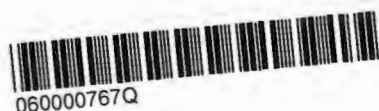


SYNTHESIS, CHARACTERIZATION AND KINETIC STUDIES OF METAL PORPHYRAZINES

FANYANA MOSES MTUNZI
PhD THESIS



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SYNTHESIS, CHARACTERIZATION AND KINETIC STUDIES OF METAL PORPHYRAZINES

BY

FANYANA MOSES MTUNZI

Submitted in fulfillment of the requirements for the Degree of Doctor of Philosophy in the Department of Chemistry in the Faculty of Agriculture, Science and Technology at the North-West University, Mafikeng campus.

SUPERVISOR

Dr. D.A. Isabirye

Date Submitted

November 2006

DECLARATION

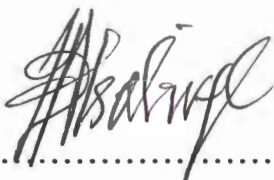
“I hereby declare that the thesis for the degree of Doctor of Philosophy, at the North-West University hereby submitted, has not previously been submitted by me for a degree at this or any other University. It is my own work in design and execution and all material contained herein has been duly acknowledged.”



FANYANA MOSES MTUNZI

CERTIFICATE OF ACCEPTANCE FOR EXAMINATION

This thesis entitled “Synthesis, characterization and kinetic studies of metal porphyrazines”, submitted by Fanyana Moses Mtunzi, student number 10350675 of the Department of Chemistry in the Faculty of Agriculture, Science and Technology is hereby recommended for acceptance for examination.



.....

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ABSTRACT

The symmetrical 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium, Mg-pz^1 , was prepared from maleonitrile via Linstead's template cyclization. The free base, Pz^1 -base and centrally metallated new compounds, M-pz^1 , $\text{M} = \text{Cu(II)}, \text{Co(II)}$ were prepared by first demetallating Mg-pz^1 with glacial acetic acid and then copper(II) and cobalt(II) metal ions in acetic acid were inserted respectively.

The N,N,N',N'-tetramethylamino porphyrazine magnesium hybrid was prepared from 2,3-dipropylmaleonitrile and 4,7-bis(isopropoxy)-1,3-iminoisoindoline. Magnesium was removed with glacial acetic acid to produce N,N,N',N'-tetramethylamino porphyrazine hybrid base which was centrally metallated to give the new compounds, Cu(II)-pz^2 and Co(II)-pz^2 respectively.

The 2,3,9,10,16,17,23,24-octa-substituted phthalocyanine was prepared from 1,2-diisocyano-4-benzyl alcohol in 1-pentanol and diazabicyclo[5.4.0]-undec-7-ene (DBU) for sixteen hours. The macrocycle was then metallated to give the new compounds, Cu(II)-pc and Co(II)-pc respectively.

Pioneering kinetic studies of the insertion of the metal ions, copper(II) and cobalt(II) into the centre of the macrocycles, 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines base, N,N,N',N'-tetramethylamino porphyrazines hybrid base, and 2,3,9,10,16,17,23,24-octa-substituted phthalocyanine showed that the reactions followed second order kinetics. The mechanism of

insertion involved a rapid loss of magnesium, followed by a slow insertion of the metal ion. Insertion into the phthalocyanine was faster.

Further pioneering study of the redox mechanism of metal porphyrazines, showed that the reduction of the copper(II) at the centre of the macrocycle followed second order kinetics. An electron tunnelling outer sphere mechanism was proposed. Just as in the case of insertion, the reduction of the Cu(II)-pc was faster than in the porphyrazines.

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ABBREVIATIONS AND FORMULAE

A	Absorbance
Aq	Aqueous
CH ₂ Cl ₂	Dichloromethane
CuCN	Copper(I) cyanide
CDCl ₃	Deuterated chloroform
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMSO	Dimethyl Sulfoxide
DMF	N,N-Dimethylformamide
HOMO	Highest occupied molecular orbital
IR	Infrared
<i>J</i>	Coupling constant (in NMR spectroscopy)
LUMO	Lowest unoccupied molecular orbital
HBr	Hydrogen bromide
MeOH	Methanol
MgSO ₄	Magnesium sulphate
Mg(OBu) ₂	Magnesium butoxide
NaH	Sodium hydride
NMR	Nuclear magnetic resonance
<i>p</i> -TsOH	<i>para</i> -Toluenesulfonic acid
K ₂ CO ₃	Potassium carbonate
Pz	Porphyrazine

Pz ¹ -base	2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine base
Mg(II)-pz ¹	2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine magnesium(II)
Cu(II)-pz ¹	2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine copper(II)
Co(II)-pz ¹	2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine cobalt(II)
Pz ² -base	N,N,N'N'-tetramethylamino porphyrazines hybrid base
Cu(II)-pz ¹	N,N,N'N'-tetramethylamino porphyrazines hybrid copper(II)
Co(II)-pz ¹	N,N,N'N'-tetramethylamino porphyrazines hybrid cobalt(II)
Pc-base	2,3,9,10,16,17,23,24-octa substituted phthalocyanine base
Cu(II)-pc	2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II)
Co(II)-pc	2,3,9,10,16,17,23,24-octa substituted phthalocyanine cobalt(II)
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV-vis	Ultraviolet-visible

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CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

The molecules from the porphyrazine ($C_{16}N_8H_{10}$) class have gained interest from the scientific community due to both their potential in technological applications¹ and their relationship to biologically important porphyrins² such as chlorophyll^{3,4} and hemoglobin molecules that play a vital role in life processes.⁵⁻⁸ Chlorophyll and hemoglobin are two efficient catalysts of nature.⁹ The remarkable construction of porphyrazines, characterized by high symmetry, planarity, and electron delocalization, made these molecules attractive for theoretical studies as well.^{10, 11}

Intensive research interest on peripherally functionalized porphyrazines during the last decade has shown that these tetrapyrrole derivatives should be considered in many respects as an alternative to phthalocyanines^{12,13} which have found extensive applications in many fields from material science to photodynamic therapy of tumors as well as pigments and dyes.^{14,15}

Due to the simple and versatile synthetic route for the preparation of porphyrazines, namely the metal-templated cyclization of the maleonitrile precursors, these macrocyclic compounds are now subject to enhanced interest.^{16,17} Recently, a variety of porphyrazines have been obtained showing interesting redox and electronic properties.¹⁸ Further more, porphyrazines with novel

physicochemical properties,¹⁹ including fluorescence and efficient intersystem crossing were also prepared, and these compounds found applications as biomedical imaging agents and as novel compounds for photodynamic therapies.²⁰

The statistical co-macrocyclization of two maleo- and/or phthalonitrile has been found to produce a mixture of six $M[Pz-(A_n; B_{4-n})]$ from which it is difficult to purify the individual component by common chromatographic methods.²¹ Symbols A and B stand for functional groups fuse to the β -position of the pyrrole. There are three general methods for the preparation of $M[Pz-(A_1; B_3)]$ pigments, namely, the polymer support route,²²⁻²⁵ the subphthalocyanine route²⁶⁻²⁸ and the statistical condensation route. On the other hand, there are few methods for the selective preparation of the *trans*- $M[Pz-(A_2; B_2)]$ pigments²⁹⁻³² (Figure 1.1.1)

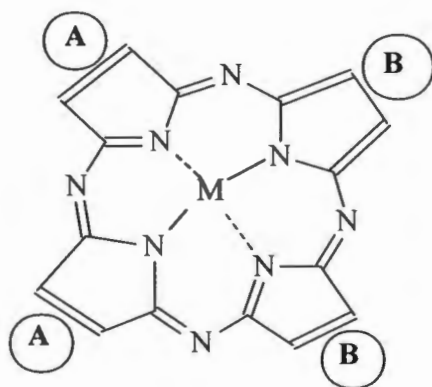


Figure 1.1.1 *trans*- $M[Pz(A_2; B_2)]$ pigment²⁹

The chemical versatility of the porphyrazine macrocycle leads to opportunity of varying the electronic structure through ligand and metal modifications; this includes, substitution, elaboration, and truncation of the macrocycle.³³ Substitutions in a very controlled manner with certain electron withdrawing groups to the

macrocycle change the electronic properties such as optical absorption, ionization and redox potential.³⁴

Peripheral substituents modulate the potential at the center of the porphyrazine macrocycle. Four peripheral nitro groups shift the 1s energies of the central nitrogens by about 2 eV, while four peripheral trifluoromethyl groups cause a shift of about 1.3 eV. Peripheral perchlorination shifts the 1s energies of the central nitrogens by about 1.35 eV, while on the other hand peripheral perfluorination causes a shift of about 1.7 eV. The most dramatic shift, of about 2.6 eV, is caused by octacyano substitution.³⁵

Peripherally functionalized porphyrazines exhibit novel optical, magnetic and electronic properties.³⁶⁻⁴⁰ In addition to the influence of the peripheral substituents, the transition metal ion in the inner core of the porphyrazine offers new ways to induce, modify and control molecular properties.⁴¹ However, metalloporphyrazines exhibit optical limiting effects comparable with phthalocyanine and naphthalocyanine derivatives.⁴²

Porphyrazines with peripheral thiol, alcohol or amine are able to complex metal ions to the edges of the macrocycle in addition to the binding within the central cavity.⁴³ The orbital interaction between the peripheral metal ions and the porphyrazine π -system mediates indirect metal-metal interactions.⁴⁴ Such peripheral binding is utilized in the formation of new sensors, an example of which is shown by the star-porphyrazine.⁴⁵ (Figure 1.1.2)

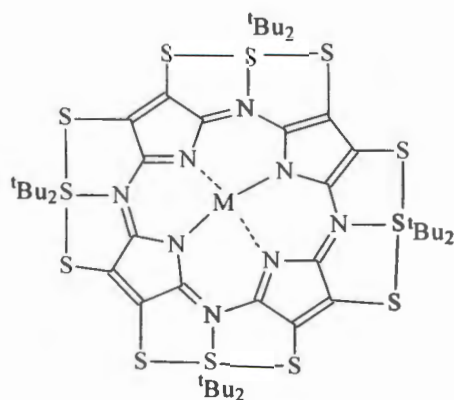


Figure 1.1.2 Structure of the star-porphyrazine⁴⁵

The other useful metal porphyrazines are the *seco*-porphyrazines that are used as sensitizers for the production of the single oxygen and they are also highly efficient as reagents for endoperoxide synthesis.⁴⁶ (Figure 1.1.3)

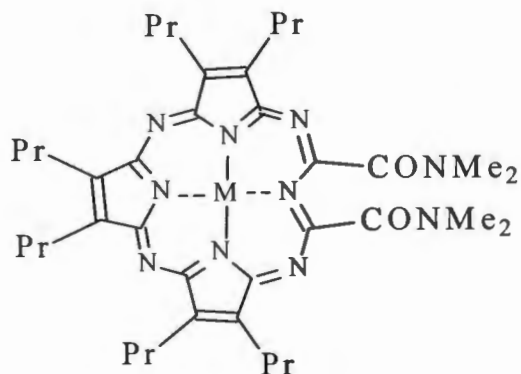


Figure 1.1.3 Structure of *seco*-porphyrazine⁴⁶

Combining the electronic character and the extended π -system of porphyrazine with peripheral metal coordination permits the preparation of a wide variety of multimetallic complexes with novel structural, spectroscopic, magnetic and electronic properties.⁴⁷

The possibility of developing tailor-made porphyrazines has resulted in a large area of technological applications and fields of scientific investigations.⁴⁷

1.2 PROBLEM STATEMENT

Porphyrazines have recently attracted interest for their nonlinear optical properties and significant potential in molecular electronics.⁴⁸⁻⁵⁰ However, the area that has been completely unexplored is that of kinetic stability of metal porphyrazines.

This includes the kinetics and mechanism of formation of metal porphyrazines. The kinetics and mechanism of oxidation-reduction between metal porphyrazines and metal porphyrazines with ordinary oxidants and reductants.

This information is necessary in order to explain the wide approach into how porphyrazines play the role they do in these applications, how they play that role, the efficiency with which they play the role and prediction of further applications. In order to achieve all these, a new set of metal porphyrazines had to be synthesized.

