.2 Preparation of the ligand (L)………………………………..21

        3.3.3 Preparation of complexes…………………………………...23

4. Result and discussion……………………………………………………..24

4.1 Conductivity data………………………………………………25

4.2 Magnetic studies…………………………………………………25

4.3 Infra red Spectra………………………………………………. 26

4.4 Electronic spectra………………………………………………28

5. Conclusion…………………………………………………………………..29

6. References…………………………………………………………………...31

APPENDIX

IR Spectra of the complexes

UV-Vis Spectra of the complexes

TO MY GOD

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LIST OF TABLES

Page

1. The solubility of complexes in Different Solvents 24

2. Conductivity Values of Complexes 25

3. Analytical Data of Metal Complexes 26

4. Infrared Data of Dione and Metal Complexes 27

5. Electronic Spectral Data of Metal Complexes 28

SYMBOLS AND ABBREVIATIONS USED

ν ⇒ Stretching

δ ⇒ Bending

λ ⇒ Wave Length

S ⇒ Siemens

μ ⇒ Magnetic Moment

IR ⇒ Infrared

nm ⇒ NanoMeter (10^{-9}m)

m.p ⇒ Melting point

M-T ⇒ Metal Complex Prepared by Template Method

M-L ⇒ Metal Complex Prepared by Direct Method

KBr ⇒ Potassium bromide

DMF⇒Dimethylformamide

DMSO ⇒ Dimethylsulfoxide

UV-Vis ⇒ Ultraviolet-Visible

^{1}H NMR ⇒ Proton Nuclear Magnetic Resonance

^{13}C NMR ⇒ Carbon Nuclear Magnetic Resonance

bQxDB ⇒ N,N-bis(3-quinoxaline-2-one)-1,2-diaminobenzene

Q-2,3-dione ⇒ Quinoxaline-2,3-dione

LIST OF FIGURES

Page

1. Structure of Quinoxaline 1

2. Tautomeric forms of Q-2,3-dione 4

3. Synthesis of derivatives of Q-2,3-dione 5

4. Structure of o-phenylendiamine 6

5. Suggested structure for the metal complexes of a new multidentate dihydrazino quinoxaline derivative 14

6. Structure of $ZnCl_2(C_8H_6N_2)_2$ complex 16

7. Complexes of macrocyclic zinc ion linked by quinoxaline ligand 17

8. Preparation of Q-2,3-dione 21

9. Reaction of Q-2,3-dione with orthphenylenediamine 22

10. Structure of Cu(II) and Ni(II) complexes 30

Abstract

Complexes of Cu(II) and Ni(II) have been synthesized using template method by the condensation of orthophenylenediamine with quinoxaline-2,3-dione in ethanolic medium in the presence of metal ion All the complexes were characterized on the basis of their molar conductance, magnetic susceptibility, IR and UV-Vis, and based on this the Cu-L complex found as square planar and Ni-L complex was octahedral.

INTRODUCTION

Heterocycles containing sulfur, oxygen and nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π-conjugation decreases Coulombic repulsion. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies [1]. The *o*-phenylenediamine and its derivatives were used as the starting material to react with carbonyl compounds through thermo-reaction and microwaveirradiation, and the benzo-fused multi-membered heteroaromatic compounds including benzimidazoles, quinoxalines and benzodiazaepines were obtained in good yields [2].

Diones are very useful functional groups amenable to a wide variety of chemical transformations. Indeed, they have been used to prepare a number of heterocyclic compounds, such as quinoxalines, dihydropyrazines, imidazoles, and pteridines.

The quinoxaline skeleton has been used as a synthetic intermediate for the preparation of numerous compounds with interesting biological properties. Due to their conformational rigidity and their wide range of properties, such heterocyclic systems play an essential role as scaffolds in biologically active compounds.

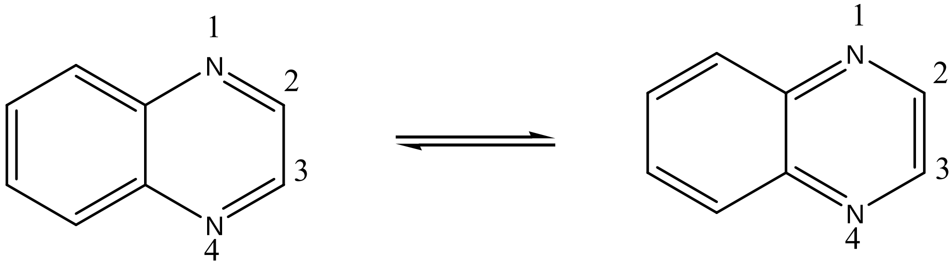


Fig.1 Structure of quinoxaline

For example, they were used in the synthesis of antibacterial agents, AMPA receptor antagonists,GABA/benzodiazepine receptor agonists/antagonists, Lck inhibitors, in addition to many other pharmacologically active compounds. Furthermore, the biological importance of quinoxaline-based inhibitors of receptor tyrosine kinases (RTKs) and protein kinase C (PKC) has led to a considerable amount of synthetic works in the field of such ring systems [3].

Quinoxaline derivatives are an interesting class of compounds possessing a broad spectrum of biological activity. Commonly are well known their antibacterial, antiviral, antifungal, antispasmodic, or even anticancer properties [4]. Quinoxaline conjugated with peptides are known for a long time as antibiotics, like echinomycin, used in pharmacological therapy. Organic compounds possessing bisbidentate heteroatom sites are important building blocks in constructing bimetallic coordination compounds. Thus, some of quinoxaline derivatives, for example 2,3-bis(2-pyridil) quinoxaline (dpq), dipyridophenazine (dppz) and 2,3-bis(2-furanyl) quinoxaline (dfq) form complexes with transition metals (Cu, Co, Ni, Ru, Rh, Pt) [5,6]. Specially interesting is dpq that can act as chelate ligand in two main ways by forming a five-membered ring involving N-atoms of the pyridine and the pyrazine rings, or by forming a seven-membered ring involving only the N-atoms of the pyridine rings [7]. Complexes of quinoxaline derivatives with metals show the high ability to covalently bind to DNA and cleavage [8]. This may suggest that conjugation of biologically active peptides with the quinoxaline analogs can lead to new therapeutic agents possessing interesting anticancer properties. There are examples of quinoxaline complexes that serve as stereochemically defined multimettalic systems for use as light absorbers and electron donor/light absorber in photoinitiated electron transfer and electron collection.

Ring-fused heterocycles that contain more than one nitrogen atom are key structures in a large variety of biochemical processes. During the last few years, quinoxalines have been of special interest due to their biological activity. This has led to the development of a new class of structural elements for mycobacteriostatic drugs based on 2,3-diaminoquinoxalines [9].

Quinoxaline 1,4-dioxides (QdNO's) are known as potent antibacterial agents, and subtherapeutic levels have been used to promote growth and improve efficiency of feed conversion in animal feed. They have also shown a selective cytotoxicity against hypoxic cells present in solid tumours. Furthermore, recent studies have put in evidence that QdNO's are endowed with antitubercular, antiprotozoal and anticandida activities. On the other hand, several authors have reported about photoallergic and mutagenic effects of some derivatives. QdNO's may also cause the development of antibiotic-resistant bacteria and influence the horizontal transfer of virulence genes between bacteria[10].

The present report shows that the synthetic quinoxaline species are used as electrochemical extraction of Cu(II). Various derivatives of this ionophore have been extensively employed as analytical reagents in the determination of metal ions.

For instance, have used quinoxaline-2-carboxylic acid in the gravimetric determination of transition metal ions such as Cu(II), Cd(II), Zn(II), Co(II), Ni(II) and Pd(II)[11].

Dicyanopyrazinoquinoxaline derivatives have strong electron-accepting properties due to the pyrazinopyrazine skeletons as well as the cyano groups. Substituents can be easily introduced at the benzene ring and control the HOMO-LUMO energy gap and the molecular packing. It was found that the compound exhibited *n*-type semiconducting behavior with carrier mobility of 3.6 × 10–6 cm^2/Vs. [12]

Quinoxaline-2,3-diones and quinoxaline-2-ones are mainly prepared by condensation of *o*-phenylenediamines with various ketoacid derivatives [13],

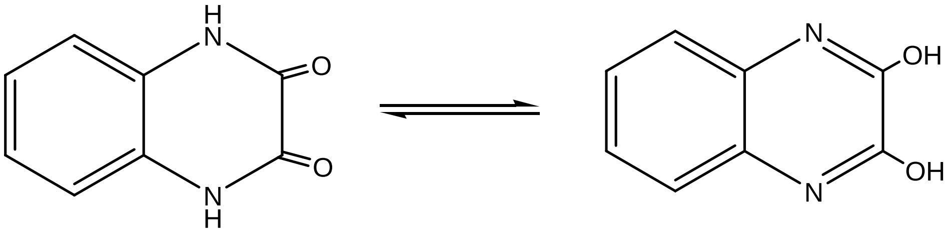


Fig.2 Tautomeric forms of quinoxaline-2,3-dione

although they can be prepared by other reactions, such as the photorearrangement of quinoxaline-1,4-dioxides [14]. Several general methods are available for preparing *o*-phenylenediamine derivatives [15]. The ring closure of an *o*-phenylenediamine with oxalate derivatives, used to form the six-member paradiazine ring of a quinoxaline-2,3-dione, is usually the last and crucial step. Normally, this step is carried out using the method of Phillips [16] under the catalysis of strong acid or at

elevated temperatures [16, 17]. Sometimes a solvent is also used [17]. With the structural modifications at other sites on 1,2- diaminobenzene completed in the

previous steps, it is desirable to perform the ring closure in the synthesis of quinoxaline-2,3-dione under mild reaction conditions in order to avoid any side reactions. The general Phillips reaction carried out under harsh conditions, as commented by Piguet[18], needs be modified for various reasons. If possible, catalysts and solvents should not be used, because any such substances are potential impurities in the final product.

