ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
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Graduate Project (Chem.774)

SYNTHESIS AND CHARACTERIZATION OF TRIMELLITIC ANHYDRIDE BASED PHTHALOCYANINE METAL COMPLEXES

By: Fitsum Bulto

June 2010

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A Project work presented to the School of Graduate Studies,
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SYNTHESIS AND CHARACTERIZATION OF TRIMELLITIC ANHYDRIDE BASED MACROCYCLIC- PHTHALOCYANINE METAL COMPLEX

BY
Fitsum Bulto

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To

My Mom
WorkituDadi

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List of abbreviations and symbols

DMSO	Dimethylsulfoxide
THF	Tetrahydrofuran
Pc	Phthalocyanine
TCPc	Tetracarboxy phthalocyanine
MPc	Metallophthalocyanine
TMA	Trimellitic anhydride
UV-vis	Ultraviolet-visible region
AAS	Atomic absorption spectroscopy
B.M.	Bohr Magneton
M.pt	Melting point
Λ_M	Molar conductance
χ_g	Gram Susceptibility
χ_m	Molar Susceptibility
μ_{eff}	Effective magnetic moment
TLC	Thin layer chromatography
Ω	Ohm
ppm	Parts per million
^{O}C	Degree centigrade
%	Percentage
cm	Centimeter
nm	Nanometer

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Abstract

A wide range of applications of phthalocyanine complexes which ranges from medical to industrial makes them interesting research area now days. Their properties can be tuned by introducing substituents on the periphery or/and the central metal. On the basis of these; Copper (II) phthalocyanine tetrcarboxylic acid and Ni (II) phthalocyanine tetracarboxylic acid; have been synthesized by template method of synthesis from trimellitic anhydride and urea in the presence of ammonium molybdate catalyst in high boiling solvent nitrobenzene. Both complexes were characterized on the basis of molar conductance, magnetic susceptibility and UV-Vis spectra analysis. The UV-Vis absorption spectra shows B(soret) and Q bands which are characteristic absorption spectra of phthalocyanine complexes. The magnetic susceptibility result indicates that, the synthesized Ni(II) complex is not square planar, but octahedral.

Keywords: phthalocyanine, tetracarboxy metallophthalocyanine, template synthesis

1. INTRODUCTION

1.1. Historical Background

The phthalocyanines were one of the earliest classes' of synthetic macrocyclic tetraamines discovered [1].The word phthalocyanine is derived from the Greek terms for naphtha (rock oil) and for cyanine (dark blue). The term was first used by R. P. Linstead in 1933 to describe a class of organic dyes, whose colors range from reddish blue to yellowish green [2].

Phthalocyanine (Pc) was first synthesized in 1907 by Braun and Tschernak as a byproduct of the preparation of *o*-cyanobenzamide from phthalimide and acetic anhydride. However, this discovery was of no special interest at that time. In 1927, de Diesbach and von der Weid prepared CuPc in 23% yield by treating *o*-dibromobenzene with copper cyanide in pyridine. In 1930-1940, Linstead et al. elucidated the structure of phthalocyanine (H_2Pc) and its metal complexes. The basic structure is represented by phthalocyanine itself:

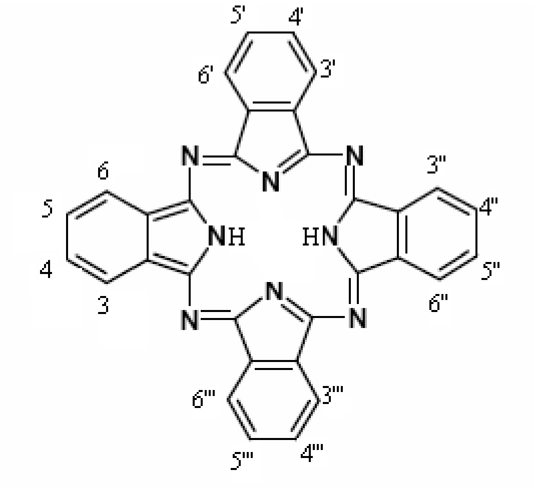
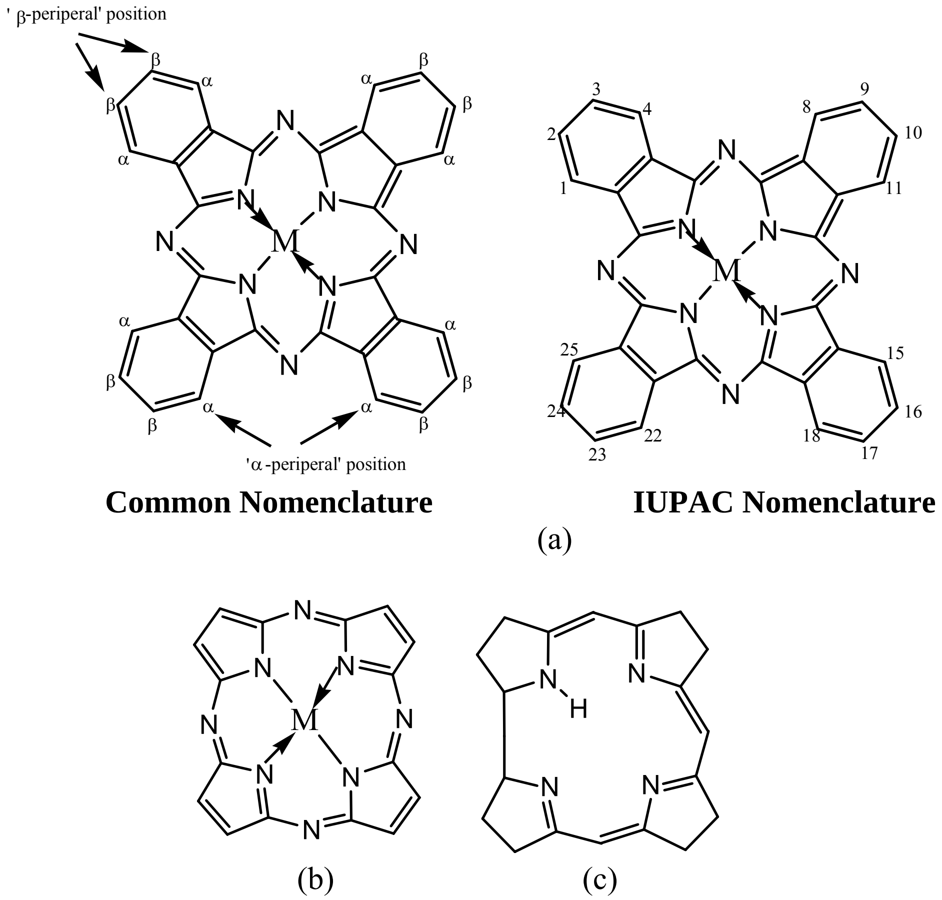


Figure 1: Molecular structure of phthalocyanine

Since the heteroaromatic Pc ligand has a strong blue color and is chemically stable, Pc complexes have been used extensively in pigments and dyestuffs for more than 70 years. Although most research results have been published as patents, academic research has become very intensive over the last 20 years. The fact that over the last decade, more than

1,000 papers have been published annually on Pc-related research, including both academic papers and industrial patents, indicates that the Pc ligand remains of interest to many researchers. The *Society of Porphyrins and Phthalocyanines* was established in the year 2000 by leading researchers within the field to help foster future collaborative research [2, 3, 4].