1.3 OBJECTIVES

The objectives of this study are therefore:

- 1.3.1 Synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II), 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base, 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines copper(II), 2,3,7,8,12,13,17,18-octakis (propyl)

porphyrazine cobalt(II) N, N, N', N'-tetramethylamino
 porphyrazine magnesium(II), N, N, N', N'-tetramethylamino
 porphyrazine base, N, N, N', N'-tetramethylamino porphyrazine
 copper(II), N, N, N', N'-tetramethylamino porphyrazine cobalt(II),
 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base,
 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II),
 2,3,9,10,16,17,23,24-octa substituted phthalocyanine cobalt(II)

1.3.2 Characterization of 2,3,7,8,12,13,17,18-octakis (propyl)
 porphyrazine magnesium(II), 2,3,7,8,12,13,17,18-octakis (propyl)
 porphyrazine base, 2,3,7,8,12,13,17,18-octakis (propyl)
 porphyrazine copper(II), 2,3,7,8,12,13,17,18-octakis (propyl)
 porphyrazine cobalt(II) N, N, N', N'-tetramethylamino
 porphyrazine magnesium (II), N, N, N', N'-tetramethylamino
 porphyrazine base, N, N, N', N'-tetramethylamino porphyrazine
 copper(II), N, N, N', N'-tetramethylamino porphyrazine cobalt(II),
 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base,
 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II),
 2,3,9,10,16,17,23,24-octa substituted phthalocyanine cobalt(II)

1.3.3 Following the kinetics of incorporation of copper(II) and
 cobalt(II) into the center of the synthesized porphyrazines and
 phthalocyanine and proposing mechanism of insertion.

1.3.4 Following the kinetics of oxidation-reduction of the central
 metal ion of the synthesized porphyrazines and phthalocyanines
 and proposing reaction mechanism.

CHAPTER TWO

LITERATURE REVIEW

2.1 PORPHYRAZINES

Porphyrazines are molecules with a highly delocalized electronic structure in which the four pyrrole moieties are linked to each other by four aza bridges as shown in Figure 2.1.1.⁵¹⁻⁵⁴

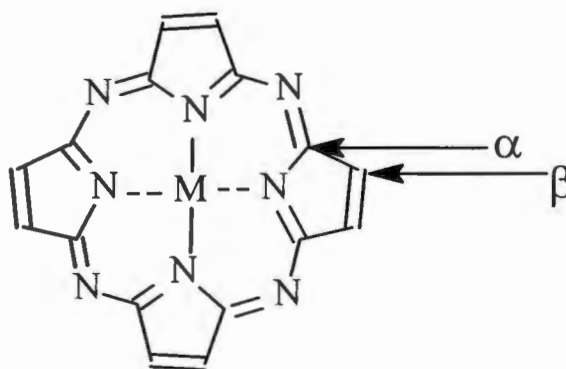


Figure 2.1.1 Structure of metal porphyrazine⁵¹

They are square planar with high symmetry and electronic delocalization.⁵⁵ The C $_{\alpha}$ -C $_{\beta}$ bonds are long compared to typical aromatic C-C distances.⁵⁶ The C $_{\alpha}$ -N-C $_{\alpha}$ internuclear angle subtended at the central protonated nitrogen is longer than the one subtended at unprotonated nitrogen.⁵⁷⁻⁵⁹ Porphyrazines are isoelectronic with porphyrins and have nearly identical molecular shape.⁶⁰ They differ only by the presence of four meso-nitrogen atoms in porphyrazines as opposed to four methine groups in porphyrines in the central ring.⁶¹

Porphyrazines, like phthalocyanines, show an intense B (Soret) band at $\lambda < 400$ nm and Q-band that has its principal absorption at $\lambda < 600$ nm. The Q-band of a 4-fold symmetric tetraazamacrocyclic shows a Q-band with a single origin, whereas compounds with reduced symmetry show a split Q-band.⁶²

Porphyrazines possess 22- π electron system, a feature that is critical for effecting a wide range of extraordinary properties such as ability to absorb visible light, to mediate the conversion of absorbed light to other forms of chemical and physical energy and to enhance thermodynamic and kinetic stability.⁶³ They also carry two negative charges in their common oxidation state and are capable of oxidation by one or two electrons and reduction with one to four electrons.⁶³ Their ring reduction processes have been found to be electrochemically reversible, whereas, their ring oxidation processes were found to be irreversible.⁶⁴

Functionalization with a wide range of different β -substituents provides porphyrazines with novel features and greatly enhanced solubility compared to their phthalocyanine counterparts.⁶⁵ Functional groups fused to the peripheral positions of metal-porphyrazines are integrated to the macrocyclic core more effectively than that of phthalocyanines.⁶⁶⁻⁶⁸

Porphyrazines display good solubility in a variety of solvents compared to phthalocyanines, however, they exhibit poor thermal and chemical stability.⁶¹ Porphyrazines and their derivatives also exhibit high electron transfer abilities and almost all their reactions and applications are based on electron transfer reactions of their conjugated π -electron ring system.^{69,70} Porphyrazine metal (II) complexes are potential photosensitizers due to their effective absorbance in the blue region of the visible spectrum as well as their low cost synthesis and lack of toxicity.⁷¹

In contrast to porphyrins, the porphyrazines have received negligible attention since their early synthesis.⁷² With the recent introduction of efficient synthesis of soluble derivatives, however, porphyrazines promise to gain in prominence over their structural relatives.⁷³ Peripherally functionalised porphyrazines and related macrocycles can bind multiple metal ion, having the potential to exhibit novel magnetic and electronic properties and to serve as building blocks in the assembly of higher order polymetallic arrays.⁷⁴

2.1.1 Structure of free base porphyrazine

The Free base porphyrazine has high delocalized geometry such that any two adjacent C_α - N_{meso} bond lengths are identical.⁷⁵ Like in magnesium porphyrazines, the C_α - C_β are longer than the aromatic C-C (Figure 2.1.3).

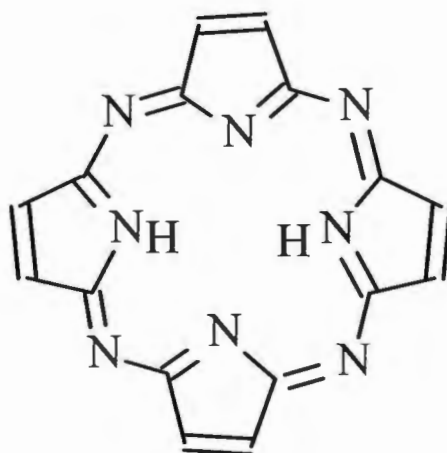


Figure 2.1.3 Structure of a free-base porphyrazine⁷⁵

The C_α -N- C_α internuclear bond subtended at the central protonated nitrogen is also larger than the one subtended at the unprotected nitrogen by about 4° .⁷⁶ Relative to porphyrins, the C_α - N_{meso} bond length in free base porphyrazine is significantly shorter than the C_α - N_{meso} bond length found in porphyrins, hence the central cavity of the free base porphyrazine is smaller than that of the porphyrin.⁷⁷

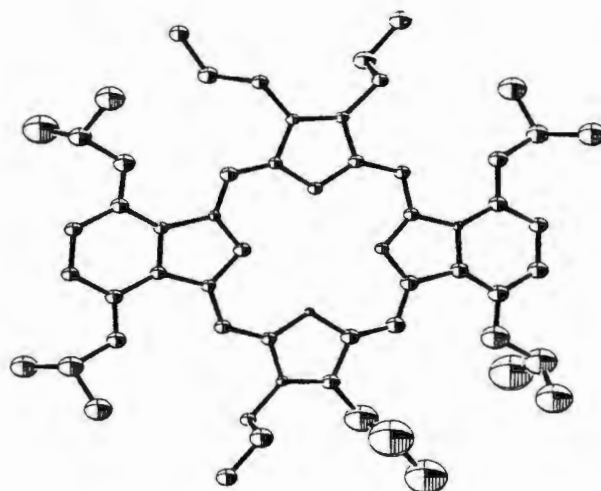


Figure 2.1.4 Typical molecular structure of a porphyrazine base⁷⁷

2.1.2 Mechanism of the inner hydrogen atom transfer in free base porphyrazines

The Free base porphyrazine has two hydrogen atoms in the inner part of the skeleton (Figure 2.1.5). The two inner hydrogen atoms are able to migrate to a framework of four nitrogen sites by a process called NH tautomerization.⁷⁸ Mostly plants use this process during photosynthesis and it is also used extensively in metal coordination chemistry.⁷⁹

NH tautomerization mechanism is believed to happen in two ways, namely, stepwise and concerted. The stepwise mechanism is characterized by a *trans-cis-trans* conversion. The *trans* isomer plays a role of a reactant and the *cis*-isomer plays the role of an intermediate. The two hydrogen atoms migrate one after another (Figure 2.1.5).

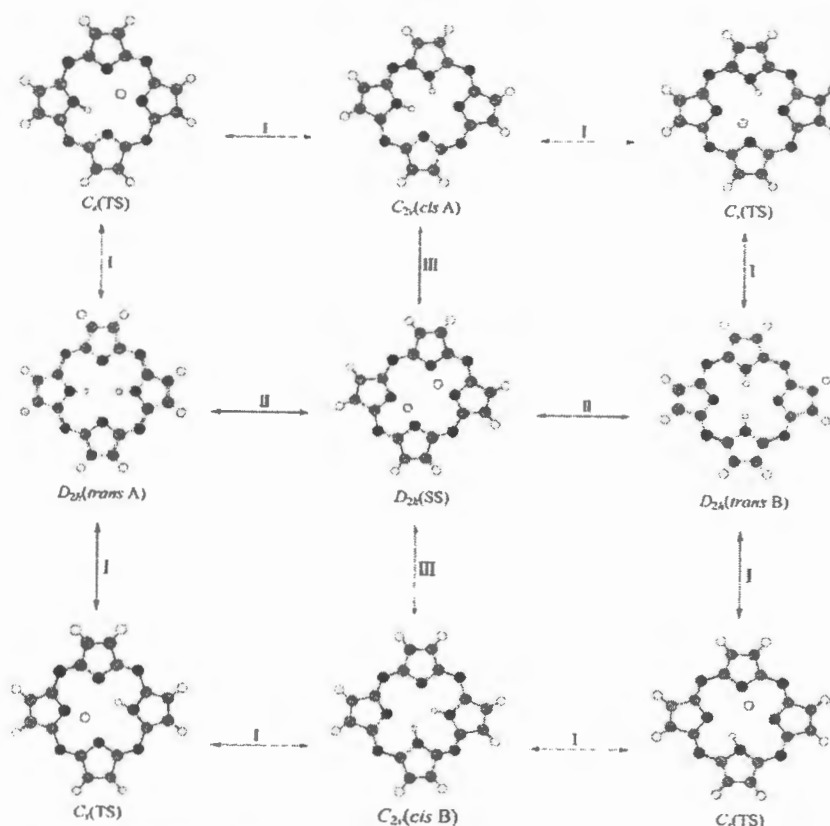


Figure 2.1.5 Schematic diagram of the inner hydrogen tautomerization process of free-base. Path I describes the stepwise mechanism, and path II describes the concerted mechanism⁷⁸

The concerted mechanism was found to involve synchronous migration of both H atoms (Figure 2.1.5, path II). The double proton transfer occurs via a two-step mechanism involving a metastable *cis*-intermediate rather than by a synchronous step (path I).^{78,79}

2.2 HISTORICAL BACKGROUND

2.2.1 Synthesis of different metal-porphyrazines

The first metallated porphyrazinediol was prepared by Bellec⁸⁰ from (L)-(+)-dimethyl tartrate via conversion into the corresponding dispoke or 2,3-dimethoxy-2,3-butanediyl protected

2,3-dihydroxymaleonitrile, Instead macrocyclization, transmetallation and deprotection. He found the stability of these products to be very dependent on the nature of the metal ion in the cavity of the porphyrazine. The reactions of these porphyrazinediols were used to synthesize new solitaire porphyrazines.