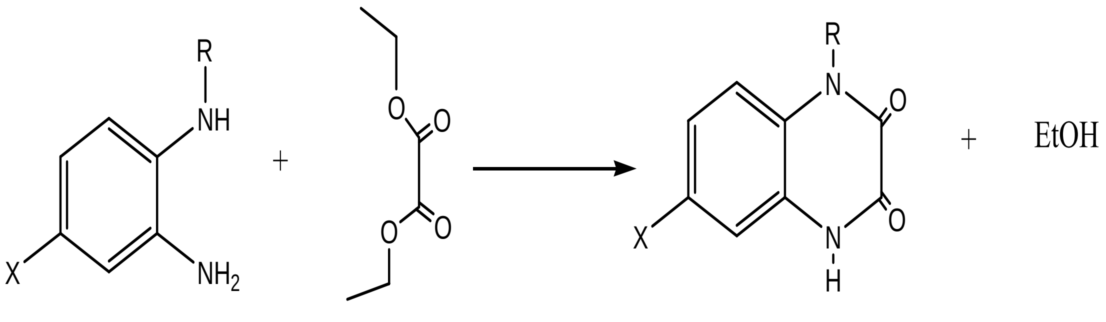


Figure.3 Synthesis of derivatives of Q-2,3-dione

Product	X	R
1	Cl	CH_2CH_2CN
2	CF_3	CH_2CH_2CN
3	H	C_6H_5
4	CH_3	H
5	Cl	H
6	H	H

1,2,3,4-tetrahydroquinoxaline-2,3-dione [19]

Ligands of o-phenylenediamine and its complexes have a variety of applications including biological, clinical and analytical. Earlier work has shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds, and that the coordinating possibility of o-phenylenediamine has been improved by condensing with a variety of carbonyl compounds

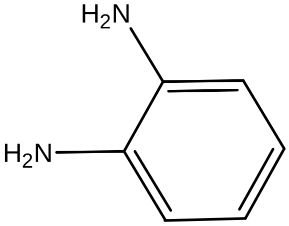


Figure. 4 Structure of o-phenylendiamine

A search through literature reveals that no work has been done on the transition metal complexes of the ligand derived from o-phenylenediamine and quinoxaline-2,3-dione. In this paper I report the synthesis of a new type of tetradentate ligand formed by the condesation of o-phenylenediamin with quinoxaline-2,3-dione in the presence of metal ion[20].

Chemistry of Nickel(II) and Copper(II) metal complexes

I) Nickel (II) complexes

The electronic configuration of the Ni (II) is d^8. Octahedral Ni (II) complexes having $^3A_{2g}$ ground state are expected to have three spin allowed transitions $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_2g \rightarrow {}^3T_{Ig}$ (P) and $^3A_{2g}\rightarrow{}^3T_{2g}$ (F) in the range of 7000-13000, 11000-20000 and 19000-27000cm^1, respectively. In addition to these three transitions, two spin-forbidden transitions $^3A_{2g}\rightarrow{}^1E_g$ and $^3A_{2g}\rightarrow{}^1T_{2g}$ are also observed one at near the second spin-allowed transition and another band between second and third spin-allowed transitions.

Five coordinate nickel (II) complexes have structures, which are generally near to one of the two limiting geometries, namely the square pyramid and the trigonal bipyramid. The electronic ground state of nickel (II) in the five coordinate complexes can be either a spin singlet (low-spine) or a spine triplet (high-spin). Low –spin trigonal bipyramidal nickel (II) species, which exhibit three transitions, namely $^1A_{1\rightarrow}{}^1B_1$, $^1A_{1\rightarrow}{}^1E$ and $^1A_{1\rightarrow}A_2$ lie in the region 15000-18000, 21000-24000 and 27000-29000 cm^{-1}, respectively[21].

The majority of four coordinate nickel (II) complexes are square planar and diamagnetic, while other are pseudo tetrahedral nickel (II) complexes have spectral transitions in the visible region with a much greater intensity than the octahedral ones.Tetrahedral Ni (II) complexes with $^3T_1$ ground state generally exhibit four transitions. They are $^3T_1 \rightarrow ^3A_2$, $^3T_1 \rightarrow ^1E$, $^3T_1 \rightarrow ^3T_1$ (P) and $^3T_2 \rightarrow ^1T_1$ [21]. The band $^3T_1 \rightarrow ^3T_1$ (P) is a strong band of high intensity when compared with others. In square planar nickel (II) complexes, three spin allowed d-d bands corresponding to $^1A_{1g \rightarrow} {}^1A_{2g}$, $^1A_{1g \rightarrow} {}^1B_{1g}$ and $^1A_{1g \rightarrow} {}^1E_g$ transitions are expected. Majority of the square planar nickel (II) complexes exhibit strong absorptions in 15000-25000 and 23000-30000 cm^{-1} regions.

The square planar nickel (II) complexes don't have any absorption band below 10000 cm^{-1}, due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes.

II) Copper (II) complexes

The Cu (II) ion with its d^9 configuration in octahedral and tetrahedral environment is highly susceptible to Jahn-Teller distortion. In tetrahedral arrangement, also Jahn-Teller distortion is operative, in spite of the fact that large spin-orbit coupling constants might produce sufficient splitting of $^2T_2$ ground state. Octahedral complexes without any distortion are expected to have only one d-d absorption band corresponding to $^2E_g \rightarrow ^2T_{2g}$ transition. For distorted octahedral complexes, several weak absorption bands are observed around 1600 cm^{-1} and often a broad band in the near IR region. In the axially elongated tetragonal distortion three absorption bands corresponding to the transitions $^2B_{1g\rightarrow}{}^2A_{1g}$, $^2B_{1g\rightarrow}{}^2B_{2g}$ and $^2B_{1g\rightarrow}{}^2E_g$ are observed.

Tetrahedral complexes are expected to give a single, broad band corresponding to $^2T_2 \rightarrow {}^2E$ transition in the near IR region.

The ground term in the square planar geometry is $2B_{1g}$ and three d-d bands corresponding to the transitions $^2B_{1g\rightarrow}{}^2B_{2g}$, $^2B_{1g\rightarrow}{}^2A_{1g}$ and $^2B_{1g\rightarrow}{}^2E_g$ are observed. In both square planar and tetragonal geometries the transitions are not well resolved. However, in parallel with nickel (II) copper (II) systems with square planar stereochemistry will have no electronic absorption below 10000 cm^{-1}. Similarly tetrahedral copper (II) will absorb primarily in the red and near IR[21].

LITERATURE SURVEY

Transition-metal Quinoxaline Complexe

During a study of the complexes formed between copper(II) compounds and substituted quinoxalines it was found that the stoicheiometry of the product depended on the nature of the substituents in the ligand. The compounds formed between copper(I) compounds and the same ligands are described .

Quinoxaline (Q) , 2-methylquinoxaline (Mq) , and 2,3-dimethylquinoxaline (Dmq) all form complexes of the type Cu_2X,L with copper(I) halides. These are of similar stoicheiometry to those reported for copper(I) complexes with substituted pyrazines. It was suggested that the pyrazine complexes were binuclear, with each pyrazine molecule coordinated to two copper atoms through the two nitrogen atoms, each copper atom being bonded to a halide atom and a nitrogen atom of the organic ligand. If these quinoxaline compounds have a similar structure to that suggested, then molecular models show that no appreciable steric hindrance will be involved. Cu,Br,Q, Cu,I,Q, and the complexes containing substituted quinoxalines were prepared by direct synthesis from the copper(I) halide and the ligand in either water or 50% aqueous ethanol both containing the sodium, potassium, or calcium halide. Attempts to prepare Cu,Cl,Q by this method gave a mixture of yellow, orange, and brown products, but this complex was obtained by reduction of an aqueous solution of the copper(II) complex with hypophosphorous acid. Only indefinite products were obtained with 2,3-diphenylquinoxaline. Molecular models show that this is not due to a steric effect and therefore may be due to the weaker basicity of this ligand. The insolubility of the complexes in all solvents except mineral acids prevented a study of their properties in solution. Thermogravimetric analyses show the complexes to decompose by loss of the organic ligand. The residue, in the case of the quinoxaline complexes, was identified as the copper(I) halide by its X-ray powder photograph. Many bisquinoline-metal(II) halides have been shown to decompose in the same way to leave the anhydrous metal halide[22].