Macrocycles which are cyclic compounds with 9 or more members including at least 3 donor atoms giving a set of four essentially coplanar nitrogen atoms have been most extensively studied, in part because of their relevance, assumed relevance, to naturally occurring systems such as Porphyrins and the corrins. The phthalocyanines are structurally similar to naturally occurring porphyrins such as hemoglobin, chlorophyll a, and vitamin B_{12}. Phthalocyanines themselves do not occur in nature [2, 5, 6].



(a)

(b) (c)

Figure 2: Molecular structure of (a) metallophthalocyanine showing α α and β positions including numbering and (b) metalloporphyrin (c) Corrin

1.2. General Aspects of Phthalocyanines

1.2.1. Properties and Functions of Metallophthalocyanines

Phthalocyanines are synthetic substances related to the naturally occurring porphyrins. They consist of a macrocycle made up of four isoindole units linked by aza nitrogen atoms in contrast to the methine carbon atoms in porphyrins.

The metal complexes of phthalocyanine called metallophthalocyanines (MPcs) are planar, 18 π -electron systems with highly conjugated structure, as shown in Figure 2. MPc complexes are well known commercially as blue-green pigments with the colour arising from their intense absorption band observed in the visible region of the spectrum called the Q band. MPcs have been found useful in many technological applications such as photovoltaic cells, fuel cells, semi-conductor devices, electronic and chemical sensors, catalysis and recently in medical applications as photosensitizers for photodynamic therapy. Have high thermal, chemical, and photochemical stabilities which make them important in pigments and dyestuffs in the paper and textile industries [3, 4, 5, 7].

MPcs have also been used as catalysts for the removal of sulfur from crude oil, as charge-generation materials in xerography, in optical read/write discs, as photodynamic reagents for cancer therapy, in deodorants, germicides and anti-bacterial reagents, and as growth promoting and retarding agents of plants. Other active fields of Pc-related research include applications in or as chemical sensors, electrochromism, conductors, and semiconductors, photovoltaic elements for electricity generation, one dimensional metals, non-linear optics, electrocatalysis, liquid crystals, and electrophotography [8, 9].

MPc complexes are also known to be chemically and thermally stable and these properties have allowed them to be used in fuel cells, as photovoltaic materials and in molecular electronics.

Applications of MPc complexes are hindered by their low solubility in organic and aqueous solutions. However, this drawback can be improved by introducing substituents either in the ring system or as axial ligands on the central metal ion. The ring substituents can be attached in one of the two positions of the MPc ring as shown in Figure -2, i.e. α -position or β -position [10, 11].

Phthalocyanine derivatives, which have a similar structure to porphyrin, have been utilized in important functional materials in many fields [12]. Their useful properties are attributed to their efficient electron transfer abilities. The central cavity of phthalocyanines is known to be capable of accommodating over 63 different elemental ions, including hydrogen (metal-free phthalocyanine, H_2-PC). Metal phthalocyanines MPc and compounds with metalloids such as B, Si, Ge, and As or nonmetals such as P display a wide variety in their coordination chemistry [5, 12].

A phthalocyanine containing one or two metal ions is called a metal phthalocyanine (M-PC). In the last decade, as a result of their high electron transfer abilities, M-PCs have been utilized in many fields such as molecular electronics, optoelectronics, photonics, (Figure -3). The functions of M-PCs are almost universally based on electron transfer reactions because of the 18 π electron conjugated ring system found in their molecular structure.

Further, particular derivatives are known to have potential as second-generation photo sensitizers for photodynamic therapy (PDT) of cancer because they show strong absorption of the far-red light between the wavelengths of 600 and 800 nm, which has greater tissue penetration properties, and satisfactory photosensitization of singlet oxygen [13, 14, 15].

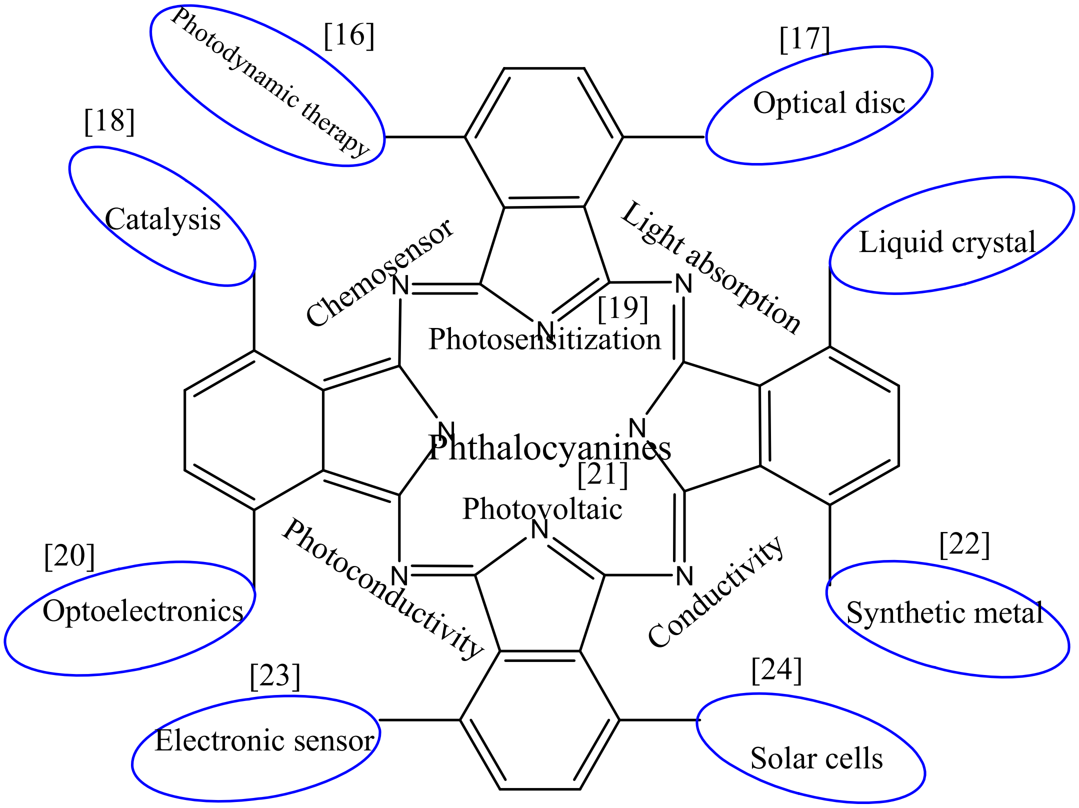


Figure 3: Typical function of phthalocyanine derivatives

1.2.2. UV-Vis spectrum of MPc

The best indications for a phthalocyanine system are given by their UV-Vis spectra. The UV-Vis absorption spectra of these phthalocyanines exhibit Q and B bands, which are the characteristic bands for the phthalocyanines [25].