The metal complexes of tetrapyridino porphyrazines were synthesized by a template procedure analogous to that of phthalocyanines. The most common methods use α -dicyanopyridine or α -dicarboxypyridine. Water soluble cationic tetra-2,3-pyridinoporphyrazines were prepared by Scott⁸¹ through quarternization of the pyridine nitrogen with dimethyl sulphate at low temperatures in dimethyl formamide.

Wang⁸² studied the synthesis of pyrazino porphyrazine derivatives functionalized with tetrathiafulvalene (TTF) units. During his studies, he synthesized the pyrazino porphyrazine system (metal-free and copper derivatives) by tetramerization of 2,3-dicyanopyrazine monomer units.

The structure of the metal free, zinc and copper derivatives were established by ^1H NMR spectroscopy, spectrophotometry, MALDI-TOF mass spectrometry, cyclic voltammetry and differential pulse voltammetry. The electrochemical redox behavior was found to be strongly solvent dependent. The two-stage oxidation of the tetrathiofulva units of the metal-free, zinc and copper porphyrazines was observed in the range of the solvent.

The reduction and oxidation of the pyrazino porphyrazine of the metal- free derivative was detected in benzonitrile. On excitation of the pyrazino porphyrazine system in the Q-band region no fluorescence was observed. This was assumed to be the consequence of the intramolecular charge transfer between the TTF moieties and the excited state of the central porphyrazine.

Kudrevich⁸³ prepared several derivatives of 2,3-dicyanopyrazine via condensation of o-quinones with diaminomaleonitrile. The metal- free tetra- 2,3-[5,6- (9,10-phenanthro)] porphyrazine was obtained from the dilithium derivative through demetallation in HCl. These compounds were found to have limited solubility in organic solvents such as quinolines and were aggregated in solutions.

To eliminate the aggregation phenomenon and to determine the spectral properties of the angularly annelated naphthalocyanine aza analogs, he prepared several isomeric tetra-2,3-[di-butyl-9, 10-phenanthro) pyrazino] porphyrazines. These complexes were synthesized via complexation of di-ter-butyl substituted 5,6-(9,10-phenanthro)-2,3 dicyanopyrazines with metal salts in the presence of urea, quinoline and tri-(n-butyl) amine.

A hypsochromic shift of the octaaza naphthalocyanines versus their carboxylic analogs was observed for all aza analogs, with the shift depending on the composition of the aromatic macrocycle. The results also showed that the first angularly annelated benzo ring addition cause a hypsochromic shift of about 25 nm of the Q-band

of the *tetra*-2,3-quinoxalino porphyrazine, whereas addition of a second condensed benzo ring had little effect.

Maizlish⁸⁴ synthesized unsymmetrical porphyrazines containing peripheral nitrogen heterocycles and chloro-, nitro or *tert*-butyl-substituted benzene rings. He managed to determine their spectral properties and their thermal stabilities in air.

On the other hand, Montalban⁸⁵ studied the synthesis and ring opening metathetic polymerization of porphyrazine benzonorbornadiene derivatives. The Benzonorbornadiene substituted porphyrazines were homo and co-polymerized with norbornene using $(C_{12}CyP)_2RUPh$ to provide dark green and blue polymers. These materials were characterized by GPC, UV-vis and EPR.

Anthony⁸⁶ assembled a series of chalcogen atom substituted porphyrazines and characterized them. He substituted the oxygen and sulphur chalcogen atom for methylene groups, sensitized and characterized heteroatom-enriched seven-membered ring dinitriles by IR, MS-UV-vis and H^1 NMR to examine the ring conformations. The unchalcogen-substituted Ni(II), Cu(II) and Zn(II) containing porphyrazines were also synthesized. The macrocycles were characterized and studied using UV-vis, IR, elemental analysis, cyclic voltammetry and electrical conductivity measurements.

2.2.2 Studies made on different metal porphyrazines

Hoffman and Barrett⁸⁷ groups did a sterling work on synthesis of quite a number of porphyrazines, which include the synthesis of porphyrazine-octathiolate $[\text{pzS}_2]_4^{-8}$, the dithiolate $[(\text{pzS}_2):(\text{pc})_3]^2$, and the two tetrathiolates *trans*- $[(\text{pzS}_2)_2:(\text{pc})_2]^4$, and *cis*- $[(\text{pzS}_2)_2:(\text{pc})_2]^{-4}$.

From their studies they could see that these porphyrazines were exhibiting unusual coordination within the macrocyclic cavity and by the peripheral ligating group. Since these macrocycles are electron rich, they also exhibited unusual UV-vis spectra, electrochemistry and magnetic properties.

Gulcema⁸⁸ studied some porphyrazines with dimethylamino or trimethyl ammoniummethyl-sulfanyl substituents in dichloromethane or dimethylsulfoxide solution by cyclic voltammetric methods. He characterized the voltammogram of the metal free octakis- (dimethyl-aminoethyl-sulfanyl)-porphyrazine by three one-electron reduction waves.

The voltammogram showed quasi-reversible behavior at all sweep rates and the same was found to hold for its cobalt(II) derivative. The quatinized octacationic derivative exhibited four one-electron reduction waves, which were reversible at all

sweep rates. He also investigated the reaction mechanism and diffusion coefficient.

Montalban⁸⁹ studied the photo-oxidation of hexapropyl bis-(dimethylamino) porphyrazine zinc(II). He found it to be autocatalytical. He also found that the triplet state of the *seco*-porphyrazine zinc(II) sensitizes the formation of excited state singlet oxygen with a quantum yield of 0.54. The subsequent cleavage of the pyrrole double bond that occurred gave the *seco*-porphyrazines zinc(II).

The photophysics of the two porphyrazines was examined using absorption, emission and transient absorption spectroscopy. The efficiency of the production of singlet oxygen was monitored by phosphorescence emission signature at 1270 nm.

Baumann⁹⁰ investigated the synthesis, structure and spectroscopy of complexes of the novel binucleating norphthalocyanine-2, 3-dithiolato ligand. During his study he found that the electronic absorption spectra of a series of porphyrazines in which the two peripheral sulphur atoms form thioether moieties with a modified benzyl-protecting group cause a strong splitting of the Q-band. He also observed that when the peripheral sulphurs bind a metal ion to form solitaire-porphyrazines the optical spectra closely resemble that of symmetrical phthalocyanine with unsplit Q-band.

Morgan⁹¹ studied synthesis and photodynamic activity of some porphyrazine derivatives. He started by synthesizing a number of porphyrazines via the cyclization of tricyanovinyl amines and dinitrile amines in pentanol solution of magnesium oxide. These porphyrazines were converted into their respective zinc chelates and tested for their ability to photoinactivate cells in the culture.

The results showed promise for application in photodynamic therapy.

The study of the synthesis and characterization of metal capped *cis*- and *trans*- porphyrazine tetrathiolates was done by Siebert.⁹² The spectroscopic and electrochemical studies showed that the physical properties of the *cis*- and *trans*- tetrathioether porphyrazines were different and this difference was found to be due to their distinct molecular symmetries.

Montalban⁹³ also studied the synthesis, structure and spectroscopy of the *seco*-porphyrazines. He found that the cleaved pyrrole rings in the *seco*- and *diseco*-porphyrazines caused about 50 to 70 nm red shifted split Q-band in the electronic absorption spectra.

Duerr⁹⁴ studied the medium effects on the photo physical properties of porphyrazine metal(II) complexes in micellar solutions. In his study he described the solubility of different porphyrazine metal complexes in cationic, neutral and anionic surfactants under various conditions. Optimal conditions were evaluated and photo physical properties of the dyes were measured. With light-scattering experiments, micellar shapes were measured and compared with theoretical models. Triplet absorption spectra of the porphyrazines were recorded and showed maxima similar to that of phthalocyanines.

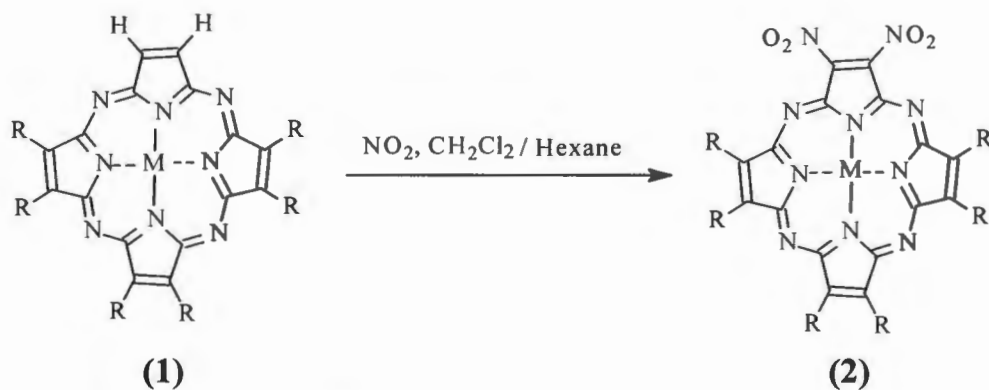
In the steady-state experiments photo induced electron transfer reactions of different porphyrazine metal(II) complexes were investigated for several electron acceptors and hydrogen was

evolved in some of the porphyrazine metal complexes in a four-component sacrificial system in order to check the photocatalytical properties of hydrophobic porphyrazines dissolved in surfactants.

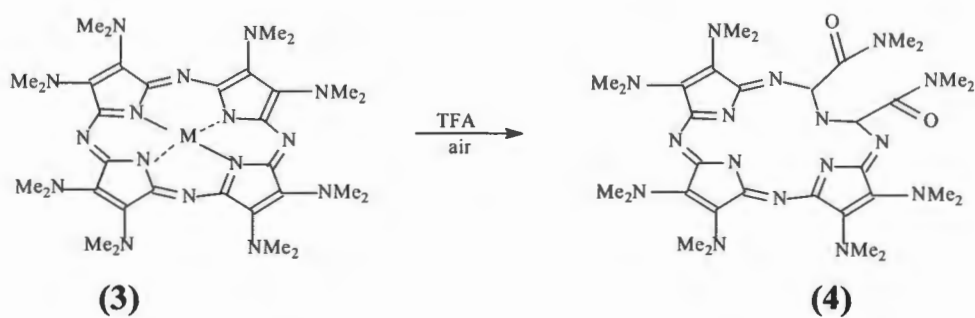
Nie⁹⁵ synthesized unsymmetrical porphyrazines with three substituted pyrroles at the periphery and one unsubstituted pyrrole, which he treated with trifluoroacetic acid. The result was the removal of the central metal to give a free base. The free base and the nickel porphyrazine were nitrated by nitrogen dioxide in dichloromethane to form dinitro porphyrazine. The porphyrazine hexaamine was easily oxidized with the first oxidation obtained at $E_{1/2}$ at -0.18V . Dinitro porphyrazine showed a 0.6V cathodic shift for the two reversible reduction waves compared to those observed for the parent porphyrazine.