Bis(quinoxaline-2,3-dithiolato-*S*,*S*')nickel(II)

The complex, [Ni($C_8H_4N_2S_2$)$_2$], is a mononuclear nickel(II) complex in which the coordination about the Ni atom to the four S atoms of the two quinoxaline-2,3-dithiolate (qt) ligands is slightly distorted square planar. The molecule has a crystallographic inversion centre[23].

Structural elucidation of manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of a new multidentate dihydrazino quinoxaline derivative

Manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of a new multidentate oxygen-nitrogen donor, *bis*(*N*-salicylidene)-2,3-dihydrazino-1,4-quinoxaline (H_2BSDHQ) were prepared and characterized by elemental analysis, conductance, thermal, spectral and magnetic data. H_2BSDHQ deprotonates to give a dibasic ONNO donor set in a trivalent iron(III) complex, which binds to the divalent metal ions in a bis-tridentate fashion, using two monobasic ONN donor sets, and resulting in polymeric complexes. Octahedral geometries are proposed for all these complexes, and preliminary studies show that they possess potential antimicrobial activity [24].

Metal complexes of a new ligand derived from 2,3-quinoxalinedithiol and 2,6-bis(bromomethyl)pyridine

The synthesis of a new ligand containing quinoxaline and pyridine subunits is described. The reaction of 2,3-quinoxalinedithiol with 2,6-bis(bromomethyl)pyridine leads to the isolation of bis(2-thio-3-mercaptoquinoxalino)-2,6-dimethylpyridine (**L**), which is a macrocyclic ligand precursor.

The reaction of transition metal ions with **L** gives [M(L)X]X complexes (where M = Mn(II), Co(II), Cu(II), Ag(I), Zn(II), or Cd(II), and X = Cl or Br). The compounds were characterized by physical and spectroscopic measurements which indicated that the ligand is probably acting as a pentadentate NS_4 chelating agent.On the assumption that four sulfur atoms and one nitrogen atom of the ligand are coordinated to the metal, as seems likely from an inspection of molecular models, it follows that the complexes would be five coordinate with respect to the ligand. As the ligand is potentially pentadentate, it is quite feasible that the metal ions are six coordinate with one halide ion at the vertices of an octahedron. When the energy of the complexes was minimized, using MM2 calculations, reasonable bond distances and bond angles around the metal were obtained, suggesting that an octahedral or distorted octahedral configuration around the metal is possible. The possibility of a square pyramidal configuration around the metal has been discarded from the conductivity measurements, which show that the complexes are 1:1 electrolytes. Despite the crystalline nature of the products none proved suitable for X-ray structure determination[25].

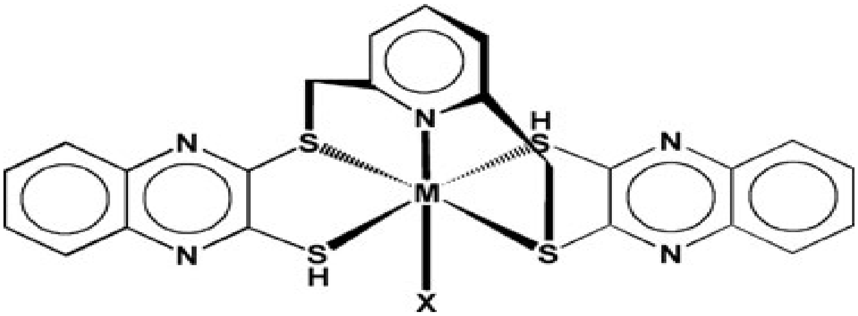


Figure.5 Suggested structure for the metal complexes of a new multidentate dihydrazino quinoxaline derivative

New Dinuclear Transition Metal Complexes with the [M2(μ-dhbq)]n+ Core and 2-(2_-Pyridyl)quinoxaline (L) as a Terminal Ligand: Preparation and Characterization (dhbq2 = the Dianion of 2,5-Dihydroxy1,4-benzoquinone; M = AgI, MnII, CoII, NiII, CuII, RuII, P dII, FeIII, RhIII; n = 0, 2, 4)

Synthetic procedures are described that allow access to the new complexes $[Mn_2(dhbq)L_2(H_2O)_4$,$[Fe_2(dhbq)L_2(H_2O)_4](NO_3)_4{\cdot}6H_2O$,$[Co_2(dhbq)Cl_2L_2(H_2O)_2][Ni_2(dhbq)Cl_2L_2(H_2O)_2]$,$[Cu_2(dhbq)Cl_2L_2(H_2O)_2]$,$[Ru_2(dhbq)L_2(H_2O)_4](ClO_4)_2$,$[Rh_2(dhbq)Cl_2L_2(H_2O)_2]Cl_2{\cdot}_2H_2O$, $[Pd_2(dhbq)L_2]Cl_2{\cdot}5H_2O$ and $[Ag_2(dhbq)L_2]$, where dhbq2 is the dianion of 2,5-dihydroxy1,4-benzoquinone and L is the biheteroaromatic ligand 2-(2-pyridyl)quinoxaline. The new complexes were characterized by elemental analyses and by a variety of physical and spectroscopic techniques. Dinuclear structures are assigned for the complexes in the solid state. The two metal ions are bridged by the bischelating dhbq2 ion, while L behaves as a bidentate chelate with the 2-pyridyl nitrogen and the nearest quinoxaline nitrogen atom as the ligand atoms. The metal ion coordination geometries are octahedral, tetrahedral or square planar[26].

Dichlorodiquinoxalinezinc(II)

In complex [$ZnCl_2(C_8H_6N_2)_2$], two quinoxaline ligands are mono-coordinated to a Zn^{II} atom. With two chloride ions, they form a distorted tetrahedral coordination

geometry. The combination of π stacking interactions between inversion-related quinoxaline ligands and the coordination to zinc creates layers parallel to the *bc* plane. [27]

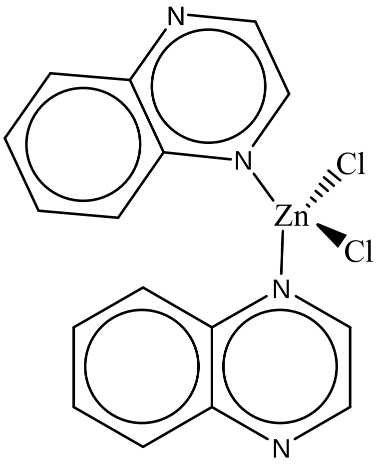
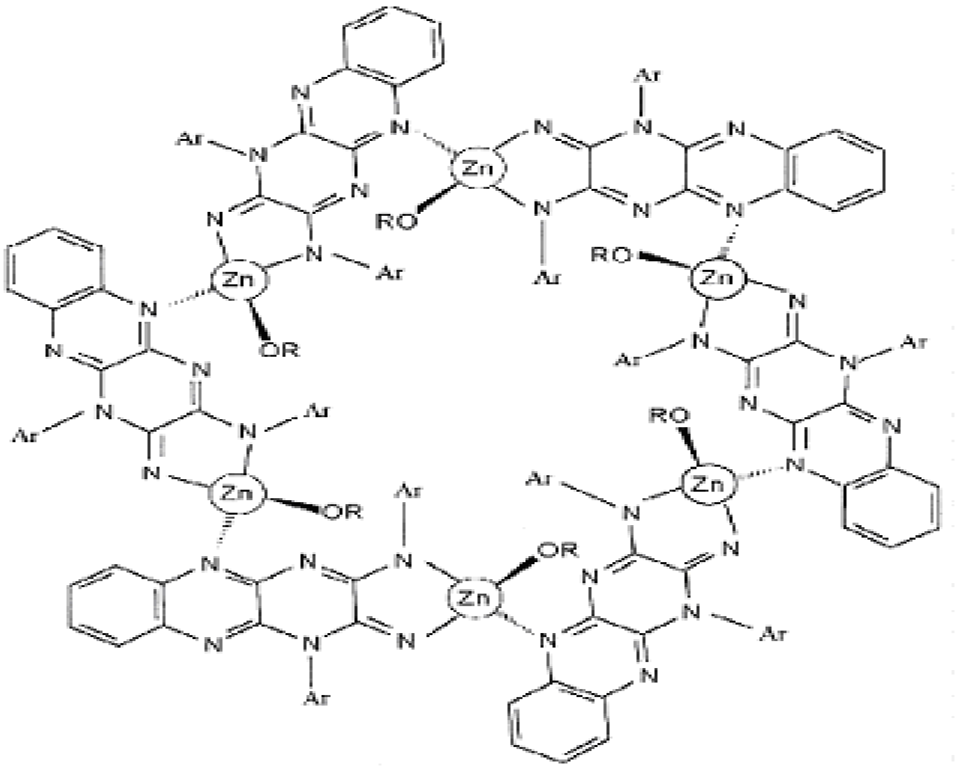