Ultraviolet-visible (UV-Vis) absorption spectrum for metallophthalocyanine can be clearly identified by its characteristic and distinct intense Q band and low intensity B band. The MPc absorption spectrum shows two bands referred to as Soret (or B) band at the blue region (300 – 350 nm) of the UV-Vis spectrum and the intense band known as Q band at the red region (600 – 800 nm) which arises from $\pi \rightarrow \pi^*$ transition.

The origins of these $\pi \rightarrow \pi^*$ transitions which gives rise to B and Q absorption bands can be understood by Gouterman's four-orbital model. The Q band for MPc complexes occur from the electron transition from the a_{1u} orbital to the e_g orbital and the B band results from the a_{2u} or b_{2u} orbital to the e_g orbital, Figure 4.

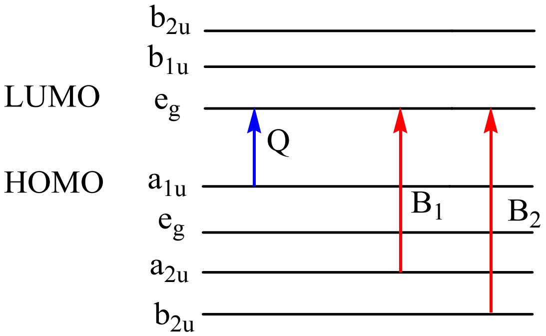


Figure 4: Gouterman's four model showing electron transitions and the origin of Q and B bands for MPc.
LUMO = Lowest unoccupied molecular orbital
HOMO = highest occupied molecular orbital

1.3. Chemistry of Trimellitic anhydride

Trimellitic anhydride (1, 2, 4-Benzenetricarboxylic anhydride), chemical compound with formula $C_9H_4O_5$, (m.p. 165^{O}C, b.p. 390^{O}C,), is a derivative of carboxylic acid and it is stable under ordinary conditions. At ordinary temperatures it is white to off white flakes with musty odor which easily converted to trimellitic acid under aqueous condition.

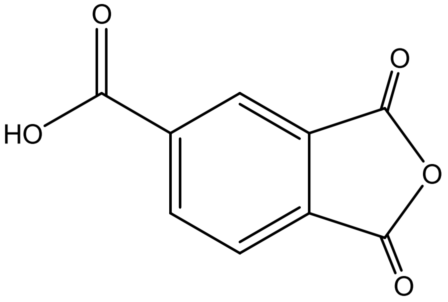


Figure 5: Trimellitic anhydride

Trimellitic anhydride reacts with alcohols forming the corresponding esters. Reactions with ammonia yield amides and imides.

Anhydrides are activated acyl compounds that are often used for the same type of acylation as acid chlorides. But they are not as reactive as acid chlorides and particularly valuable when the appropriate acid chlorides are too reactive, do not exist and are more expensive. Anhydrides are occasionally found in nature; such as cantharidin [26].

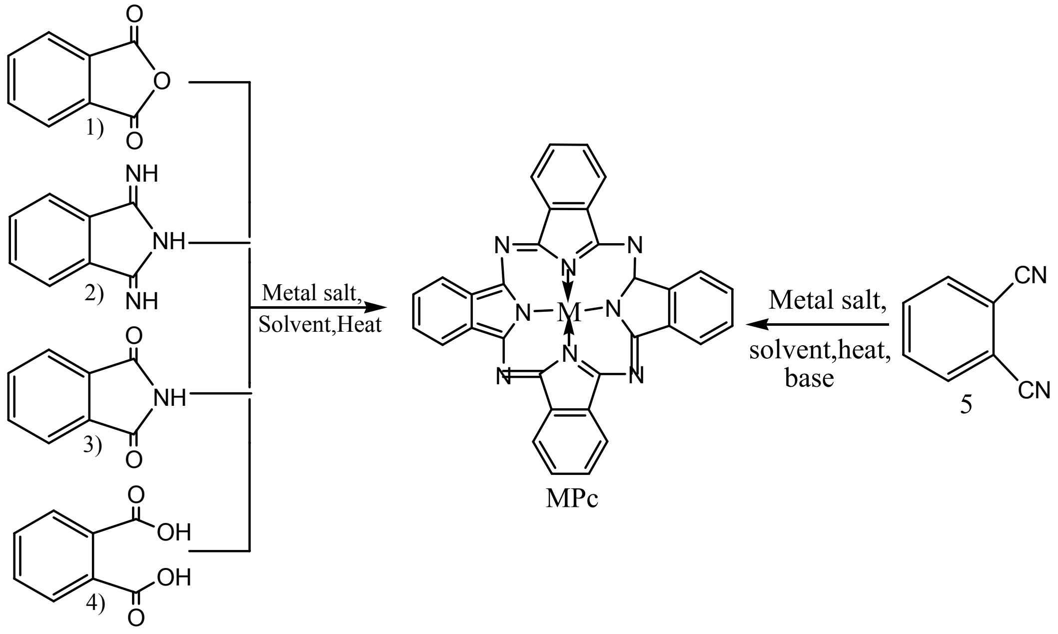
Trimellitic anhydride is used as a curing agent for epoxy and other resins. It is also used in vinyl chloride plasticizers, various polymers and polyesters, agricultural chemicals, dyes and pigments, paints and coatings, pharmaceuticals, surface active agents, numerous modifiers and intermediates, and specialty chemicals. A number of epoxy resin and surface coating systems, containing between 2-10% TMA, are available as dry powder formulations and are intended for application either by electrostatic dry powder spraying or by dipping pre-heated articles into fluidized beds.

1.4. Synthetic routes of metal complexes of phthalocyanine

One pot template condensation reactions lie at the heart of macrocyclic chemistry. Therefore template reactions have been widely used for the synthesis of macrocyclic complexes, where, generally, transition metal ions are used as the templating agent. The metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products [27].

Phthalocyanine complexes have been synthesized with nearly all the metals of the periodic table. Despite the apparently complex structure of the Pc system, it is formed in a single-step reaction from readily available starting materials. The reaction is strongly exothermic.

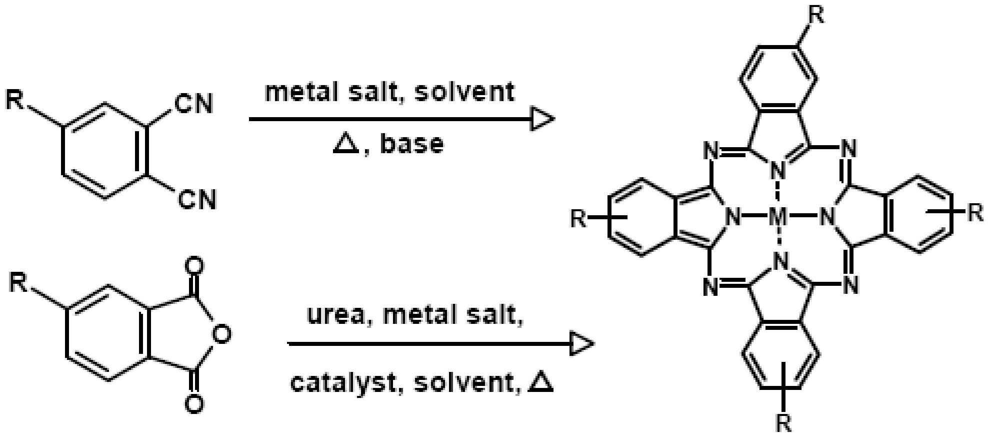
There are several methods for the synthesis of metallophthalocyanine complexes; the common method is shown in Scheme-1.