2.3 CHEMISTRY OF PORPHYRAZINES

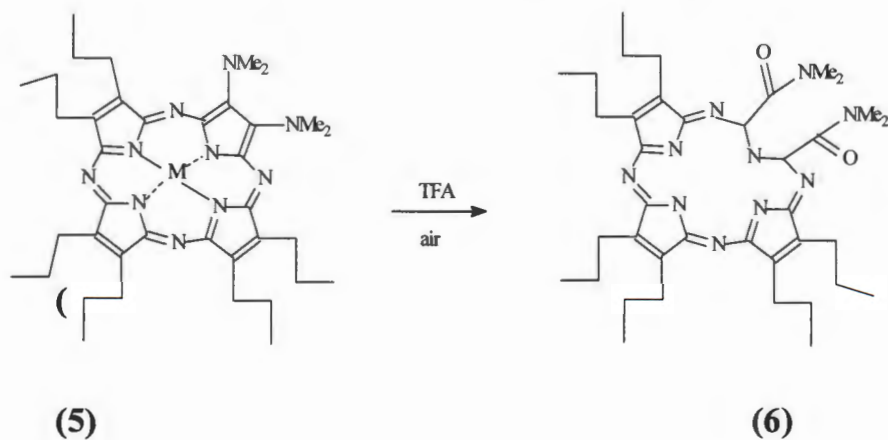
As compared to porphyrins and phthalocyanines, a lot of work is still to be done in order to understand the chemistry of porphyrazines.⁷⁸ At present, the chemistry of porphyrazines is wide open for exploratory research.⁷⁹ Treatment of porphyrazine (1) in dichloromethane with a solution of nitrogen dioxide in hexane at room temperature results in the rapid formation of dinitroporphyrazine (2)⁹⁶



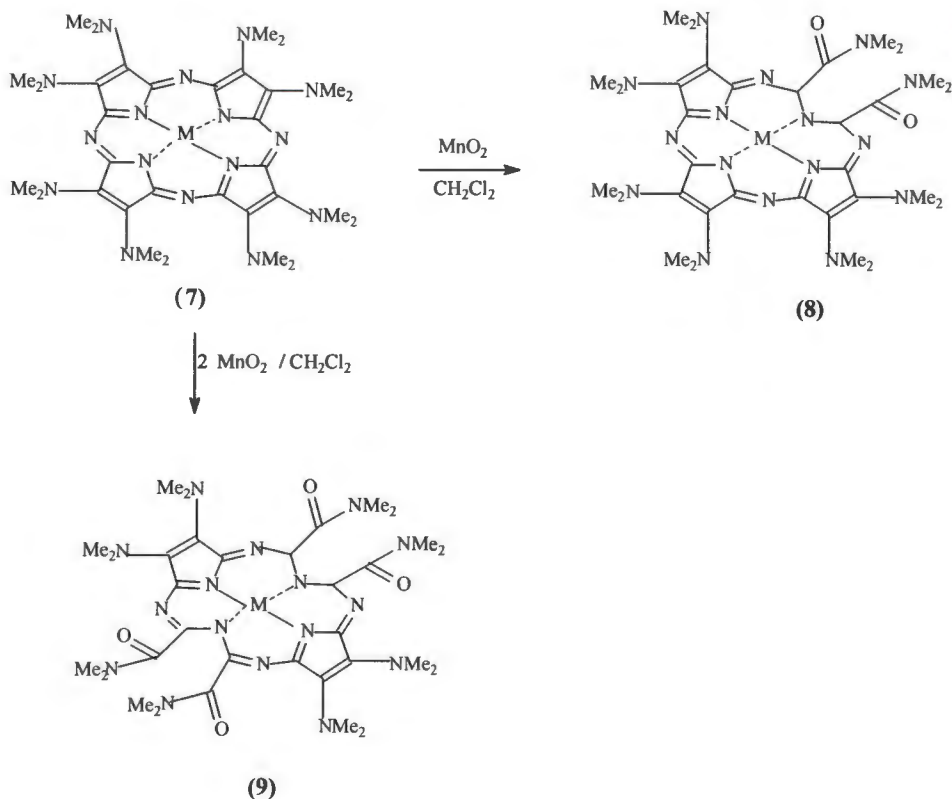
When compound (3) is treated with trifluoroacetic acid in the presence of air compound (4) is obtained.



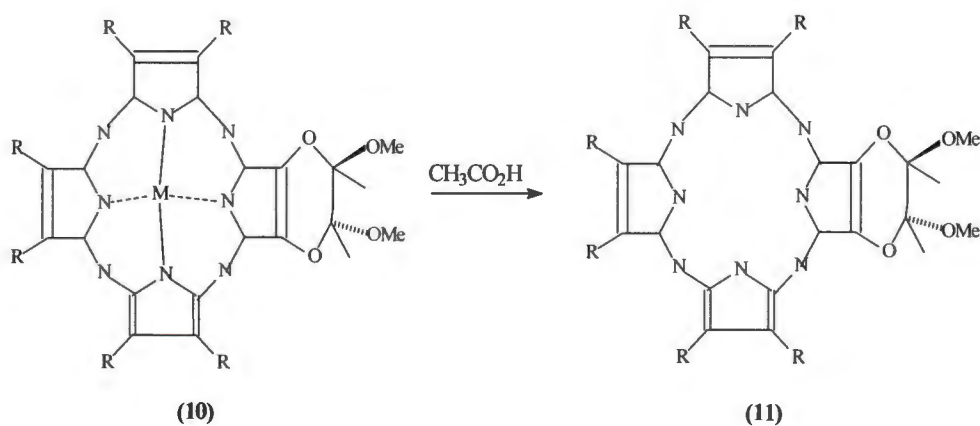
When porphyrazine (5) is reacted with trifluoroacetic acid in dichloromethane, a *seco*-porphyrazine (6) is obtained.⁹⁶



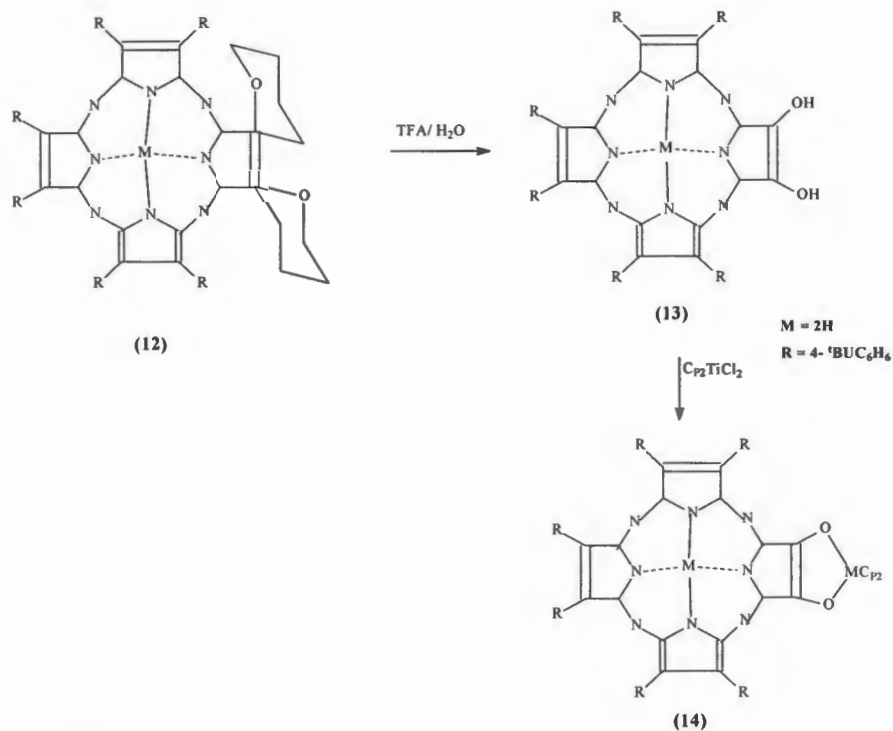
When porphyrazine (7) is treated with 1 and 2 equivalents of manganese dioxide for 4 and 24 hours respectively, compounds (8) and (9) are obtained respectively.^{96,97}



Reaction of porphyrazine (10) with glacial acetic acid gives the free base (11)⁹⁸



Treatment of porphyrazine (12) where $M = \text{Zn}$ with aqueous trifluoroacetic acid (95%) lead to the unstable diol (13). When the metal in the porphyrazine complex is nickel and the complex is reacted with metallocene dichloride, porphyrazine (14) is obtained.⁹⁹



2.4 RELATED MACROCYCLES

2.4.1 Porphyrins

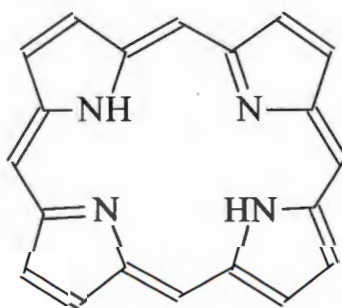


Figure 2.4.1 Structure of a porphyrin¹⁰⁷

Porphyrins were originally studied for their importance in oxygen transport, photosynthesis, energy production, metabolism and the disease porphyria.¹⁰⁷ There are a number of synthetic porphyrins prepared for several purposes ranging from basic research to functional application in society.¹⁰⁸ Photofrin, for example, is used for treatment of viral infections and cancer.¹⁰⁹

Other porphyrins are used as commercial oxidation catalysts to make fine chemicals and have applications in controlled-polymer synthesis.¹¹⁰ In addition to these current uses, there have been several hundred patents issued in the past few years for the use of porphyrins in molecular electronics and applications in novel functional materials.¹¹¹ Metallated porphyrins are able to mediate reactions such as epoxidation, cleavage of amides alkane hydroxylation, Diels-Alder cycloadditions and cyclopropanation. There has also been an interest in using porphyrins to make conjugated polymers with unusual electronic properties.¹¹¹

Conjugated porphyrin polymers are low band-gap organic semi-conductors and this high polarisability, intense absorption in the near infra-red and strong optical non-linearity makes them interesting materials for fabricating ultra-fast telecommunication switches.¹¹²

The different nature of porphyrin and porphyrazine ring is observed on the metal-to-ligand charge transfer and ligand-to-metal charge transfer transitions appearing in the spectra of transition metal complexes.¹¹³ The different size of the coordination cavity

causes the metal-ligand interaction to change going from porphyrin to porphyrazines.¹¹⁴

This simply means that, a metal atom complexed to a porphyrazine will experience a higher electrostatic potential than the one complexed to a similarly substituted porphyrin.¹¹⁵ The reason behind all these is that, the central nitrogens of porphyrazine have higher 1s ionization potential's than those of porphyrins.¹¹⁶

2.4.2 Phthalocyanines

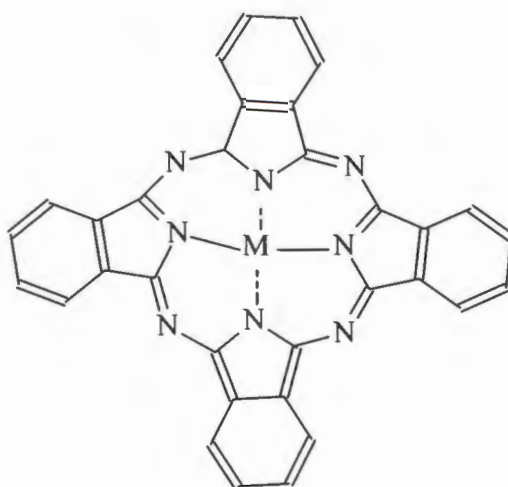


Figure 2.4.2 Structure of a phthalocyanine¹¹⁷

Phthalocyanines are by far the most investigated from the above-mentioned tetrapyrrole molecules.¹¹⁷ The metal-free phthalocyanine (H_2Pc) was first synthesized by Braun³⁸ and Tcherniac³⁸, while De Diesbach³⁸ and Von der Weid³⁸ originally obtained $CuPc$. In the following years many other metal phthalocyanines have been obtained, and Linstead³⁹ and coworkers initiated comprehensive study of their properties. Ever since,

phthalocyanines have been used as blue and green dyes, and pigments.¹¹⁸

Most of phthalocyanines were found to be chemically and thermally stable,¹¹⁹ subliming without decomposition, which makes them particularly attractive for the preparation of thin films by vacuum sublimation.¹¹⁹⁻¹²² Therefore, they were used practically in different technology sectors, applications including, chemical sensors,^{123,124} computer read/write discs,^{124,125} Langmuir-Blodgett films,^{126,127} photoconducting materials in laser printers,¹²⁸ as well as sensitizers for photodynamic therapy,¹²⁹⁻¹³³ liquid crystals, energy conversion (photovoltaic and solar cells),^{134,135} and non-linear optics.¹³⁶ Despite all the positive properties of phthalocyanines, a major detraction to their general use is their limited solubility.

2.4.3 Naphthalocyanines

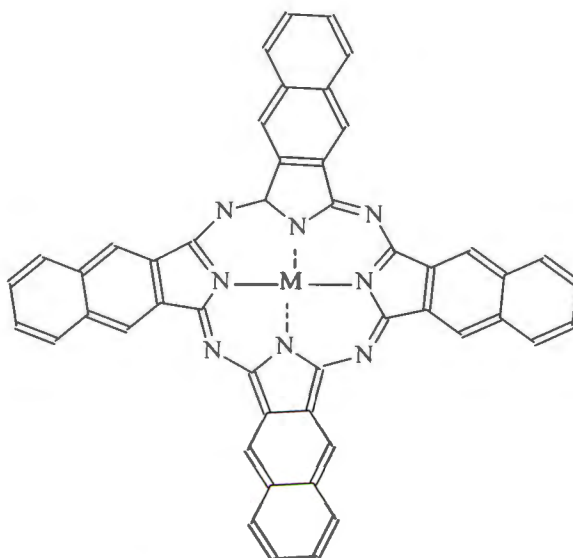


Figure 2.4.3 Structure of a Naphthalocyanine¹³⁷

Naphthalocyanine compounds have been the object of studies mainly because of their electrooptic characteristics and application in the field of the solar energy conversion, laser, electrophotography, photosensitization and electrocatalysis.¹³⁷⁻¹³⁹

When compared to phthalocyanines and porphyrazines, Nalwa¹⁴⁰, observed a progressive red-shift in optical absorption peaks in the Q-band region and an increase in the third-order non-linear optical susceptibility with sequential increase of benzo substitution from the porphyrazine to naphthalocyanine ring.