Figure.6 Structure of $ZnCl_2(C_8H_6N_2)_2$ complex

New Derivatives of Quinoxaline- Synthesis, Complex Formation and their Application as Controlling Ligands for Zinc Catalyzed Epoxide-CO^2- CO polymerization

The tricyclic derivatives containing an additional quinoxaline ring which, in principle, could also coordinate with the zinc ion. The 1H NMR spectrum of the complex showed that only one phenolate group coordinates to the Zn atom, thus indicating that the quinoxaline acts as a monoanionic ligand. This was confirmed by X-ray crystallography . Rather surprisingly, the complex exhibits a 36-membered macrocyclic ring system composed of six monomeric units. All zinc ions are

tetrahedrally coordinated with the quinoxaline ligand bridging two zinc cations. Both the imine nitrogen N2 und the amide nitrogen N1 in the quinoxaline binds to one zinc center to form a five-membered chelate ring. In addition, the amine nitrogen N5 acts as a bridging donor to connect two zinc centers. This results in the formation of an unusual macrocyclic system in which six zinc ions in a chair conformation are linked by six quinoxaline ligands (Fig.) [28]



. **Figure.7 Complexes of macrocyclic zinc ion linked by quinoxaline ligand**

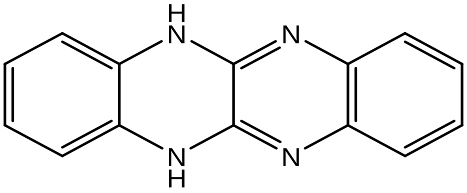
Objectives and the scope of the present investigation

Literature survey reveals that the metal complexes of N-heterocyclics like quinoxaline derivatives has got a great application in biomedical aspects, such as antibacterial, antifungal, anti HIV agent, and anti diabetic agent.

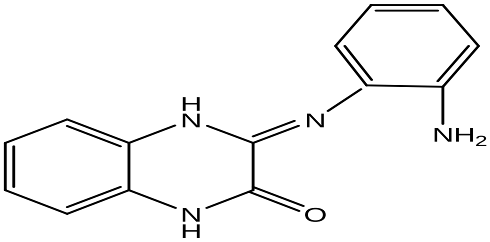
In view of the wide rang of applications and the potential metal binding abilities of N-hetrocyclics, it has been aimed to synthesize a new ligand derived from orthophenylenediamine and quinoxaline-2,3-dione, and study and characterization of its metal complexes.

The expected ligand which would be derived from the condensation of orthophenylenediamine and quinoxaline-2,3-dione could be as follows.

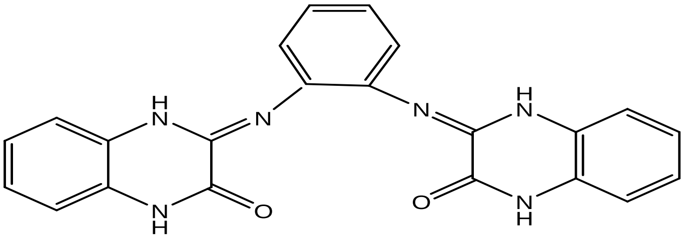
A,

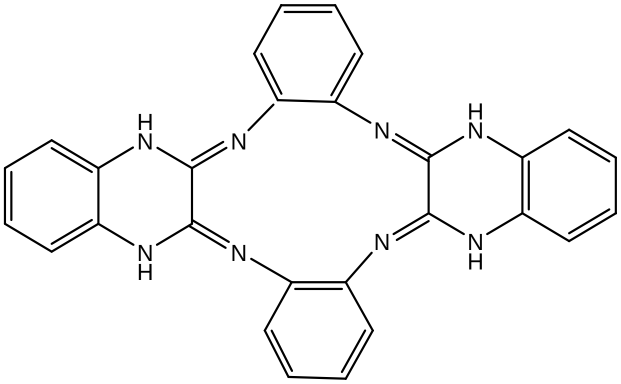


B,



C,





D,

In general ligand A is not a good chelating system, ligand B is likely to be tridentate and can be neutral, dibasic or monobasic due to NH deprotonation, ligand C is expected to be tetradentate and the basicity can not be predicted, ligand D is a macrocyclic tetradentate. And it will be interesting to study which system A,B,C or D will be preferably formed in the presence of metal ion.

The investigation is aimed at the synthesis and characterization of Cu(II) and Ni(II) complexes using quinoxaline-2,3-dione and o-phenylenediamine.

EXPERIMENTAL

Chemicals and solvents

All chemicals used were of analytical grade. Metal salts $NiCl_2$ (from BDH), $CuCl_2.2H_2O$ (GRAVE), orthophenylene diamine and oxalic acid (from Riedel-deHaen). Solvents like MeOH, DMSO, EtOH, DMF, 4N HCl, 0.5 M NaOH

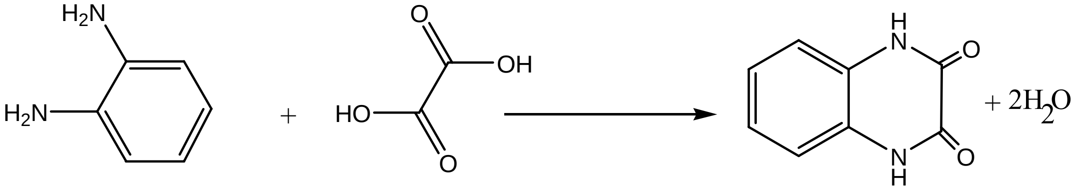
Instruments and Experimental conditions

Melting point determination was performed using LEICA GALEN ™ (III) compound microscope as well as Electro thermal melting point apparatus. ^{1}H NMR and ^{13}C NMR analysis using BRUCKER 400 ultra shielded NMR Instrument. Results were expressed in parts per million down fielded from teramethylsilane as internal reference, in deuterated dimethylsulphoxide. The Uv-Vis spectras were recorded using SPECTRONIC GENESYS 2pc using mixture of DMF and ethanol(3:1).The metal content were estimated by using BULK SCIENTIFIC ATOMIC ABSORPTION SPECTROPHOTOMETER MODEL 210 VGB. IR spectroscopy was measured using Perkin Elmer BX between the range of 400-4000 nm using KBr discs as reference compound. The conductivity of the solution of the metal complexes was measured by EC 214 Bench conductivity meter (Hanna Instrument). Magnetic susceptibility was measured using MSB Auto, Sherwood. Elemental analysis of C, H, and N was done using Exter Analytical CE 440 EA.

Synthesis

Preparation of quinoxaline-2,3-dione

Orthophnylenediamine (60 mmol), oxalic acid dihydrate (60 mmol) and 4N HCl (0.036 lit) were refluxed for half an houre. A crystaline solid appeared which was cooled, collected, washed with water, methanol and dried. The target compound was dissolved in alkali and then acidified with HCl to obtain a pure product. Yield 57%, m.pt > 350 ^{o}C. [29]



Orthophenylenediamine oxalic acid quinoxaline-2,3-dione

Figure.8 Preparation of Q-2,3-dione

Preparation of the ligand (L)

Attempts to prepare the ligand was done with the procedure as follows. Quinoxaline-2,3-dione (7.28 mmol) orthophenylenediamine (3.64 mmol) and 12 ml of ethanol were heated for 3 houres. A crystalline solid appeared which was coold, collected, washed with ethanol, and dried. Yield 70%, m.pt > 350 ^{o}C. The pssible products of this reaction are as follows.