Scheme 1: General synthesis route for MPc complexes.

Where; phthalic anhydride (**1**), 1, 3-diiminoisoindoline (**2**), phthalimide (**3**), phthalic acid (**4**) and phthalonitrile (**5**) are utilized.

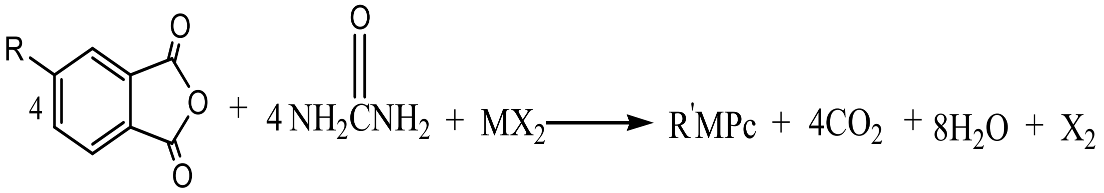
Substituted MPc complexes have been widely used; the substituents on the MPc enhance solubility and are useful in tailoring the use of MPc for various applications. The synthesis of the substituted MPc in Scheme-2 is achieved by cyclotetramerization of mono substituted phthalonitrile and substituted phthalic anhydride respectively.



Scheme 2: Synthetic route for substituted metallophthalocyanine tetra substitution.
R = substituents

Scheme-2 shows the two general methods of synthesis, which are *phthalic anhydride–urea process* and *dinitrile process* of synthesis. Inexpensive starting materials such as phthalic anhydride and trimellitic anhydride for anhydride method; and phthalonitrile for nitrile method are utilized. The anhydride method involves heating the mixture of one of the starting materials in the presence of other reagents such as metal salt, urea, solvent and the catalyst to yield the MPc complex. The solvent used should have a high boiling point as the formation of MPc is accomplished at high temperatures [28, 29].

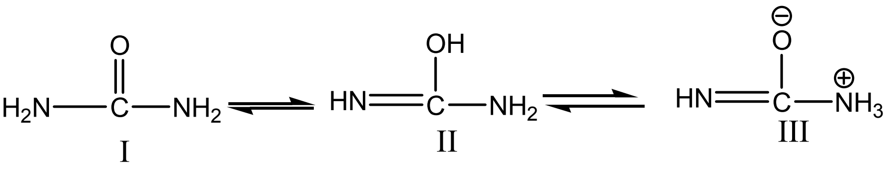
The reaction can be carried out either as melt (without solvent) at higher temperature of 300^0C or in the solvent at a relatively lower temperature of 190^0C. The overall reaction for synthesis of metallophthalocyanine by anhydride method described by the following reaction as;



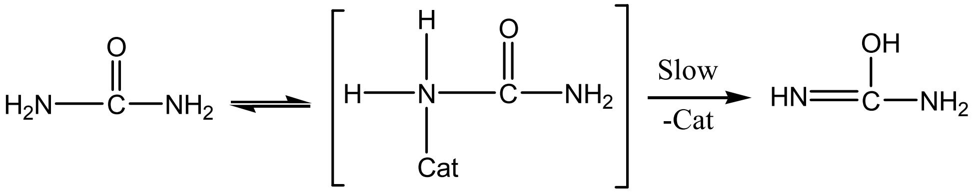
Where **R’** = indicates 4R groups on the MPc.

Even if the detailed mechanism involves more investigation, the following mechanism was proposed for the anhydride method:

Urea has the following tautomeric forms;



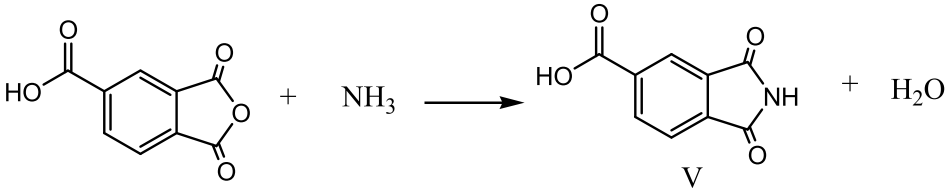
Because the Keto form(I) is the most stable, its conversion is due to external factors. Catalysts are responsible for this conversion since they are Lewis acids. Thus a reaction between catalyst and urea rather than phthalic anhydride is to be expected because urea is the only which affect the reaction order.



Since three tautomers shouldn't be stable and undoubtedly decompose into ammonia and isocyanic acid as:

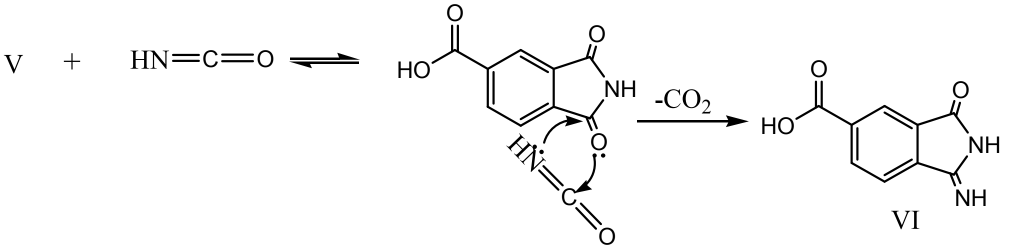
IV
Isocyanic acid

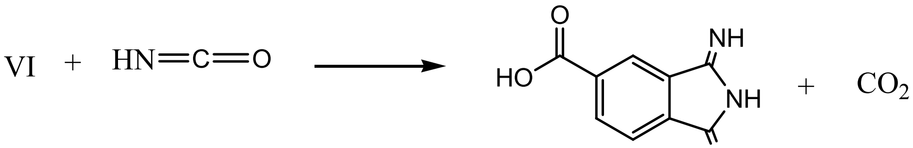
Once ammonia is formed it reacts with trimellitic anhydride to form phthalimide;