On the other hand, Kobayashi¹⁴¹ found that the Q-band shift was not linear with respect to the number of benzene units, but its extent decreases with increasing molecular weight. In other words, the substituent effect of the outer benzene unit of naphthalocyanine is smaller than that of the inner one compared with phthalocyanine and porphyrazine.

Chen¹⁴² and co-workers also observed that gallium naphthalocyanines have their Q-bands shifted about 100 nm towards the longer wavelength when compared to corresponding gallium phthalocyanine.

Isaacs¹⁴³ found that the redox processes on cobalt-phthalocyanine are more reversible than the cobalt-naphthalocyanine. In the case of cobalt-naphthalocyanine, the redox couples observed were found to involve the macrocyclic ligand instead of the metal for cobalt-phthalocyanine. They also have aggregation problems which must always be prevented by ether, alcohol and amines.

2.5 KINETIC STUDIES

Kinetics is the description of reaction rates. The order of a reaction defines the dependence of reaction rates on the concentrations of reacting species. Order is governed by the mechanism of the reaction, that is, by the number of species that must collide in order for the reaction to occur.¹⁴⁴

As indicated, not much work has been done on kinetics of insertion of metal ion into the inner core of porphyrazines. However, noticable contribution in this regard was done by . Nyokong.¹⁴⁵ et. al and Wöhrle¹³⁴ D.et. al.

The study which was undertaken by Nyokong et. al was based on redox properties and interactions of palladium(II) tetramethyl pyridino porphyrazine $[\text{Pd} (\text{Tmtppa}(-2))]^{4+}$ and Platinum(II) tetramethyl pyridinoporphyrazine $[\text{Pt} (\text{Tmtppa}(-2))]^{4+}$ complexes with cysteine and histidine. The spectral changes of these reactions with time were monitored by UV-vis.

On bulk electrolysis the colour of the reactions changed from blue to purplish-blue. The Q-band decreased in intensity and a new broad and weak band was observed near 525 nm. The newly formed spectrum of $[\text{Pd} (\text{Tmtppa}(-3))]^{3+}$ and $[\text{Pt} (\text{Tmtppa}(-3))]^{3+}$ maintained isosbestic points at 641, 545 and 368 nm respectively.

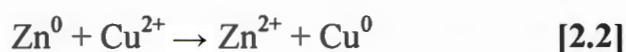
With regard to Wöhrle¹³⁴ et. al. studies, one electron reduction of $[\text{Zn} (\text{Tmtppa}(-2))]^{4+}$ was used. The absorption band for the reduction product of $[\text{Zn} (\text{Tmtppa}(-2))]^{4+}$ which is $[\text{Zn} (\text{Tmtppa}(-$

3))] $^{3+}$ was observed at 570 nm. Comparing both these studies, it was concluded that the differences in their absorption spectra was due to the effects of the central metal ions and reduction was due to one electron transfer.

2.6 MECHANISMS OF INORGANIC OXIDATION-REDUCTION REACTIONS IN OCTAHEDRAL COMPLEXES

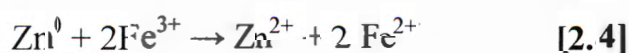
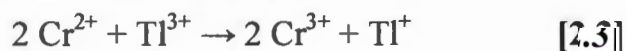
Inorganic oxidation-reduction reactions involving the transfer of at least one electron from a reducing agent to an oxidizing agent are widely used in analytical procedures and are important in many biological processes. The change in oxidation state of the reducing agent and the oxidizing agents in a reaction could also be classified as either complementary or non-complementary.¹⁴⁶⁻¹⁴⁹

A typical oxidation reduction reaction involving chromium and silver (equation 2.1) or zinc and copper (equation 2.2) could be represented as follows:



This is an example of a complementary stoichiometric oxidation reduction reaction.

When the oxidizing agents and reducing agents undergo different net changes in oxidation state, a non-complementary stoichiometric reaction takes place (Equation 2.3 and 2.4)



Complementary reactions have been observed to be faster than the non-complementary reactions. The mechanistic rationale for this observation is based on the fact that reactions take place in bimolecular steps.¹⁴⁶⁻¹⁴⁹

2.7 INNER SPHERE AND OUTER SPHERE MECHANISMS

The determination of the type of mechanism involved in a reaction requires the application of kinetics. The kinetic features of a reaction could be employed in determining if a reaction proceeds by an 'Inner-sphere electron transfer' or an 'Outer-sphere electron transfer' process.¹⁴⁹

2.7.1 Inner sphere electron transfer

Inner-sphere electron transfer requires that the oxidant and the reductant be firmly bonded during the act of electron transfer and that a bridge is formed by at least one ligand that is common to the coordination sphere of the oxidant and reductant through which the electron is transmitted.¹⁴⁹ An example of such a reaction is shown in Figure 2.7.1

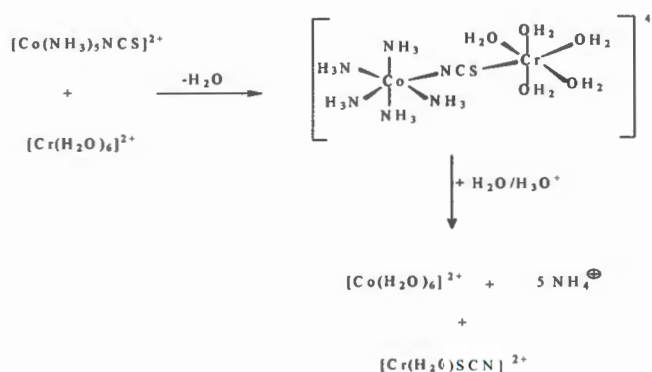


Figure 2.7.1 Figure showing the inner-sphere electron transfer mechanism¹⁴⁹

A wide range of bridging ligands are known. These include halide ions, hydroxide ions and carboxylate ions. Ammonia cannot act as a bridging ligand because it does not have a second unshared pair of electrons, which is necessary for simulating bonding to the oxidizing and reducing centre.¹⁴⁴

2.7.2 Outer sphere electron transfer

In an outer-sphere electron transfer, the interaction between the oxidant and the reductant at the time of electron transfer is small and they go through the process with the coordination sphere of the oxidant and reductant remaining intact during the electron transfer.¹⁴⁴ The general reaction is represented in equation 2.5 while a typical reaction is shown in Figure 2.72

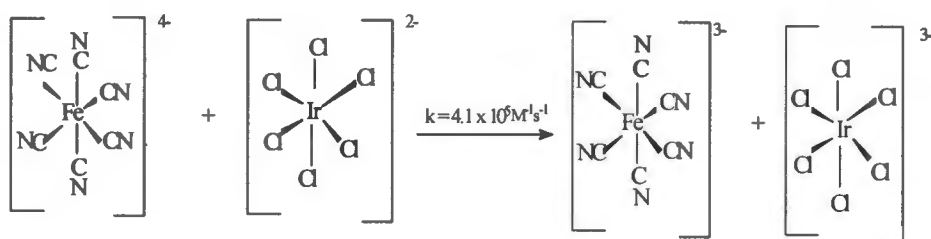
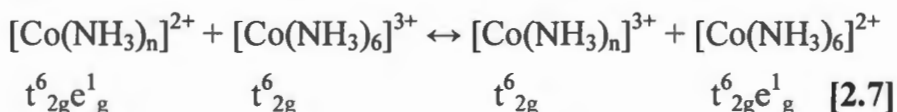
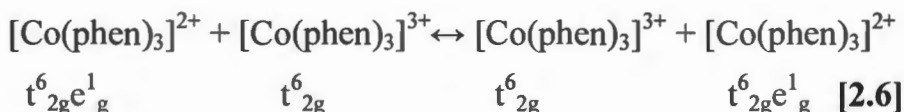


Figure 2.7.2 Figure showing the outer-sphere electron transfer mechanism¹⁴⁴

These types of reactions are believed to occur via an electron tunnelling mechanism takes place. A mechanistic decision between the inner- and outer-sphere possibilities is often based on whether or not the reaction rate corresponds reasonably to the predictions of the outer-sphere theory.¹⁴⁴

2.8 FRANCK-CONDON RESTRICTION

Electron transfer processes must satisfy the Frank-Condon restrictions, which arise in principle from the fact that the act of electron transfer takes place with a time of about 10^{-15} seconds. This means that the atomic nuclei remain frozen in position during the act of electron transfer.



In the reaction **2.6** an electron is transferred from the e_g orbital of one cobalt to that of another cobalt, whilst in the second reaction **2.7** there is an electron transfer as well as a change in spin multiplicity.¹⁵⁰ It is therefore against this background that oxidation reduction in this research is explained.

CHAPTER THREE

EXPERIMENTAL

3.1 Materials

All materials were purchased from Aldrich and used as received

3.1.1 Analytical and chemically pure solvents

All solvents used for column chromatography were dried or distilled. Hexane (CP) was purified by distillation. Ethyl acetate (CP) was distilled from anhydrous potassium carbonate. Methanol (AR) which was distilled from Mg and dichloromethane was dried from CaCl_2 under reflux. THF used for column chromatography was of analytical grade and was used without distillation. The DMSO was stored under molecular sieves (4A, 3.2 mm) for a long period before use. Reactions were performed under nitrogen atmosphere.

3.1.2 Dry solvents

Tetrahydrofuran (THF) was heated over sodium benzophenone under nitrogen (N_2) until a blue colour persisted with subsequent distillation under nitrogen prior to use.

Dimethylformamide (DMF) and dichloromethane were heated under reflux with CaH_2 under nitrogen atmosphere. Both DMF and dichloromethane over molecular sieves were stored under argon

3.1.3 Chromatography

Thin-layer chromatography was performed using Merk 60 F254 silica gel sheets. Chromatograms were eluted using different solvents systems as indicated for column chromatography. Solvent system ratios refer to volume per volume (v/v) ratios. Detection of compounds was

accomplished by their fluorescence under ultraviolet light (245 nm) and iodine. 'Flash column chromatography' was carried out on Merck Kieselgel 60 (230-400 mesh) under nitrogen pressure. Eluents were mixed in different ratios depending on the nature of the compounds.

3.1.4 Spectroscopic data and methods

NMR spectra were recorded at University of Johannesburg (RAU) on a Varian Gemini 300 MHz spectrometer in CDCl_3 . ^1H NMR data (300 MHz) are listed in the order chemical shift (δ) reported in ppm and referenced to the residual solvent peak of CDCl_3 (7.24 ppm). The coupling constant J (Hertz) was reported to the nearest 0.1 Hz and multiplicities were given as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), q (quartet), hp (heptet) and m (multiplet). Proton decoupling experiments were performed to assist in the assignment of proton signals.

^{13}C NMR data are listed in the order: chemical shift (δ) in ppm and referenced the residual solvent peak of CDCl_3 ($\delta = 77.0$ ppm)

Infra-red spectra were recorded on a Nicolet 410 impact fourier transform infrared spectrophotometer using nujol and potassium bromide cells. The range of interest was between 4000 cm^{-1} and 500 cm^{-1} .