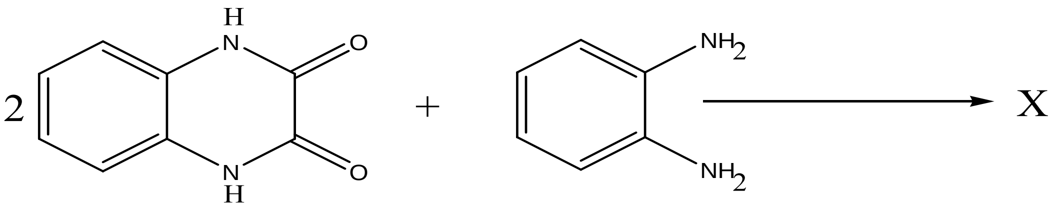
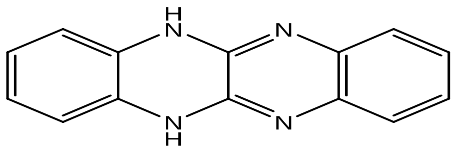


Figure.9 Reaction of Q-2,3-dione with orthophenylenediamine

Where X = Ligand 1, 2, 3 or 4



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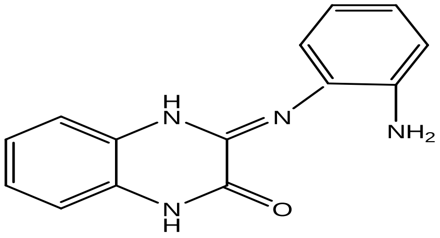

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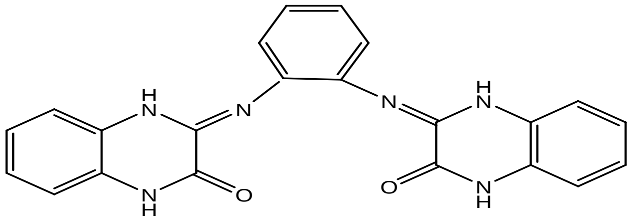

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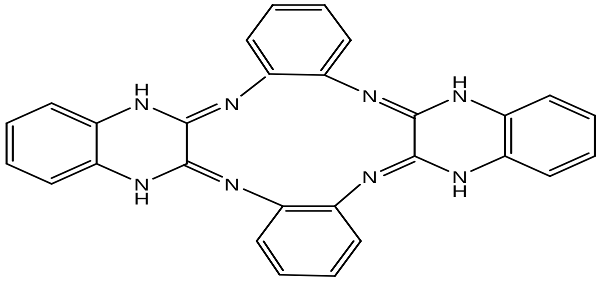


4,

As the structural studies indicated that non of this compounds were formed, the synthesis of the metal complexes was subsequently done using template method in which quinoxaline-2,3-dione and o-phenylenediamine were reacted in the presence of metal ion.

Preparation of the complexes using template procedure

A, Preparation of Ni-L complex

Anhydrous nickel chloride ($NiCl_2$) (0.526 mmol), mixture of o-phenylenediamine and quinoxaline-2,3-dione (expected ligand sample) (0.526 mmol) were adissolved in 20 ml ethanol, and refluxed for 11 hours. The final product was light green in color. Yield 40%, m.pt > 370

B, Preparation of Cu-L complex

Dihydrated copper chloride ($CuCl_2.2H_2O$)(0.3947 mmol), mixture of o-phenylenediamine and quinoxaline-2,3-dione (expected ligand sample)(0.3947 mmol) in 20ml ethanol, and refluxed for 11 hours. The final product was yellow in color. Yield 43%, m.pt > 330

RESULTS AND DISCUSSION

The Cu-L and Ni-L complexes were obtained as powders with high melting points and low solubility in organic solvents. The Nickel(II) and Copper(II) complexes are colored . They are air and moisture stable solids; both complexes are soluble in a mixture of DMF and ethanol (3:1). The solubility in other solvents are listed in table-1. The conductivity values of the complexes measured in DMF and ethanol at room temperature fall in the range that indicates both are non-electrolytes. The chloride test indicates the presence of chlorine in Ni-L but not in Cu-L complexes. Attempts to prepare the ligand (bQxDB) were unsuccessful and were confirmed by IR, NMR and elemental analysis.

TABLE-1. The solubility of complexes in different solvents

Solvent	Ni-L Complex	Cu-L Complex
Water	Insoluble	Insoluble
Ethanol	Partially Soluble	Partially soluble
DMSO	Partially soluble	Partially soluble
DMF	Insoluble	Soluble
Acetonitrile	Insoluble	Soluble
Nitro methane	Insoluble	Soluble
1,4-Dioxane	Insoluble	Partially soluble

Conductivity data

The low conductance of all the complexes measured in 10^{-3}M solutions of DMF and ethanol supports the non-electrolytic nature of the metal complexes.

TABLE-2. Conductivity values of complexes

Complex	Solvent	Molar conductance $Ohm^{-1}cm^{2}mol^{-1}$	Type of electrolyte
Ni-L complex	Ethanol	32	Non electrolyte
Cu-L complex	DMF	30	Non electrolyte

Magnetic susceptibility

Effective magnetic moments were calculated using the formula $\mu_{eff} = 2.824(X_M T)^{1/2}$, where X_M is the molar susceptibility. The Cu(II)-L complex has a magnetic moment of 1.734 BM, indicating that it has one unpaired electron and consistent with square planar geometry around the central metal ion[30]. The Ni(II)-L complex has a magnetic moment of 2.977BM, typical of d^8 systems with two unpaired electrons and is in agreement with octahedral structure [31,32] since

magnetic moments of octahedral Ni(II) complexes are thus expected to be well in excess of the spin only value, and typically lie in the range 2.9- 4BM[33]. The observed value of magnetic moment for Ni-L complex were higher than the spin

only value which indicates the presence of orbital contributions, that arise because of the mixing of ground state orbitals with higher orbitals of degenerate state.

TABLE-3 Analytical Data of Metal Complexes

Compound	**Color %Yield**	**M.p**	**%Found (Calcd)**				μ_{eff} **(BM)**
			C	H	N	M	
Q-2,3-dione	White 80	>370	- (59.259)	- (3.703)	- (17.283)	-	-
Ni-L complex	Light green 40	>370	- (51.917)	- (3.539)	- (16.519)	- (16.602)	2.977
Cu-L complex	Yellow 43	>330	- (57.391)	- (3.478)	- (18.260)	12.535 (13.913)	1.734

IR spectra

The IR spectroscopy can provide valuable information as to whether or not reaction has occurred. In order to study the binding mode of the ligand to the metal ion in the complexes, the IR spectrum of the free ligand must be compared with the spectra of the complexes. But this was not possible since both the ligand and the dione show identical IR spectra, which consequently confirms the ligand was not formed. The IR spectrum of the dione shows three characteristic bands at 3250 ν (NH), 1681 ν(C=O) and 1614 cm^{-1} νδ (N-H) amide vibrations. In the complexes the

C=O band is found at the lower values ($\Delta\nu=34^{-1}$), this indicates the binding of oxygen with the metal during complexation.

The IR data of the complexes studied are presented in Table 4. IR spectrum of the complexes shows bands at 3250 ν (NH) [34-36], 1650 ν(C=O), 1500 ν(C=C) [30], 1457 ν(N=N) [37-40] and 1614 cm^{-1} νδ (N-H) [31] amide vibrations. The IR spectra of all the complexes show two absorption bands in the far infrared region, 477-489 cm^{-1} and 555-591 cm^{-1}, which are assignable to ν (M-O) and ν (M-N) vibrations respectively. The appearance of C=N stretching frequency and disappearance of asymmetric and symmetric stretching bands due to NH of o-phenylenediamine clearly indicates the condensation of the reactants o-phenylenediamine and quinoxaline-2,3-dione in the presence of metal ions occurs.

TABLE-4 Infrared Data of Dione and Metal Complexes

Compound	ν NH	ν C=O	ν C=N	New bands on fingerprint region
Q-2,3-dione	3450-3400	1682	-	-
Ni-L complex	3450-3300	1653	1457	489,591,654,787, 1457
Cu-L complex	3450-3250	1648	1458	477, 555, 648, 719, 772,1458

Electronic Spectra

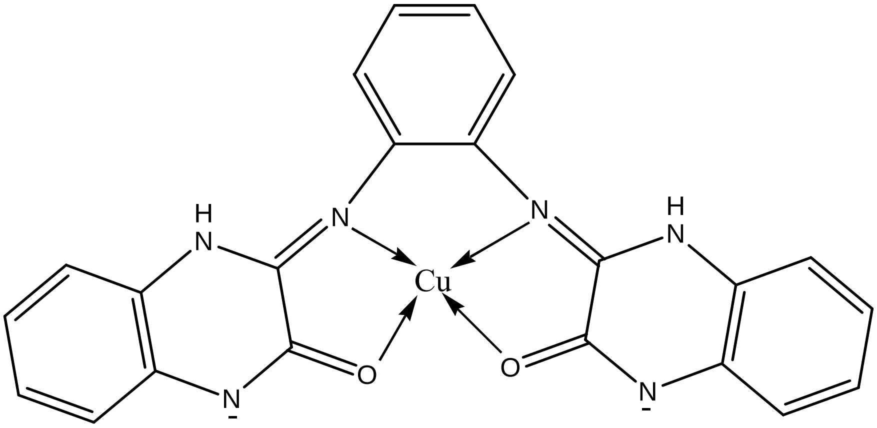
The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectra measurements were used for assigning the stereochemistries of metal ions in the complexes based on the positions and number of d-d transition peaks. The electronic absorption spectra of the Cu(II) and Ni(II) complexes were recorded at room temperature using DMF as a solvent. The Ni-L and Cu-L complex shows broad band at 409 and 440nm respectively due to n→π* transition. And also shows bands at 274 and (313-349) in both complexes due to C=O and N=C π→π* transition. However, the expected d-d transitions have not been resolved under the experimental condition.