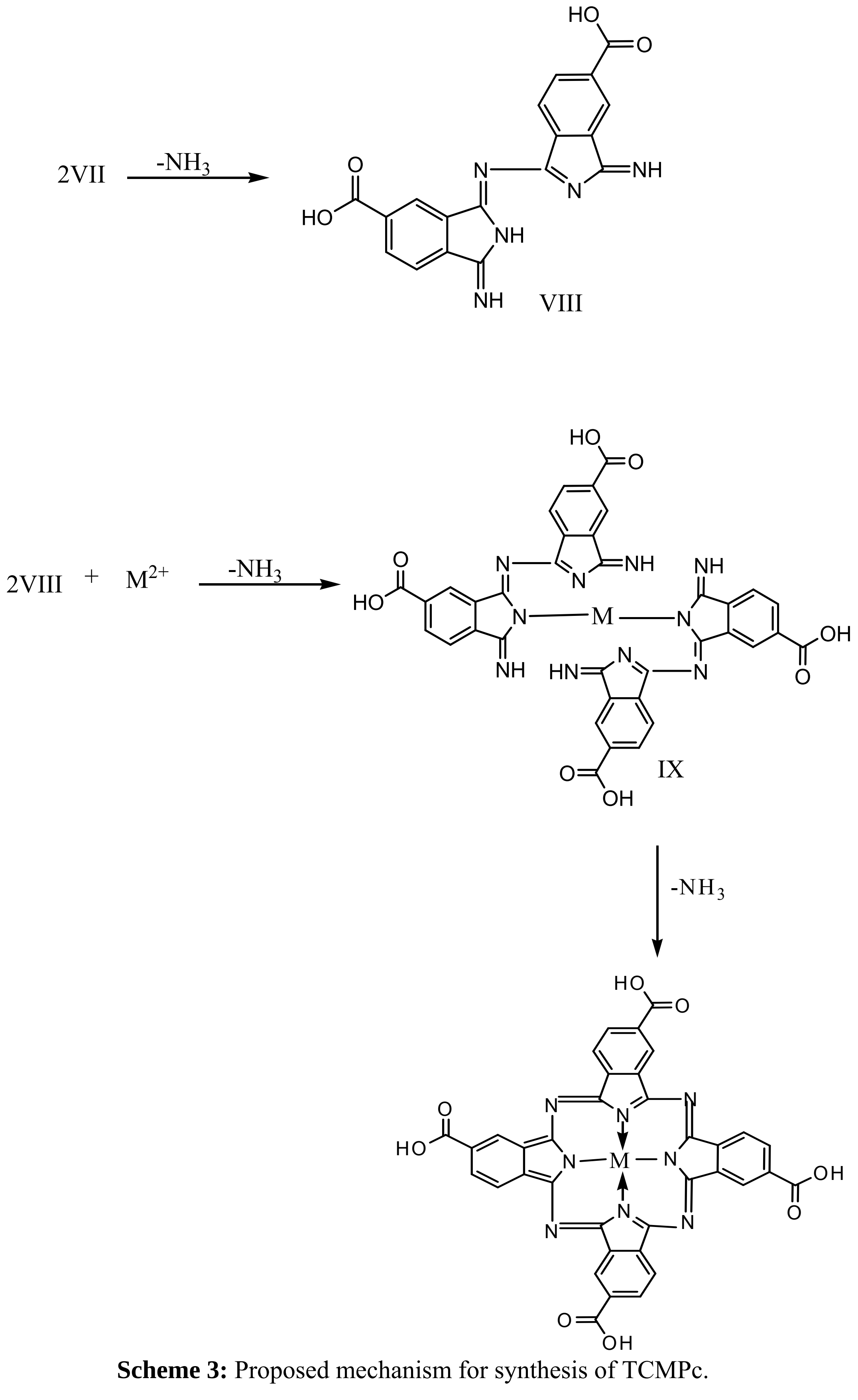
V
Phthalimide

Then;





VII



Scheme 3: Proposed mechanism for synthesis of TCMPc.

Even if the halogen from the metal salt removed as X_2 according to this reaction, there is also an explanation that it is removed as X^- with the decomposition product of urea without detailed reaction mechanism of the reaction in both cases. There is formation of H_2O and NH_3 under reaction condition which can coordinate to the metal.

1.5. Chemistry of metal ions

1.5.1. Cu (II) Chemistry

Copper (II) has d^9 electronic configuration. It is the most important oxidation state of copper. Throughout copper (II) chemistry, Jahn–Teller distortions are observed as predicted for an octahedral d^9 ion if placed in an octahedral or tetrahedral environment, although the degree of distortion varies considerably. Octahedral complexes without any distortion are expected to have only one d-d absorption band corresponding to $E_g \rightarrow T_{2g}$ transition. For distorted octahedral complexes, several weak absorption bands are observed 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. However, tetrahedral complexes are expected to give a single, broad band corresponding to $^2T_2 \rightarrow {}^2E$ transition in the near IR region. In both square planar and tetragonal geometries the transitions are not well resolved. Magnetic moments of monomeric Cu (II) complexes are generally in the rage 1.7 to 2.2B.M.

The Cu (II) ion is classified as a borderline hard acid; therefore nitrogen and oxygen donors followed by chlorine and sulphur have dominated its coordination chemistry. This can be one of the reasons for its biological importance such as in; electron transfer systems (blue copper proteins); O_2 storage and transport (haemocyanin); Cu transport proteins (ceruloplasmin) [30, 31].

1.5.2. Ni (II) Chemistry

The electronic configuration of the Ni (II) is d^8.In this divalent state it forms a very extensive series of compounds; and it is the most common oxidation state of nickel.

A range of coordination geometries is observed for nickel (II) complexes with coordination numbers from 4 to 6 being common and 6 it's maximum coordination number. Structurally, it encompasses all the main structural type; octahedral, trigonal bipyramidal, square-pyramidal, tetrahedral, and square planar. Octahedral and square planar geometries are the most usual. Some structures are complicated by interconversions between square planar and tetrahedral, or square planar and octahedral coordination.

Three spin-allowed transitions are expected for octahedral nickel complexes which assigned to $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$, $^3A_{2g}\rightarrow{}^3T_{1g}(P)$.

Magnetically, square planar complexes of Ni(II) are diamagnetic. Octahedral nickel (II) complexes have relatively simple behavior. Ni(II) should have two unpaired electrons, and the magnetic moments ranging from 2.83-3.4 B.M. depending on the magnitude of the orbital contribution [30, 31].

1.6 Objectives and Scope of the Present Investigation

Literature review reveals that a lot of work has been done on metal complexes of phthalocyanines. This is due to their wide range of applications in dyes, pharmaceutical, medical, polymer chemistry, catalysis, and electronics; and also due to the binding ability of phthalocyanines to a wide range of transition metal ions.

In view of these applications, this paper presents an investigation on the synthesis and characterization of tetracarboxy metallo phthalocyanine, which is important since it presents an improvement in solubility of phthalocyanine due to its carboxylic substituents which also leads to further investigation on phthalocyanine since the OH groups can be substituted with Cl ($SOCl_2$). This substitution opens a route for further substitution by other ligands/groups.

Overall, the investigation is aimed at the synthesis of Cu(II) and Ni(II) tetracarboxy phthalocyanine complexes using the precursors trimellitic anhydride, urea and metal salt. The complex will be characterized on the basis of chemical analysis, UV-Vis spectral, conductance and magnetic susceptibility data.

2. MATERIALS, INSTRUMENTS AND METHODS

2.1 Chemicals

All the chemicals used for synthesis of the metal complex were of Analytical grade. The chemicals used in the synthesis were 1,2,4 benzene tricarboxylic anhydride (Trimellitic anhydride-TMA) , urea, copper(II)chloride, nickel(II)chloride, ammonium molybdate, hydrochloric acid, sodium hydroxide and $AgNO_3$. Solvents used during the investigation include; MeOH, petroleum ether, EtOH, DMSO, THF, DMF, $CHCl_3$, CH_2Cl_2, nitrobenzene, formic acid and HNO_3.

2.2 Instruments

Determination of melting point or decomposition temperature of the metal complex was done with Stuart SMP3 Digital Melting Point apparatus.

UV-Vis spectrophotometric studies were done in the range 200-800 nm using spectronic Genesys 2PC spectrophotometer.

Magnetic susceptibility measurements were performed using MSB Auto, (Sherwood Sciencetific).