The ultraviolet-visible absorption spectra were measured in a 1 cm quartz cell using either a Unicam SP 8700 spectrophotometer or a Varian Cary 50 ultraviolet-visible spectrophotometer. Measurements were made from 300 nm to 800 nm

3.2 SYNTHESIS OF COMPOUNDS

3.2.1 Synthesis of 4,5-dibromo-4E-octene

Bromine (12.060 ml, 0.149 mol) in acetic acid (300 ml) was added dropwise to 4-octyne (**1**) (67 ml, 0.151 mol), which was dissolved in acetic acid (75 ml). Addition was done for 4 hours after which the reaction mixture was allowed to run for 2 hours. After 2 hours, the reaction contents were poured in ice-cold water (800 ml). This was followed by extraction with dichloromethane (300 ml x 4) and the dichloromethane extract was washed with sodium hydrogen carbonate (300 ml x 3) followed by water (300 ml x 3). The extract was then dried with anhydrous magnesium sulphate and filtered. Evaporation of the solvent left the yellowish brown oil, which was distilled under reduced pressure of 110° C.

Yield = 55.011 g, 0.068 moles, %Yield = 45.3, R_f = 0.31 (Hexane, 100%). ^1HNR (300MHZ, CDCl_3) δ 0.93 (t, 4H, $J=7.4$ Hz), 1.60 (m, 4H), 2.64 (t, 6H, $J=7.5$ Hz) ^{13}C (300 MHz, CDCl_3) 13.02, 22.63, 42.56, 121.62

3.2.2 Synthesis of 2,3-dipropylfumaronitrile

Copper cyanide (23.664g, 0.268 mol) in DMF (250 ml) was heated to 145° C until the solution turned clear. The contents of the flask were then cooled to 130° C followed by addition of 4,5-Dibromo-4E-octene (**2**) (23.120g 0.088 mol). The reaction was left heating at 130° C for 18 hours after which it was cooled to room temperature. The mixture was then poured in concentrated ammonium hydroxide (600 ml) and stirred for 40 minutes. This was followed by filtration of the solids, which were washed with ethyl acetate. The filtrate was extracted with ethyl acetate (200 ml x 3). The ethyl acetate extract and washing from the solids were washed with water (200 ml x 3), followed by sodium chloride (200 ml x 2). The organic layer was then dried with anhydrous magnesium sulphate. The

solvent was removed under reduced pressure and the resulting brown oil was distilled under reduced pressure to give clear oil, which was collected at 110° C.

Yield = 5.240g, 0.035 mol. %Yield = 40, R_f = 0.51 (hexane, 100%).

^1H NMR (300MHz, CDCl_3) δ 0.97(t, 4H, $J=7.5\text{Hz}$), 1.65(m, 4H), 2.52(t, 6H, $J=7.4\text{Hz}$) ^{13}C (300MHz, CDCl_3) 13.08, 21.23, 35.67, 115.34, 129.10

3.2.3 Synthesis of 2,3-dipropylmaleonitrile

2,3-Dipropylfumaronitrile (**3**) (6.335g, 0.043 mol) in acetonitrile (120 ml) was dissolved in a Rayonet photochemical reactor round bottom flask that was sealed with parafilm. Nitrogen was bubbled through the solution, which was stirring. The solution was irradiated with light for 39 hours after which the solvent was removed under reduced pressure. The dark brown solution was distilled under reduced pressure to give clear oil, which was collected at 130° C.

Yield = 2.007g, 0.014 mol; %Yield = 32.5; R_f = 0.20 (hexane, 100%).

^1H NMR (300MHz, CDCl_3) δ 0.97 (t, 4H, $J=7.5\text{Hz}$), 1.66(m, 4H), 2.52(t, 6H, $J=7.4\text{Hz}$); ^{13}C (300MHz, CDCl_3) 8.69, 16.83, 31.27, 110.94, 124.70

3.2.4 Synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium

Butanol (20 ml), magnesium (77 mg, 3.17) and iodine crystal were refluxed for 24 hours after which 2,3-dipropylmaleonitrile (**4**) (300 mg, 0.831 mol) was added in suspension of magnesium butoxide and the reaction mixture refluxed for the 24 hours away from direct light. After 24 hours the brownish purple solution was evaporated and the residue was re-dissolved in ethyl acetate. It was then purified using flash column

chromatography with the solvent system ethyl acetate: dichloromethane (1: 10).

Yield = 92mg, 0.136 mol; %Yield = 4.3; R_f = 0.61, ethyl acetate: dichloromethane (1:10). ^1H NMR (300MHz, CDCl_3) δ 1.35 (t, 24H, $J=7.5\text{Hz}$), 2.52 (hp, 16H, $J=7.4\text{Hz}$), 4.06(t, 16H, $J=7.5\text{Hz}$); ^{13}C (300MHz, CDCl_3) δ 15.20, 26.22, 28.84, 30.08, 30.59, 122.78, 123.17, 123.50, 123.83, 134.81, 135.17, 135.50, 135.82, 143.92, 149.47, 149.83, 150.19, 158.82

3.2.5 Synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine base

Removal of magnesium from 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine magnesium (**5**) (0.58g) was accomplished by heating at reflux in a $\text{CHCl}_3/\text{AcOH}$ (20:1) solution (200 ml), which was made basic by the addition of NaOH. The organic layer was separated, washed once with 10% aqueous NaOH (50 ml) dried (Na_2SO_4), and filtered. The 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine base was adsorbed onto a silica gel, column chromatographed and eluted with $\text{CH}_2\text{Cl}_2/\text{Hexanes}$ (1:1). Slow evaporation of the solvent gave a microcrystalline solid, which was recrystallized by slow diffusion of benzene into a CHCl_3 solution of the. 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine base (**6**)

Yield = 0.48g, %Yield = 0.827, R_f = 0.413 (Hexane: ethyl acetate, 10:1) ^1H NMR (CDCl_3) δ = -2.11 (s, 2H, NH), 1.86 (t, 24H, $J = 7.7\text{ Hz}$, CH_3), 3.98 (q, 16H, $J = 7.7\text{ Hz}$, CH_2CH_3)

3.2.6 Synthesis of 3,6-bis(isopropoxy)-1,2-benzenedinitrile

To 3,6-dihydroxy-1,2-benzenedinitrile (**9**) (21.62g, 0.135mol) and excess potassium carbonate (41.800g, 0.299mol) in DMF (300 ml), 2-bromopropane (34.8 ml, 0.371 mol) was added. The reaction mixture was heated at 60° C for 68 hours. After 68 hours the contents of the flask were then poured in water (1000 ml) and stirred vigorously. The resulting precipitate was filtered under reduced pressure and washed with water (7 times). It was repeatedly purified by mixing with hot methanol and the solids vigorously stirred for 10 minutes and filtered (5 times). The crystalline material was washed with hot methanol and collected as white crystals.

Yield = 21.993g, %Yield = 66.7, R_f = 0.41 (hexane: dichloromethane, 1:1.5) ^1H NMR (300MHz, CDCl_3) δ 1.37(d, 12H, $J=6.0\text{Hz}$), 4.55(hp, 2H, $J=6.1\text{Hz}$), 7.13(s, 2H); ^{13}C (300MHz, CDCl_3) 21.91, 73.69, 106.69, 113.20, 120.54, 154.33

3.2.7 Synthesis of 4,7-bis(isopropoxy)-1,3-diiminoisoindole

The 3,6-Bis(isopropoxy)-1,2-benzenedinitrile (**10**) (14.48g, 0.059 mol) was suspended in 1,2-ethanediol (250 ml). 1.0g of sodium was added and the mixture was heated to 130°C for 20 minutes. This was followed by bubbling ammonia into the mixture for 4 hours 30 minutes at a temperature of 145°C. The solution was then allowed to cool down to room temperature and then poured in water (700 ml). The resulting precipitate was filtered and recrystallised in methanol. Yellowish crystals of 4,7-Bis(isopropoxy)-1,3-diiminoisoindole were collected.

Yield = 9.98g, 0.038 mol; %Yield = 64.4; R_f = 0.13 (Dichloromethane: Hexane, 3:2) ^1H NMR (300MHz, CDCl_3) δ 1.39 (d, 12H, $J = 6.0 \text{ Hz}$); 4.63 (hp, 2H, $J = 6.1 \text{ Hz}$), 6.93 (s, 2H), 8.18 (s, 1H) ^{13}C (300 MHz, CDCl_3) 22.20, 71.55, 117.51, 123.41, 148.11

3.2.8 Synthesis of bis(dimethylamino) maleonitrile

Diaminomaleonitrile (2.290g, 0.021 mol) in DMF (70 ml) was added dropwise to sodium hydride (4.300g) in DME (50 ml) at -30° C. The reaction mixture was warmed to -10° C and dimethyl sulphate (10.4 ml) was slowly added until finished after which the reaction mixture was stirred for 1 hour at -10° C and left stirring for 19 hours at room temperature. This was followed by filtration of the mixture and the precipitate washed with DME (200 ml). The combined filtrate and washing were concentrated by evaporation of the solvent under reduced pressure. The residue was dissolved in dichloromethane and washed with water (100 ml x 5). The organic layer was then dried with anhydrous MgSO₄, filtered and the solvent evaporated under reduced pressure. The mixture of bis(dimethylamino)fumaronitrile and bis(dimethylamino) maleonitrile was separated by flash column chromatography using solvent system of ethyl acetate: hexane (1:8).

Yield = 1.620g, 0.010 mol, %Yield = 46.6, R_f = 0.16 [hexane:ethyl acetate, (4:1)] ¹H NMR (300MHz, CDCl₃) δ 2.74(s, 12H) ¹³C (300MHz, CDCl₃) 43.68, 113.64, 119.34

3.2.9 Synthesis of N, N, N', N'-tetramethylamino porphyrazine hybrids

Butanol (30 ml) and magnesium (210 mg, 8.64 mmol) were refluxed for 24 hours. This was followed by addition of bis(dimethylamino) maleonitrile (**16**) (270 mg, 1.642 mmol) in butanol (5 ml) and 4.7-(isopropoxy)-1,3-iminoisoindoline (**15**) (1230 mg, 4.701 mmol) in butanol (5 ml) in suspension of magnesium butoxide. The reaction mixture was refluxed for the next 24 hours away from direct light. After 24 hours the brownish purple solution was evaporated under reduced pressure after which the residue was re-dissolved in dichloromethane (60

ml) followed by addition of acetic acid (20 ml). The reaction contents were vigorously stirred for 2 hours in ice-bath. After 2 hours the reaction mixture was poured in ice with concentrated ammonium hydroxide (50 ml) and stirred for 30 minutes. After 30 minutes, the aqueous and organic layers were separated. This was followed by extraction of the aqueous portion with dichloromethane (3 x 150 ml) and the two organic layers were mixed and dried with anhydrous sodium sulphate. Sodium sulphate was filtered and the solvent evaporated under reduced pressure. The sample mixture was purified by column chromatography on flash silica gel using the solvent system of ethyl acetate: dichloromethane: toluene (1:8:6) as eluent. Three components were separated as pure fractions. The bulk sample was re-separated using a mixture of ethyl acetate: dichloromethane: toluene (0.5: 1: 4) as eluent on flash silica. Major product (N,N,N',N'-tetramethylamino porphyrazine hybrid) (**17**) was separated as pure.

Yield = 97 mg, 0.108 mmol, %Yield = 6.6 ^1H NMR (300MHz, CDCl_3) δ (s, 6H), 4.95 (m, 1H), 5.10 (m, 1H), 5.17 (m, 1H), 7.37 (d, 2H, $J=9\text{Hz}$), 7.46 (d, 2H, $J=8.7\text{Hz}$); ^{13}C (300MHz, CDCl_3) δ 22.71, 22.78, 30.97, 44.57, 70.77, 75.24, 75.53, 114.50, 122.58, 124.26, 125.06, 128.54, 128.77, 130.84, 131.02, 135.05, 140.73, 140.80, 148.63, 150.48, 150.97

3.2.10 Synthesis of 1,2-diisocyano-4-phenoxybenzene

To NaH (0.15g), phenol (0.353g, 0.0375 mol) in THF (15 ml) was added and 4-nitrophthalonitrile (0.50g, 0.0028 mol) in THF (15 ml) was added to the solution and the reaction was allowed to run for 8 hours. The resulting 1,2-diisocyano-4-phenoxybenzene (**20**) was filtrated and the solid washed with ethyl acetate and both the filtrate and the washing were mixed and evaporated under reduced pressure. The resulting white

precipitate was purified by flash column chromatography using solvent system, ethyl acetate: hexane (1: 4).