TABLE-5 Electronic Spectral Data of Metal Complexes

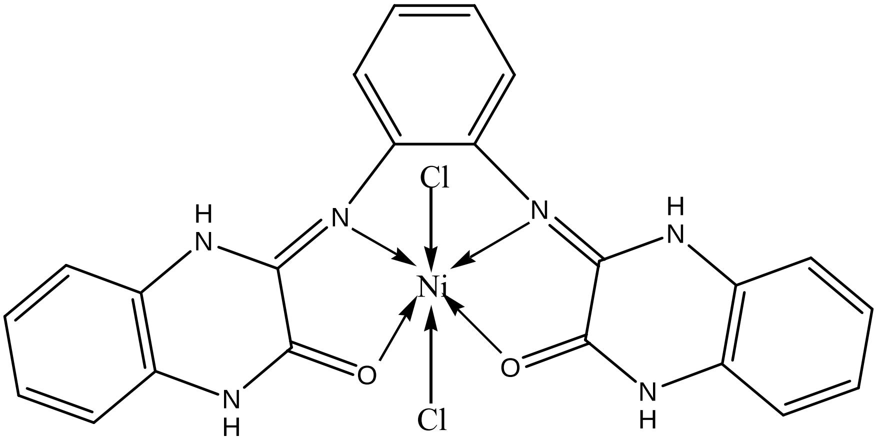
Complex	**π→π* Λ(nm)**	**π→π* Λ(nm)**	**n→π* Λ(nm)**
Ni-L complex	274	313	409
Cu-L complex	274	349	440

Conclusion

As the expected ligand could not be successfully synthesized, the modified route to obtain metal complex through template method was followed. The ligand which was formed in the presence of metal ion has several potential donor atoms, but due to steric constraints the ligand can provide a maximum of four donor atoms at any one time for coordinating to a metal. On assumption that two oxygen atoms and two nitrogen atoms of the ligand are coordinated to the metal and hence the complexes are four coordinates with respect to the ligand. As the ligand is potentially tetra dentate, it is quite feasible that the Ni-L complex is six coordinate and Cu-L complex is four coordinate as shown below. The absence of C=N stretching frequency on the IR spectrum of the expected ligand sample ruled out the formation of the ligand (N,N'-bis(3-quinoxaline-2-one)-1,2-diaminobenzene) but it was formed in the presence of metal salts by undergoing condensation between orthophenylenediamine and quinoxaline-2,3-dione.The complexes were characterized on the basis of IR, Uv-Vis, magnetic susceptibility and conductivity measurements.



Suggested structure for Cu complex



Suggested structure for Ni complex

Figure.10 Structure of Cu(II) and Ni(II) complexes

References

1. Kumagai, Tsutomu; Tomura, Masaaki; Nishida, Jun-ichi; Yamashita,Yoshiro Tetrahedron Lett. 44, 6845–6848 (**2003**)
2. Cui, Yong Tang, Xiu-Bo Shao, Chang-Xing LI, Ji-Tai SUN, Wen-Hua Chinese Journal of Chemistry, **2005**, *23*, 589—595
3. Jiangning Ji and Kee-In Lee Journal of the Korean Chemical Society **2005**, Vol. 49, No. 2
4. Z. Wu, N. J Ede, Tetrahedron Lett., 42, 8115-8118, **2001**
5. J.Z. Wu, Z.G. Xu, Y. Li, J.Chem.Crystall., 32, 75-80, **2002**.
6. A.M. Thomas, M. Nethaji, S. Mahadevan, J.Inorg.Bioch., 94, 71-178, **2003**.
7. A. Esquer, S. B. Kumar, M. Font-Bardia, Inorg.Chim.Acta, 286, 62-66, **1999**.
8. B.K. Santra, P.A.N. Reddy, G. Neelakanta, J.Inorg.Chem., 89, 191-196, **2002**.
9. O. Hampela, C. Rodeb, D. Waltherb, R. Beckerta and H. Görlsb **2002** Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com
10. http://www.bentham.org/cmc/contabs/cmc
11. Laure Tomaszewski , Zhifeng Ding , David J. Fermın , Helena M. Cac¸ote , Carlos M. Pereira , Fernando Silva , Hubert H. Girault Journal of Electroanalytical Chemistry, 453 (**1998**) 171–177

12. Nishida, Jun-ichi; NARASO; Murai, Shiro;Fujiwara, Eiichi; Tada, Hirokazu; Tomura,Masaaki; Yamashita, Yoshiro *Org. Lett.* **6**, 2007– 2010 (**2004**)
13. Cheeseman, G. W. H.; Cookson, R. F. Condensed Pyrazines. In The Chemistry of Heterocyclic Compounds; vol. 35, Weissberger, A.; Taylor, E. C. series editors; John Wiley & Sons, Inc.: New York, **1979**; pp.78-111.
14. Jarrar, A. A.; Fataftah, Z. A. Tetrahedron, **1977**, **33**, 2127.
15. Patai, S. Chemistry of the Amino Group; Interscience: New York, 1968; Patai, S. The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives; Wiley: New York, **1982**
16. Phillips, M. A. J. Chem. Soc. **1928**, 2393-2399.
17. Obafemi, C. A.; Pfleiderer, W. Helv. Chim. Acta. **1994**, *77*, 1549-1556.
18. Piguet, C.; Bocquet, B.; Hopfgartner, G. Helv. Chim. Acta. **1994**, *77*, 931-942.
19. Shu-Kun Lin Molecules **1996**, *1*, 37 – 40
20. N. Raman, Y. Pitchaikani Raja and A. Kulandaisamy, Indi. Chem. Sci, **2001**, Vol. 113, No.3, pp 183-189
21. D. Sandhaya Rani, Ph.D. Thesis "synthesis and structural studies of transition metal compounds derived from multidentate 2,3-Distrubited Quinoxalines", submitted to Osmania university, **1995.**

22. a, D. A. Dows, A. Haim, and W. K. Wilmarth, J. Inorg. Nuclear Chem., **1961**, **21,** 33.

    b, D. H. Brown, R. N. Nuttall, and D. W. A. Sharp, J. Inorg. Nuclear Chem., **1964**,**26,** 1151.

23. J.Acta Cryst. (**2003**). **59**, 496-498

24. Dikonda S. Rani, Parupalli V. A. Lakshmi and Vuppalapati Jayatyagaraju, Department of Chemistry, Osmania University, 500-700 Hyderabad, India, January **1993**