The molar conductivity measurements were carried out using EC 214 Bench type conductivity meter (Hanna Instrument) in DMF.

The metal complex was analyzed for its metal content using Buck Model Scientific 210 VGB atomic absorption spectrometer.

2.3 Methods

2.3.1 Qualitative Tests

i. Thin Layer Chromatography

Thin layer chromatography was used to check the purity of the compounds. Thus, the purity of the Cu(II) and Ni(II) complexes was checked by TLC using suitable solvent, methanol/chloroform(being 4:1) as a mobile phases.

ii. Chloride Test

Complexes dissolved in HNO_3 acid were subjected to chloride identification after digestion. 0.5M solution of $AgNO_3$ was added to check the presence/absence of chloride in the samples

iii. Nickel test

The qualitative test of nickel in the complex was performed by the addition of 5ml of an alcoholic solution of dimethyl glyoxime to HNO_3 solution of the complex and then neutralized with aqueous ammonia.

2.3.2 Quantitative Determinations

i. Metal Determination

The metal contents of the complexes were determined spectroscopically using atomic absorption spectroscopy.

20 mg of the metal complex dissolved in 10 ml of concentrated nitric acid was digested with gradual and repeated addition of 10 ml portions of the acid until the organic content of the complexes decomposes. After the decomposition, only the metal salts remain in the solution. The residue was dissolved and diluted in 50ml deionized water. The solution was subjected to AAS studies after appropriate dilutions. Based on the absorbance data, the concentrations of the metal complexes were calculated and the result was given in table 4.

ii. Molar Conductance Measurements

The specific conductance of the complexes were determined by using EC 214 Bench type conductivity meter (Hanna Instrument) after preparing 10^{-3}M solutions of complexes in DMF. The molar conductance of the complex is derived from the specific conductance by the following formula.

$\Lambda_M = \frac{L\ \mathrm{x}1000}{M}$ Where; L=specific conductance (μS)
Λ_M =molar conductance (S cm^{2}mol^{-1})
L=concentration (mol cm^{-3})

The k values obtained for Cu(II) and Ni(II) complexes were 6.4 and 9.3 μS respectively. Their molar conductance is shown in table 5.

3. EXPERIMENTAL PART

3.1. Synthesis of Cu(II)tetra carboxyphthalocyanine [CuTCPc(H_2O)$_2$]

A mixture of trimellitic anhydride (1.25g, 6.5 mmol), urea (1.56g, 26mmol), ammonium molybdate (0.006g, 0.004 mmol) and the required metal salt, di hydrated copper (II) chloride (0.28g, 1.65mmol) were finely ground and added to nitrobenzene (35 ml). The mixture was refluxed for 4 hours at 160-190°C. A dark green solid resulted which was filtered off and washed with methanol until the smell of nitrobenzene could no longer be detected. Sodium hydroxide, 2M, was added to the solid mixture and refluxed for 2 hours at 90°C, allowed to cool to room temperature. The resulting fluid was acidified with hydrochloric acid (6M) to precipitate the complex, which was filtered, washed with methanol and dried over $CaCl_2$. Yield: 0.58g (45.3%) [32].

3.2. Synthesis of Ni(II)tetra carboxyphthalocyanine [NiTCPc(H_2O)$_2$]

A mixture of trimellitic anhydride (1.25g, 6.5mmol), urea (1.56g, 26mmol), ammonium molybdate (0.006g, 0.004 mmol) and the required metal salt, hex hydrated Nickel(II) chloride (0.39g, 1.64mmol) were finely ground and added to nitrobenzene (35 ml). The mixture was refluxed for 4 hours at 160-190°C. A dark blue solid resulted which was filtered off and washed with methanol until the smell of nitrobenzene could no longer be detected. Sodium hydroxide, 2M, was added to the solid mixture and refluxed for 2 hours at 90°C, allowed to cool to room temperature. The resulting fluid was acidified with hydrochloric acid (6M) to precipitate the complex, which was filtered, washed with methanol and dried over $CaCl_2$. Yield: 0.56g (44%) [32].

4. RESULTS AND DISCUSSTION

4.1. Physical characteristics

Both Ni(II) and Cu(II) complexes were obtained as colored crystalline products with high melting point and low solubility in most common solvents as described below.

Compound	**Molecular formula**	**Molecular Weight** (g/mole)	**Appearance**	**Color**	**Mpt.^{0}C**	**Yield (%)**
Trimellitic anhydride	$C_9H_4O_5$	192	Crystalline	white	165	----
Urea	$CO(NH_2)_2$	60	Crystalline	white	132 ± 3	----
Cu(II)TCPc	$CuC_{36}N_8H_{16}O_8$	751.5	Crystalline	Dark green	327	45.3%
Ni(II)TCPc	$NiC_{36}N_8H_{16}O_8$	746.7	Crystalline	Dark blue	>347	44%

Table 1: Physical Properties of starting materials and complexes

Solvents	Chemical formula	Bpt.^{0}C	Dielectric constant	Density (g/ml)	Solubility	
					CuTCPc	NiTCPc

Table 2: Solubility test of MTCPcs

Non-Polar						
Benzene	C_6H_6	69	2	0.655	Insol.	Insol.
Diethyl ether	CH_3CH_2-O-CH_2CH_2	35	4.3	0.879	Insol.	Insol.
Chloroform	$CHCl_3$	61	4.8	1.498	Insol.	Insol.
Polar Aprotic						
1,4-Dioxane	-CH_2-CH_2-O-CH_2-CH_2-O-	101	2.3	1.033	Insol.	Insol.
THF	-CH_2-CH_2-O-CH_2-CH_2-	66	7.5	0.886	Sl.sol.	Sl.sol.
Acetonitile	CH_3-CN	82	37	0.786	Sl.sol.	Sl.sol.
DMF	H-C(=O)N$(CH_3)_2$	153	38	0.944	Sl.Sol.	Sol.
DMSO	CH_3-S(=O)-CH_3	189	47	1.092	Sol.	Sl.sol.
Polar protic						
Methanol	CH_3OH	79	24	0.789	Insol.	Insol.
Water	H_2O	100	80	1.00	Sl.Sol.	Sl.sol.

*Sol. =soluble *Insol. = insoluble *Sl.sol= slightly soluble

4.2. Qualitative Tests

4.2.1. Thin Layer Chromatography

The complexes purity was confirmed by TLC.

4.2.2. Chloride Tests

The absence of any white precipitates after addition of 0.5M solution of $AgNO_3$ indicated the absence of chloride in the samples.

4.2.3. Nickel test

Red precipitate was observed after procedural step, which indicates the formation of nickel dimethyl glyoxime [33]. So, the presence of nickel was confirmed.

4.3. Quantitative Determinations

4.3.1. Metal Determination

The molar ratios of the metal to ligand of both the complexes were obtained from absorbance measurements using atomic absorption spectroscopy. The result obtained was given in table 3.

Table 3: Metal Determination and metal to ligand ratios

Metal Complexes	Percentage of metal (%)		Metal to ligand ratio
	Calculated	Found	
Ni(II) complex	7.54	8.14	1:1
Cu(II) complex	8.13	7.91	1:1

4.3.2. Molar Conductance Measurements

The molar conductance values of the Ni(II) and Zn(II) complexes obtained from specific conductance are given in table 4.