Yield = 0.737g, %Yield = 86.4, R_f = 0.36 (ethyl acetate: hexane, 1:4)

^1H NMR (300MHz, CDCl_3) δ -0.90 (s, 2H), 3.46 (m, 5H, CH) 7.07 (m, 3H, ArH), ^{13}C NMR (300MHz, CDCl_3) δ 71.01, 117.45, 119.69, 119.92, 126.95, 127.34, 134.43, 135.20

3.2.11 Synthesis of 2,3-Benzo[3,6-bis(isopropoxy)]-7,8,12,13,17,18-hexapropyl porphyrazine

A mixture of magnesium (60.0 mg, 2.50 mmol) and iodine crystal in butanol (40 mL) was refluxed for 24 hours after which it was allowed to cool to room temperature. This was followed by addition of 2,3-dipropyl maleonitrile (200 mg, 1.23 mmol) and 4,7-bis(isopropoxy)-1,3-diiminoisoindoline (32.0 mg, 0.123 mmol). The reaction mixture was heated for additional 24 hours and allowed to cool to room temperature. Butanol was evaporated under reduced pressure and the residue was dissolved in ethyl acetate and filtered to remove impurities. The crude mixture was partially purified using gradient column chromatography (hexane: ethyl acetate, 8:1 then 1:1). Magnesium was removed by treatment of dichloromethane solution of the crude product with acetic acid for 3 hours. The mixture was neutralized with NaOH solution and the precipitate formed was filtered and taken up into ethyl acetate. The aqueous solution was extracted with ethyl acetate and the combined ethyl acetate solutions were washed with water and dried over anhydrous MgSO_4 . Purification was performed using flash column chromatography (hexane: dichloromethane, 1:1) to yield 2,3-Benzo[3,6-bis(isopropoxy)]-7,8,12,13,17,18-hexapropyl porphyrazine (24.0 mg, 27 %) as a blue solid product after precipitation from methanol.

Yield = 24.0 mg, %Yield = 27.0, $R_f = 0.17$ (hexane: dichloromethane, 1:1) ^1H NMR (300MHz, CDCl_3) δ 7.53 (2H, s, H-2, H-3), 5.35 (2H, sept, $J = 5.9$ Hz, 2 x CH_3CHCH_3), 4.07 (4H, t, $J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.98 (4H, t, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.79 (4H, t, $J = 7.1$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.30 (12H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.81 (12H, d, $J = 5.7$ Hz, 2 x CH_3CHCH_3), 1.26 (18H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), ^{13}C NMR (300MHz, CDCl_3) δ 162.0 (C-1, C-4), 2 x 158.9, 2 x 149.3, 2 x 145.9 and 2 x 145.1 (C-1, C-4, C-6, C-9, C-11, C-14, C-16, C-19), 2 x 144.7, 2 x 141.6, 2 x 140.8 and 2 x 130.0, (C-2, C-3, C-7, C-8, C-12, C-13, C-17, C-18), 2 x 118.3 (C-2, C-3), 2 x 71.8 (2 x CH_3CHCH_3), 29.7, 2 x 28.3, 2 x 28.1 and 27.9 (6 x $\text{CH}_2\text{CH}_2\text{CH}_3$), 2 x 25.5, 2 x 25.4, 2 x 25.2 and 22.9 (6 x $\text{CH}_2\text{CH}_2\text{CH}_3$), 3 x 14.8 and 3 x 14.7 (6 x $\text{CH}_2\text{CH}_2\text{CH}_3$).

3.2.12 Synthesis of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine

1,2-Diisocyano-4-phenoxybenzene (**20**) (0.300g, 1.36×10^{-3} mol) was refluxed in 1-pentanol (14 ml) in the presence of 1 mol 1,8-Diazabicyclo[5.4.0]-undec-7-ene (0.21 g, 1.36×10^{-3} mol) for 16 hours. Methanol (20 ml) was added and the precipitate (**21**) filtered off, soxhlet extracted with methanol and acetone and dried at 60°C .

Yield = 0.294g, %Yield = 43 $R_f = 0.23$ ((ethyl acetate: hexane, 3:8) ^1H NMR (300MHz, CDCl_3) δ -2.01 (s, 2H, NH), 3.66 (m, 4H, CH), 6.99 (m, 4H, ArH), 7.23 (m, 4H, ArH), 7.50 (m, 4H, ArH) 8.04 (m, 4H, ArH), 8.99 (m, 4H, ArH), 9.23 (m, 4H, ArH), ^{13}C (300MHz, CDCl_3) δ 71.01, 76.57, 76.99, 77.41, 117.45, 119.69, 119.92, 126.95, 127.48, 127.63, 128.53, 128.85, 128.94, 134.43, 135.20

3.2.13 Synthesis of tetranitro phthalocyanine base

4-Nitrophthalic anhydride 13.5 g (0.078 mol) was heated to 160°C until it melted completely. Then 5.0 g (0.020 mol) of lead monoxide was added in small portions with constant stirring. The reaction mixture was maintained at 140°C with constant stirring for 4 hours. The deep green solid was obtained by washing the product with glacial acetic acid and hot ethanol and dried at 70°C for 2 hours

Uv-visible electronic absorption bands, λ_{max} (nm): 302, 654, 715 (DMSO). IR absorption bands (cm^{-1}): 3095 m, 1610 m, 1521 s, 1483 m, 1337 s, 1252 m, 1135 m, 1081 s, 921 m, 846 s, 749 s, 728 s, 671 m, 477 s, 435 s.

3.2.14 Elemental Analysis

The elemental analyses of metal porphyrazine complexes were performed at the instrumental analysis laboratory of the University of Cape Town. The microanalytical results are displayed in Table 4.5.1-4.5.10

3.3 KINETIC STUDIES

A chemical reaction can be investigated by means of three approaches:

- ❖ *Thermodynamic* approach – According to this approach, a plausible reaction path can be predicted by determining energy differences between reagents and products. Equilibrium concentrations of the reagents and products can also be predicted. However it gives no indication of how fast equilibrium is reached.
- ❖ *Quantum mechanical* approach – This approach focuses on the structural aspects of the reagents and products in their isolated forms. It gives no kinetic information, but can be useful to assist in postulating a reaction mechanism.
- ❖ *Kinetic* approach – It is based on the study of the reaction rate as a function of process-controlling factors. These process-governing

factors include: the nature of the reagents, reagents concentration, the solvent, the presence of a catalyst in the reaction mixture, the pH of the reaction mixture, ionic strength, temperature as well as pressure at which the reaction proceeds

The advantage of a kinetic approach is that it leads to an understanding of the mechanism of a reaction and its analysis into a sequence of elementary reactions. Information about the mechanism of the reaction can be gathered by varying the process-governing factors, and normally only one factor is changed at a time in a monovariance fashion. Since a kinetic approach is the only approach giving information about reaction rates, it is therefore the most appropriate method to achieve the goals set for this research.

3.3.1 Procedure for the kinetic studies of the insertion of copper(II) metal ion to 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base

A spectrophotometric procedure was employed to study the reaction of insertion of copper(II) metal ion into the inner core of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base. In this method a solution of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base (5×10^{-6} M) in dichloro methane was made and allowed to equilibrate at 20°C. Another solution of copper(II) acetate (5×10^{-6} M) in acetic acid was also allowed to equilibrate at the same temperature. The two were mixed in the proportion of 3: 1 [copper(II) acetate: 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base] and quickly transferred to a 1 cm quartz cell in the thermostatted compartment of the Cary 50 spectrophotometer. The UV-vis absorption spectrum from 300 nm to 800 nm was then scanned at 5-minutes intervals. The reaction was also done

at 25°, 30°, 35°, and 40° C respectively. Readings were taken at $\lambda = 588$ nm

Maintenance of isosbestic point throughout the entire reaction meant that a simple reaction was being followed, that is, one reagent (A) is converted into another reagent (B) and where the two reagents have the same molar absorptivities, and an isosbestic point was obtained. This was important in the diagnosis of this reaction because it eliminated other possible reactions that could be occurring like, reduction of Cu^{2+} , reaction with the double bonds in the macrocycle, impurities in the solution or simple dissolution where more compound is dissolving as time goes by or decomposition of the final product.

3.3.2 Procedure for the kinetic studies of the insertion of cobalt(II) metal ion to 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base

A spectrophotometric procedure was employed to study the reaction of insertion of cobalt(II) metal ion into the inner core of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base. In this method a solution of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base (1.1×10^{-5} M) in dichloro methane was made and allowed to equilibrate at 50°C. Another solution of cobalt(II) acetate (1.1×10^{-5} M) in acetic acid was also allowed to equilibrate at the same temperature. The two were mixed in the proportion of 4: 1 [cobalt(II) acetate: 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base] and quickly transferred to a 1 cm quartz cell in the thermostatted compartment of the Cary 50 spectrophotometer. The UV-vis absorption spectrum from 300 nm to 800 nm was then scanned at 5-minutes intervals. The reaction was also done at 55°, 60°, 65°, and 70° C respectively. Readings were taken at $\lambda = 588$ nm

3.3.3 Procedure for the kinetic studies of direct metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium with copper(II) metal ion

A spectrophotometric procedure was employed to study the reaction of direct replacement of magnesium at the centre of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium by copper(II) metal ion. In this method a solution of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium (1.6×10^{-5} M) in dichloro methane was made and allowed to equilibrate at 25°C. Another solution of copper(II) acetate (1.6×10^{-5} M) in acetic acid was also allowed to equilibrate at the same temperature. The two were mixed in the proportion of 3: 1 [copper(II) acetate: 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium] and quickly transferred to a 1 cm quartz cell in the thermostatted compartment of the Cary 50 spectrophotometer. The UV-vis absorption spectrum from 300 nm to 800 nm was then scanned at 5-minutes intervals. The reaction was also done at 30°, 40°, 50°, and 60° C respectively. Readings were taken at $\lambda = 588$ nm

3.3.4 Procedure for the kinetic studies of the insertion of cobalt(II) metal ion to the central cavity of N, N, N', N'-tetramethylamino porphyrazine hybrid

A spectrophotometric procedure was employed to study the reaction of insertion of cobalt (II) metal ion into the central cavity of the N, N, N', N'-tetramethylamino porphyrazine hybrid base. In this method a solution of N, N, N', N'-tetramethylamino porphyrazine hybrid base (0.72×10^{-6} M) in dichloro methane was made and allowed to equilibrate at 15°C. Another solution of cobalt acetate (0.72×10^{-6} M) in glacial acetic acid was also allowed to equilibrate at the same temperature.

The two were mixed in the proportion of 5: 1 (N, N, N', N'-tetramethylamino porphyrazine hybrid: cobalt acetate) and quickly transferred to a 1 cm quartz cell in the thermostatted compartment of the Cary 50 spectrophotometer. The Uv-vis absorption spectrum from 300 nm to 800 nm was then scanned at 0.5-minute intervals. The reaction was repeated at 15°, 20°, 25°, 30°, 35°, and 40°C respectively. Readings were taken at $\lambda = 779$ nm.

3.3.5 Procedure for the kinetic studies of the insertion of copper(II) metal ion to N, N, N', N'-tetramethylamino porphyrazine hybrid

A spectrophotometric procedure was employed to study the reaction of insertion of copper(II) metal ion into the central cavity of the N, N, N', N'-tetramethylamino porphyrazine hybrid base. In this method a solution of N, N, N', N'-tetramethylamino porphyrazine hybrid base (0.82×10^{-5} M) in dichloro methane was made and allowed to equilibrate at 40°C. Another solution of copper acetate (0.82×10^{-5} M) in acetic acid was also allowed to equilibrate at the same temperature. The two were mixed in the proportion of 4: 1 [N, N, N', N'-tetramethylamino porphyrazine hybrid: copper acetate] and quickly transferred to a 1 cm quartz cell in the thermostatted compartment of the Cary 50 spectrophotometer. The UV-vis absorption spectrum from 300 nm to 800 nm was then scanned at 5-minute intervals. The reaction was repeated at 45°, 50°, and 60°C respectively. Readings were taken at $\lambda = 779$ nm.