25. J. R. AnaconA, Thais Martell and Ivonne Sanchez J. Chil. Chem. Soc. v.50, **2005**

26. Sahar I. Mostafa, Spyros P. Perlepes, and Nick Hadjiliadis Z. Naturforsch. 56b**,** 394-402 **(2001)**

27. B. M. E. Markowitz, M. M. Turnbull and F. F. Awwadi Acta Crys, (**2006**). 62, 1278-1280

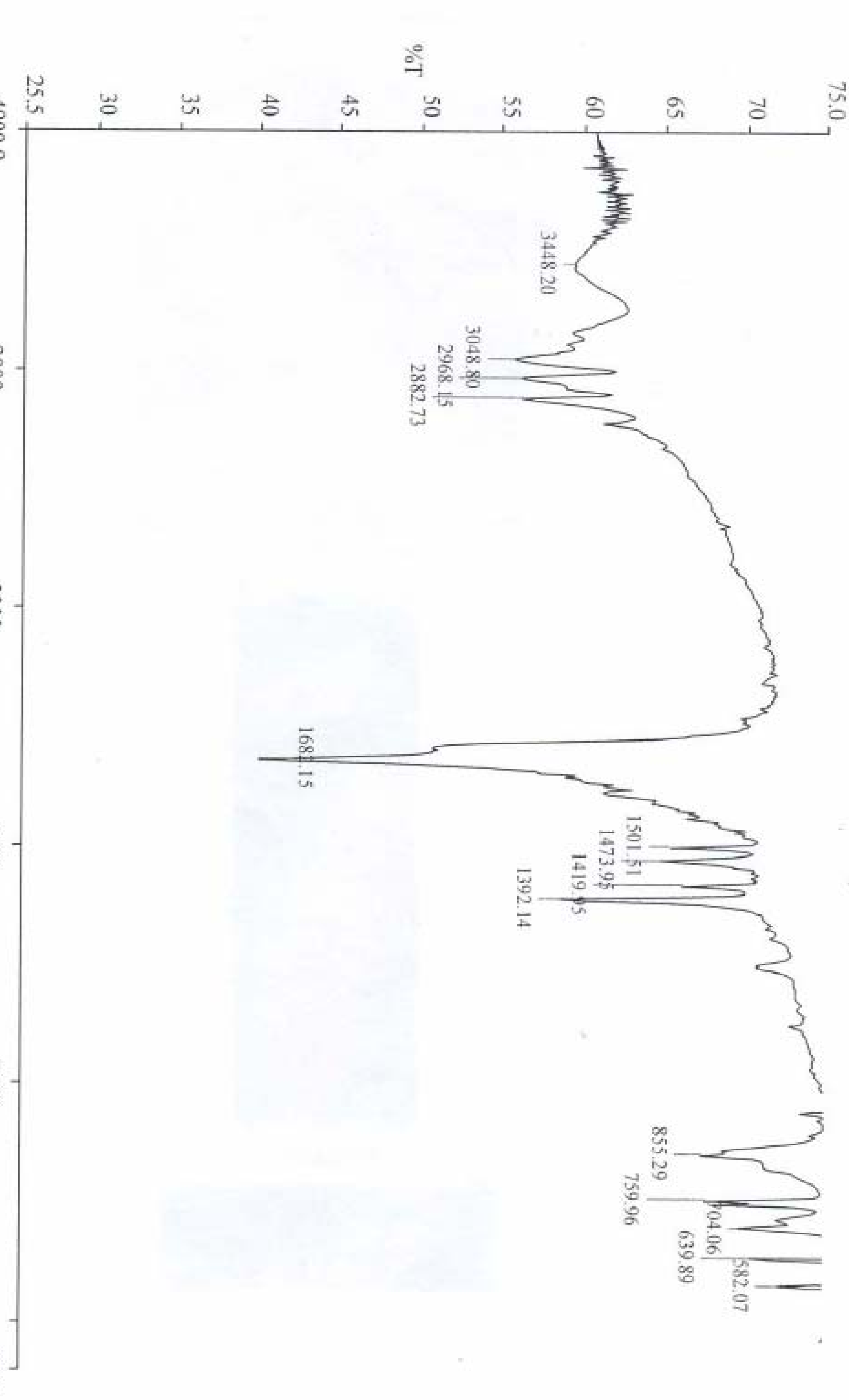
28. O. Hampel, C.Rode, D. Walther, R. Beckert and H. Gorls, Z. Naturforsch, 57b, . 946-956 (2002)

29. Mulu Gebre, V.J.T. Raju and Negussie Retta Department of chemistry, Addis ababa University, **2000**

30. L.Oprean, A.Comsa, L.David, O.Crisan, M.Coman and M. Neamtu, Studia University, Special Issue, **2001**

31. Chirantan Roy Choudhury, Subrata Kumar Dey, Sutapa Sen, Bappaditya Bag, Samiran Mitra, and Volker Gramlich, Z. Naturforsch. 57 b, **2002**,1191-1194
32. N. Raman, V. Muthuraj, S. Ravichandran and A. Kulandaisamy, Indian. Chem. Sci, Vol.115, No. 3, **2003**, pp 161-167
33. Mehmet Sonmez, Turk. J. Chem, Vol. 25, **2001**, 181-185
34. Fouzia Rafat, M.Y. Siddiqi and K.S.Siddiqi, J.Serb. Chem. Soc, Vol.69 (8-9), pp 641-649, **2004**
35. Mohammad Shakir, Yasser Azim, Hamida T. N. Chishti, Nishat Begum, Poonam Chngsubam, and Mohammad Y.Siddiqi, J. Braz. Chem. Soc. Vol. 17. No.2 Mar./Apr. **2006**
36. Frantisk Brezina, Martin Biler and Richard Pastorek, Department of Inorganic and Physical Chemistry, Palacky University, May 31. **1998**
37. H.Kara, Y. Elerman, and A. Elmali, Z. Naturforsch. 58b, 955-958 (**2003**)
38. Chullikkattil P. Pradeep, Panthapally S. Zacharias and Samar K. Das, J. Chem. Sci., Vol.117, No.2, March **2005**, pp 133-137
39. Cezar Spinu and Angela Kriza, Acta Chem. Slov. **2000**, 47, 179-185
40. Srecko R. Trifunovic, Zorica Markovic, Dusan Sladic, Katarina Andjelkovic, Tibor Sabo and Dragica Minic, J. Serb. Chem. Soc. 67(2)115-122(**2002**)