Table 4: Conductivity values of Complexes

Complex	Solvent	Molar Conductance ($S\ cm^2 mol^{-1}$)	Type of electrolyte
Ni(II) complex	DMF	9.3	Non electrolyte
Cu(II) complex	DMF	6.4	Non electrolyte

The molar conductance values of both complexes are less than $65\Omega^{-1}\ cm^2\ mol^{-1}$ indicating their non-electrolyte nature since in DMF Λ_M is less than 65 for nonelectrolyte [34].

i.e. in DMF Λ_M b/n 0-65→ non electrolytes

b/n 65-90→ 1:1 electrolyte

Thus it is concluded that the ligand is in L^{-2} deprotonated form.

4.4. UV-Vis spectra of Ni(II) and Cu(II) Complexes

The electronic absorption spectra of the Cu(II) and Ni (II) complexes were recorded at room temperature in H_2SO_4. Both synthesized complexes exhibited B or Soret band between 300 – 350 nm which results from the transition of the deeper π orbitals (b_{2u} and a_{2u}) to the π* orbitals (e_g);and Q band between 600-800 nm which assigned to transition of π orbital (a_{1u}) to the π* orbitals (e_g) .i.e. N=C π→π* transition. The weak band to the shorter wavelength of Q band is also characteristic band of phthalocyanine which is vibronic origin. The peak around 400 nm is assigned to the n→π* transition of C=N groups.

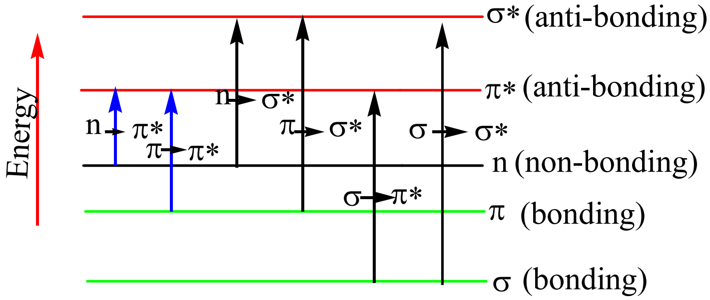


Figure 6: Electron transition and energy relation ship.

Of the six transitions outlined, only the two lowest energy ones (left-most,) are achieved by the energies available in the 200 to 800 nm spectrum.

Charge transfer bands normally occur when the central metal ion has d-orbital lying within the HOMO-LUMO gap of the phthalocyanine ring, and the transitions that gives rise to these bands are either metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT).

The UV-Vis absorption spectra of Cu(II) and Ni(II) complexes are given in appendix 1and 2, page 27 and 28, respectively.

Table 5: UV-Vis Spectral data of Complexes

Complex	π→π* (B) **Λ(nm)**	π→π*(Q) **Λ(nm)**
Ni(II) complex	308.9	761.4
Cu(II) complex	304.9	741

The d-d transitions also observed for both complexes as shown in appendix 3 and 4. For Ni(II) complex, the bands at 617 nm and 526 nm assigned to $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$

respectively which are expected for octahedral complexes. Cu(II) complex also shows the expected bands of octahedral complex at 624 nm, 538 nm, 498 nm which are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ respectively.

4.5. Magnetic Susceptibility Measurements of Metal Complexes

The magnetic susceptibility of the complexes was determined as gram susceptibility (χ_g), and was obtained to be 0.803 x 10^{-6} for CuTCPc and 1.689 x 10^{-6} for NiTCPc at $22^{O}C$. This indicates paramagnetic since they are positive values. To arrive at the effective magnetic moment of the complexes, the following calculations were made.

Molar magnetic susceptibility **(χ_M) =** χ_g x Molecular weight of the complex, and

$\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

Table 6: Magnetic Susceptibility Data of Metal Complexes

Complex	χ_g, gram susceptibility ($cm^3\ g^{-1}$)	χ^{corr}_{M}, molar susceptibility ($cm^{-3}\ mol^{-1}$)	μ_{eff}, effective magnetic moment(BM)	Spin only value (BM)
Cu(II)TCPc	0.803 x 10^{-6}	1.09 x 10^{-3}	1.55	1.73
Ni(II)TCPc	1.689 x 10^{-6}	2.24 x 10^{-3}	2.30	2.83

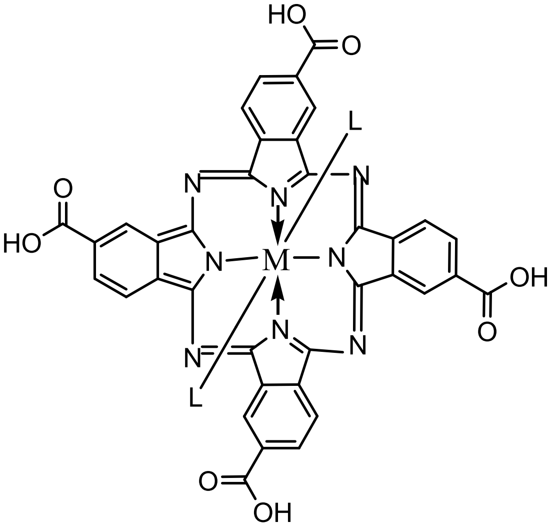
Magnetic moments of octahedral Ni (II) complexes are usually close to the spin-only value of 2.83 BM. In contrast, tetrahedral complexes possess magnetic moments 4 BM due to orbital contributions, and square planar complexes are diamagnetic.

Cu(II) complex possesses magnetic moment in the range $\mu_{eff} = 1.55$ B.M in agreement with the spin only value of Cu(II) with slight lowering. This indicates the presence of one unpaired electron. For Ni(II) complex the magnetic moment is found to be 2.3B.M which again confirms the presence of two unpaired electrons. This is in agreement with octahedral geometry for the complex even if there is lowering of the room temperature magnetic moments of the complexes compared to spin only values which may be due to the highly conjugated cyclic ligand surrounding the metal ion “Electron delocalization” and also due to “anomalous” properties of Ni(II) complexes [35].

The paramagnetic nature suggests that nickel(II) assumes an octahedral geometry rather than a square planar geometry.

CONCLUSIONS

A highly Pi conjugated macrocyclic system-phthalocyanine complexes of Ni(II) and Cu(II) were synthesized from trimellitic anhydride and urea precursors by template method. The formation of the metal phthalocyanine complexes was confirmed from their characteristic UV-Vis spectra. The complexes were subjected to chloride test and the absence of chloride was confirmed. Metal content is also determined to reveal metal to ligand ratios in the complexes. Accordingly, metal to ligand ratio was found to be 1:1. Conductivity studies on both complexes indicated that the complexes were non-electrolytes. Based on the data obtained, octahedral coordination has been suggested for both complexes. The complexes are represented by general formulas [$MPcL_2$] (M = Cu(II), Ni(II); and L =H_2O or NH_3 which are produced under the reaction conition as described in section 1.4) are proposed with octahedral geometry.



M = Cu(II) ,Ni(II)

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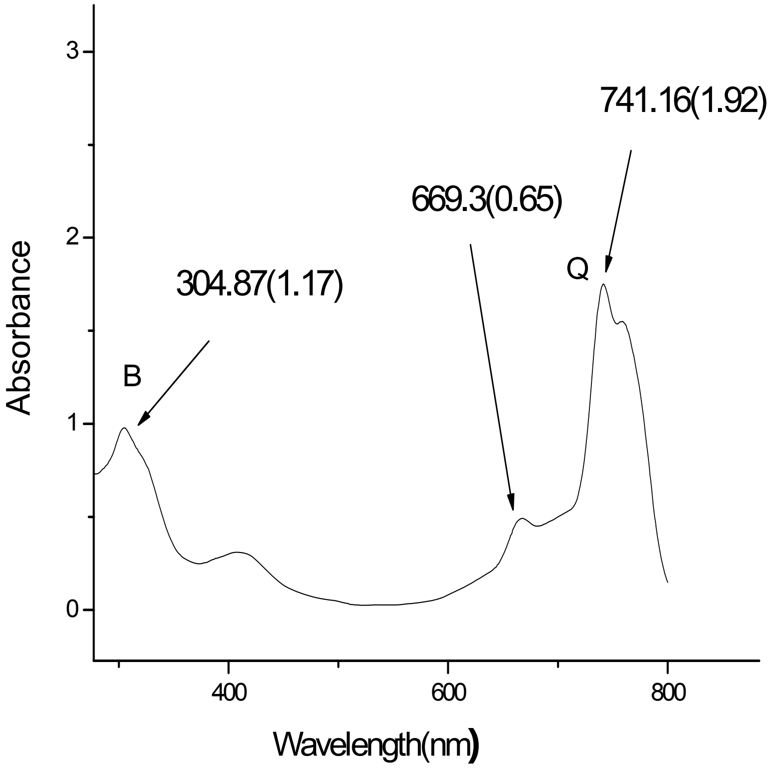
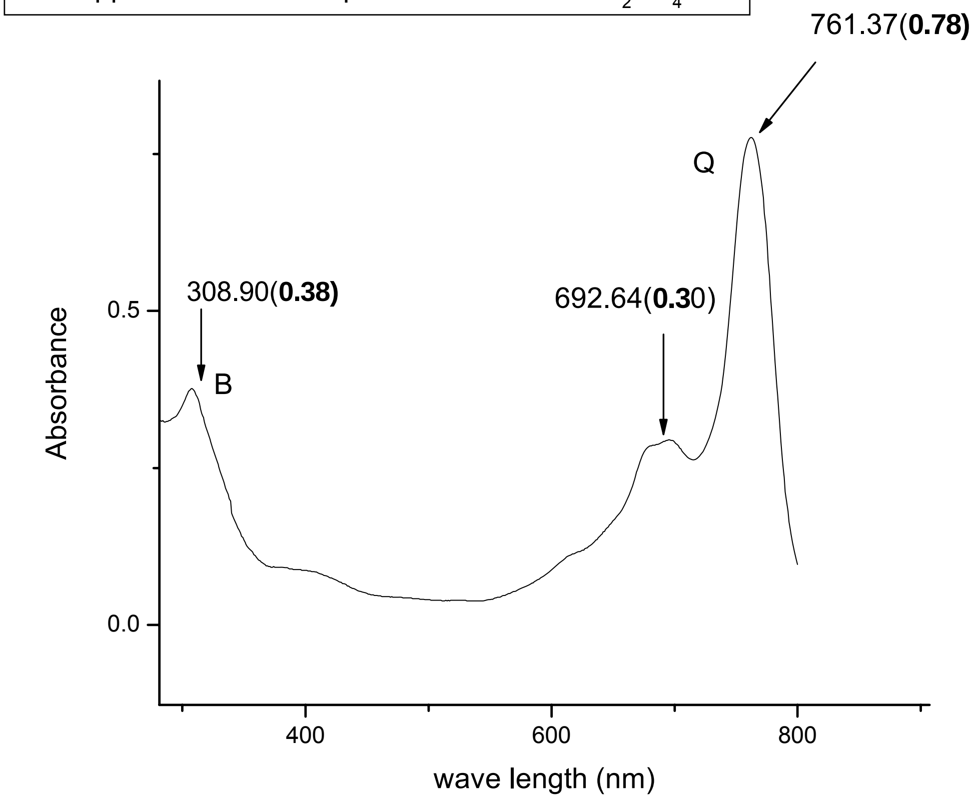
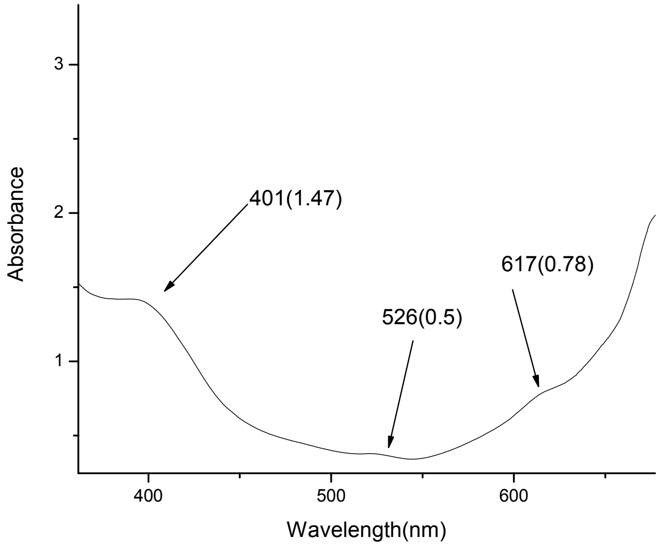
Appendix 1. Uv-vis spectra of Cu(II)TCPc in H_2SO_4



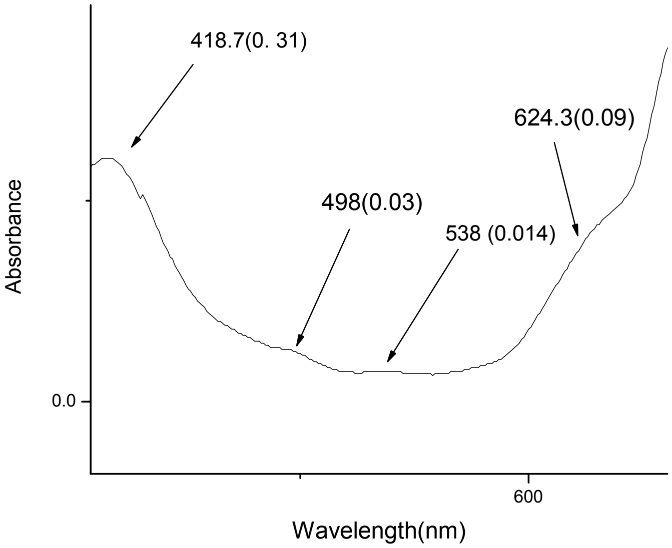
Appendix 2. UV-vis spectra of NiTCPc in H_2SO_4



Appendix 3. NiTCPc in H_2SO_4(expaned for d-d)



Appendix.4 Uv-vis spectra of CuTCPc in H_2SO_4(expanded for d-d)



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: Fitsum Bulto
Signature: _____________

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

Name: Prof. V. J. T. Raju

Signature: ______________

Place and Date of Submission: Department of Chemistry
Addis Ababa University
June 2010