APPENDIX



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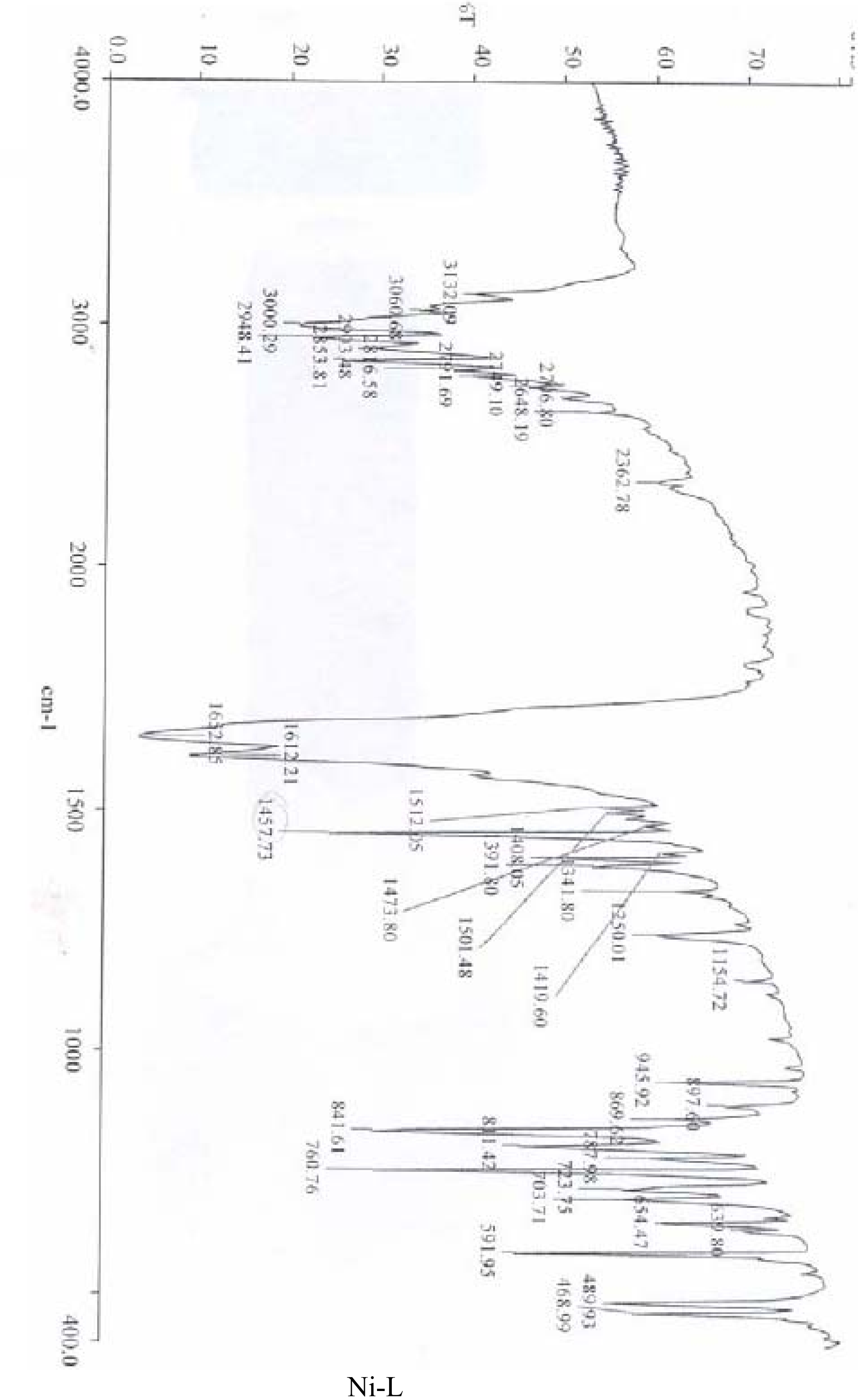
Q-2,3-dione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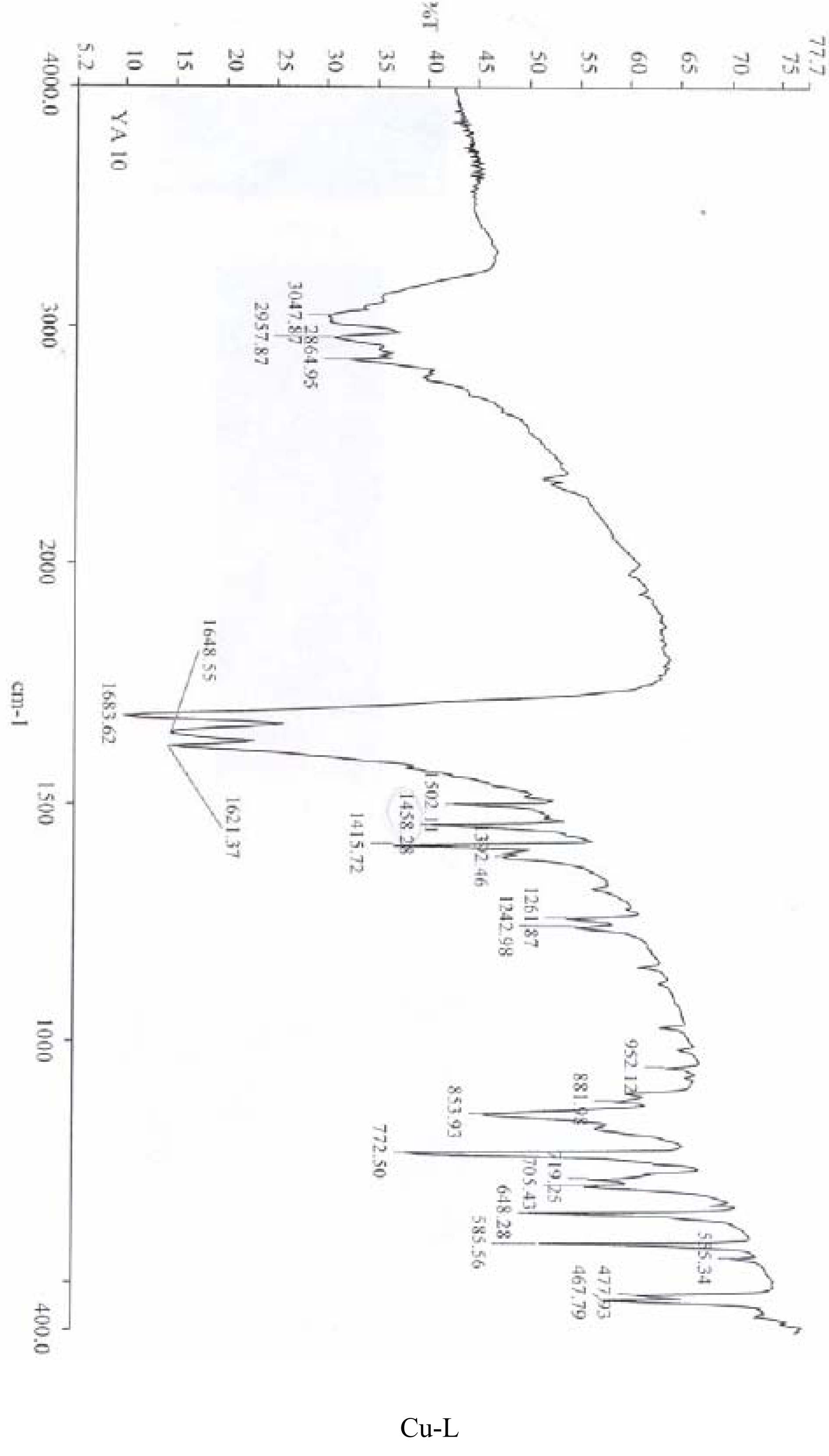
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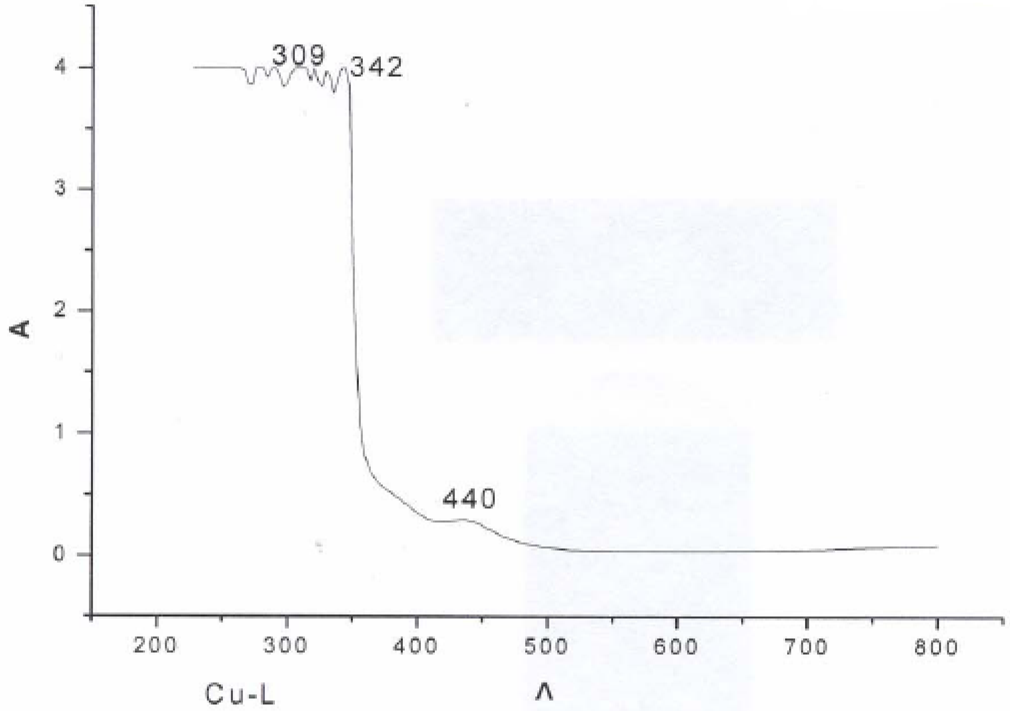
Cu-L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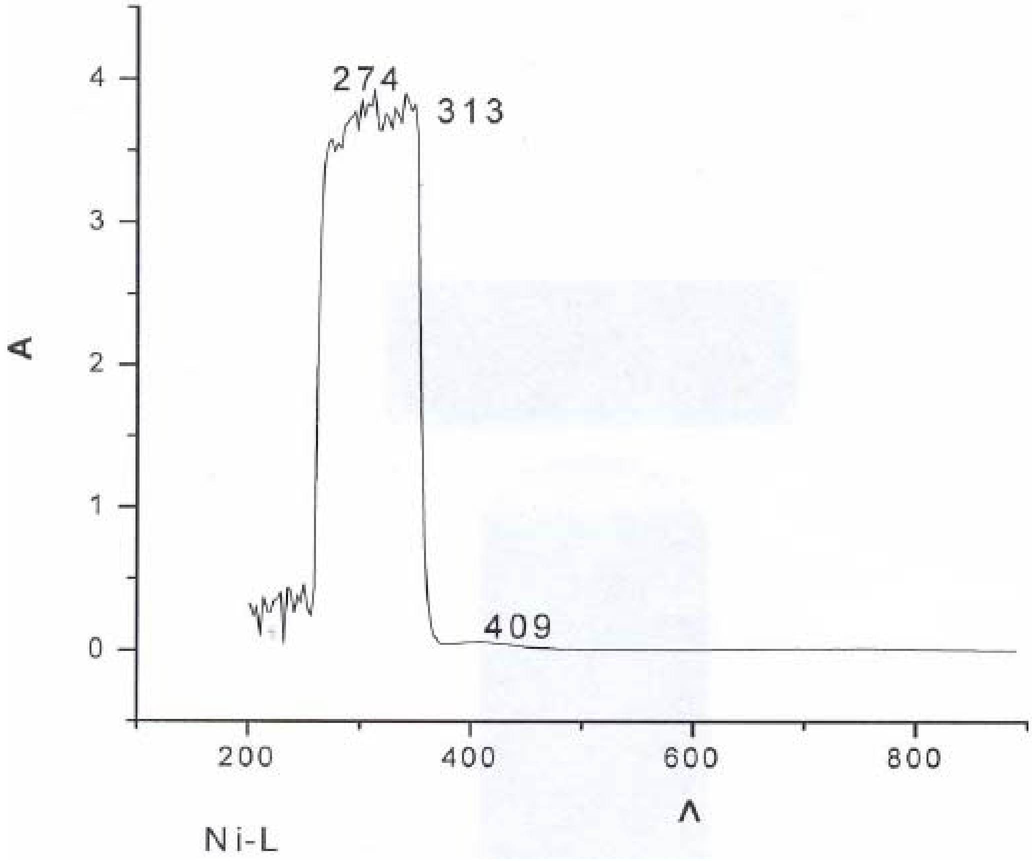
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Ni-L

DECLARATION

I, the undersigned, declare that this project is my original work and has not been presented for a degree in any other university and that all the sources of materials used for this project has been duly acknowledged.

Name: Yosef Alemayehu

Signature: ______________

This project has been submitted for examination with my approval as university advisor.

Name: 1. Prof. V.J.T. Raju, __________________

2. Dr. Yonas Chebude, __________________

Place and Date of Submission: Department of Chemistry
Addis Ababa University
JULY 2006