3.3.6 Procedure for the kinetic studies of the insertion of cobalt(II) metal ion to the central cavity of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine

A spectrophotometric procedure was employed to study the reaction of insertion of cobalt(II) metal ion into the central cavity of the

2,3,9,10,16,17,23,24-octa substituted phthalocyanine. In this method a solution of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base (0.32×10^{-6} M) in dichloro methane was made and allowed to equilibrate at 45°C. Another solution of cobalt acetate (0.32×10^{-6} M) in glacial acetic acid was also allowed to equilibrate at the same temperature.

The two were mixed in the proportion of 2: 2 [2,3,9,10,16,17,23,24-octa substituted phthalocyanine: cobalt acetate] and quickly transferred to a 1 cm quartz cell in the thermostatted compartment of the Cary 50 spectrophotometer. The Uv-vis absorption spectrum from 300 nm to 800 nm was then scanned at 5-minutes intervals. The reaction was repeated at 35°, 40°, and 45°C respectively. Readings were taken at $\lambda = 700$ nm.

3.3.7 Procedure for the kinetic studies of the insertion of copper(II) metal ion to the central cavity of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine

A spectrophotometric procedure was employed to study the reaction of insertion of copper(II) metal ion into the central cavity of the 2,3,9,10,16,17,23,24-octa substituted phthalocyanine. In this method a solution of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base (0.45×10^{-5} M) in dichloro methane was made and allowed to equilibrate at 20°C. Another solution of copper acetate (0.45×10^{-5} M) in glacial acetic acid was also allowed to equilibrate at the same temperature.

The two were mixed in the proportion of 4: 1 [2,3,9,10,16,17,23,24- octa substituted phthalocyanine: copper acetate] and quickly transferred to a 1 cm quartz cell in the thermostatted compartment of the Cary 50 spectrophotometer. The ultraviolet-visible absorption spectrum from 300 nm to 800 nm was then scanned at 0.20-minutes intervals. The reaction

was repeated at 25°, 30°, and 35°C respectively. Readings were taken at $\lambda = 666$ nm.

3.3.8 Procedure for kinetic studies of Redox reactions of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II) with 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II)

A spectrophotometric procedure was employed to study the reaction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II) with 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II). In this method, the solutions were prepared under nitrogen to eliminate the presence of oxygen. A solution of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II) (0.53×10^{-5} M) in dichloromethane was prepared and allowed to equilibrate at 25° C under nitrogen. Another solution of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.53×10^{-5} M) in glacial acetic acid under nitrogen was also prepared and allowed to equilibrate at 25°C. The two solutions were mixed in the proportion of 4: 1 [2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II): 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II)] and quickly transferred to a 1 cm quartz cell in a thermostated compartment of the Cary 50 spectrophotometer. The Uv-vis absorption spectrum from 300 to 800 nm was scanned and readings were taken at $\lambda = 588$ nm at 1-minute intervals. The reactions were repeated at 55° and 60° C.

3.3.9 Procedure for kinetic studies of Redox reactions of N, N, N', N'-tetramethylamino porphyrazine hybrid copper(II) with 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II)

A spectrophotometric procedure was employed to study the reaction of N, N, N', N'-tetramethylamino porphyrazine hybrid copper(II) with 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II). In this method, the solutions were prepared under nitrogen to eliminate the

presence of oxygen. A solution of N, N, N', N'-tetramethylamino porphyrazine hybrid copper(II) (0.88×10^{-5} M) in dichloromethane was prepared and allowed to equilibrate at 25° C under nitrogen. Another solution of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt (II) (0.88×10^{-5} M) in glacial acetic acid under nitrogen was also prepared and allowed to equilibrate at 25°C.

The two solutions were mixed in the proportion of 3: 1 [N, N, N', N'-tetramethylamino porphyrazine hybrid copper(II): 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II)] and quickly transferred to a 1 cm quartz cell in a thermostated compartment of the Cary 50 spectrophotometer. The Uv-vis absorption spectrum from 300 to 800 nm was scanned and readings were taken at $\lambda = 640$ nm at 2-minutes intervals. The reactions were repeated at 30° and 40° C.

3.3.10 Procedure for kinetic studies of Redox reactions of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) with 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II)

A spectrophotometric procedure was employed to study the reaction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) with 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II). In this method, the solutions were prepared under nitrogen to eliminate the presence of oxygen. A solution of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) (0.53×10^{-5} M) in dichloromethane was prepared and allowed to equilibrate at 30° C under nitrogen. Another solution of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt (II) (0.53×10^{-5} M) in glacial acetic acid under nitrogen was also prepared and allowed to equilibrate at 30°C.

The two solutions were mixed in the proportion of 3: 1 [2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II): 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine cobalt(II)] and quickly transferred to a 1 cm quartz cell in a thermostated compartment of the Cary 50 spectrophotometer. The Uv-vis absorption spectrum from 300 to 800 nm was scanned and readings were taken at $\lambda = 588$ nm at 1-minute intervals. The reactions were repeated at 30° and 40° C.

3.3.11 Computation of rate constants and activation parameters

All the reactions studied in this research were over 95% complete and the observed rate constants were obtained from plots of $1/[A]_t$ against time, which gave a straight line where:

A_t = absorbance at time t.

The integrated rate equation used was second order:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad [3.1]$$

A_0 = Absorbance at time zero

The concentration of A at any time t was given by the relationship:

$$[A]_t = \frac{[A]_0}{1 + [A]_0 kt} \quad [3.2]$$

The activation parameter E_a was obtained from the Arrhenius equation:

$$k = Ae^{E_a/RT} \quad [3.3]$$

Where k is the rate constant

A is an exponential factor

E_a is the activation energy

R is the gas constant

T is the absolute temperature in Kelvin degrees

The above equation was used in its simplified form, which is:

$$\ln k = \ln A - \frac{E_a}{RT}$$

[3.4]

The gradient of a plot of $1/T$ against $\ln k$ from equation [3.4] gave the activation energy.

Since the reactions were second order reactions, their half-lives were calculated thus:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

[3.5]

The activation parameters for the process were determined by measuring the temperature dependence of the reaction rate using the Eyring equation:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^*}{R}\right) - \left(\frac{\Delta H^*}{RT}\right)$$

[3.6]

where k = rate constant, k_B = Boltzmann's constant,
 h = Plank's constant.

A graph of $\ln\left(\frac{k}{T}\right)$ versus $\frac{1}{T}$ gave a slope of $-\left(\frac{\Delta H^\ddagger}{RT}\right)$ with $\Delta H^\ddagger$ = standard enthalpy change of activation and the intercept yielded

$$\ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right) \quad , \text{ with } \Delta S^\ddagger = \text{standard entropy change of activation.}$$

CHAPTER FOUR

RESULTS

4.1 SYNTHESIS AND ISOLATION OF COMPOUNDS

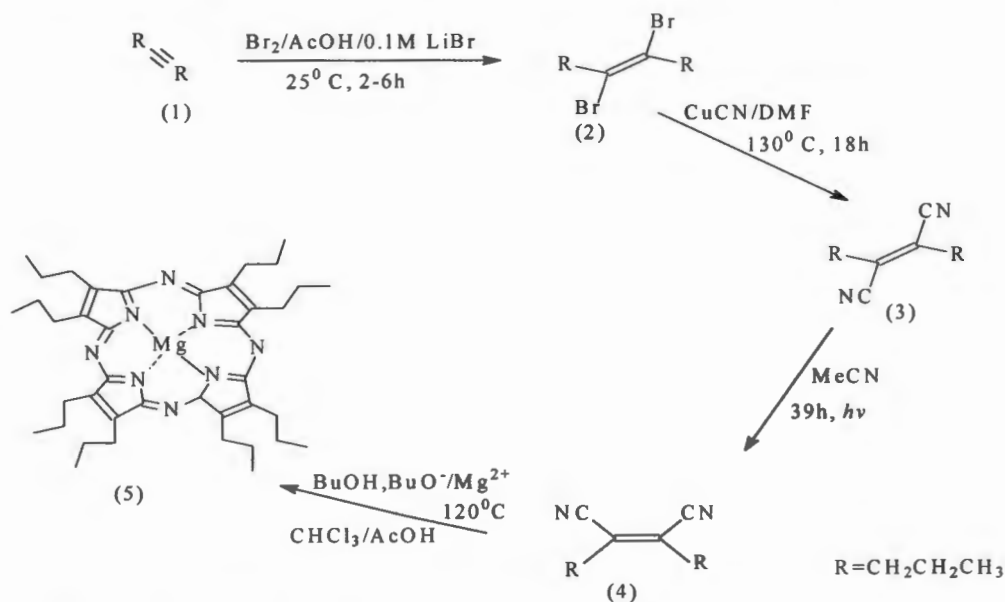


Figure 4.1.1 Figure showing synthetic route of 2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine magnesium⁷⁸

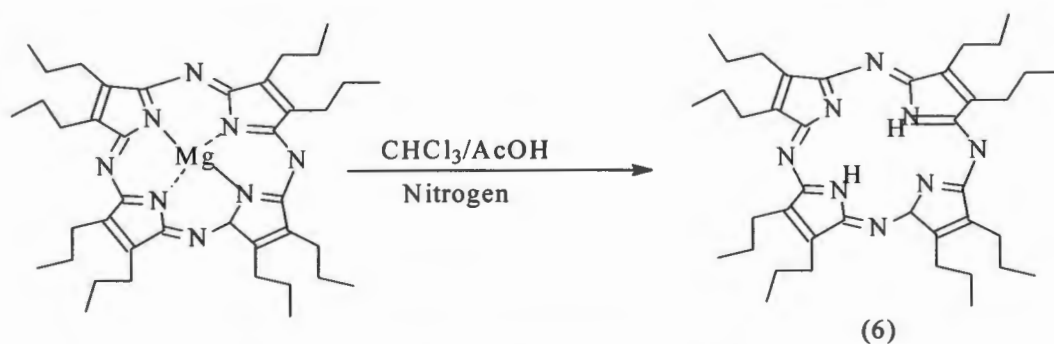


Figure 4.1.2 Figure showing synthesis of 2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine base⁷⁸

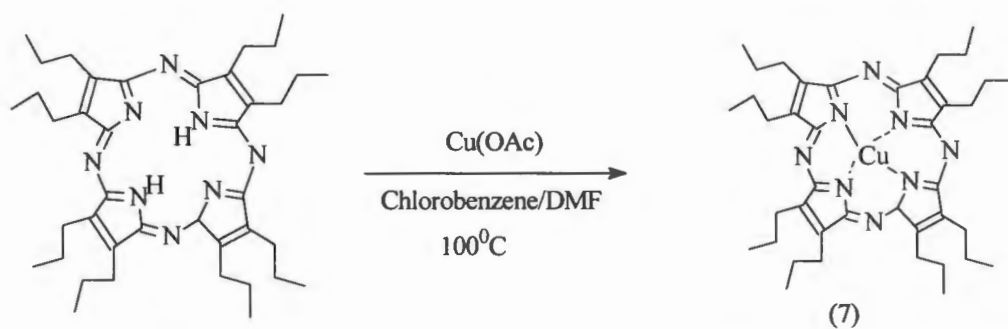


Figure 4.1.3 Figure showing synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II)⁷⁸

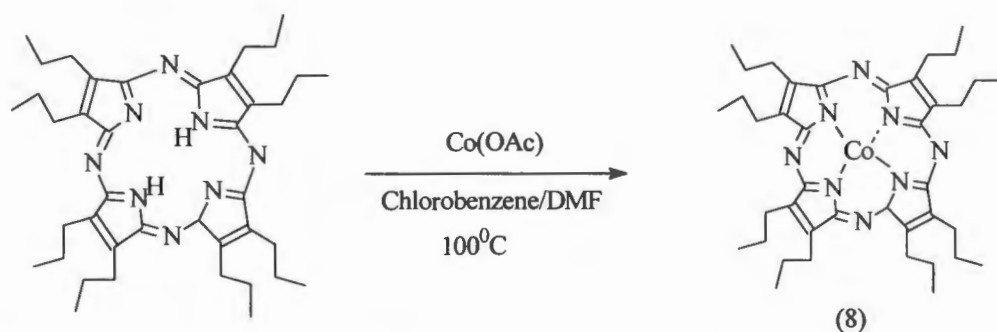


Figure 4.1.4 Figure showing synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II)⁷⁸

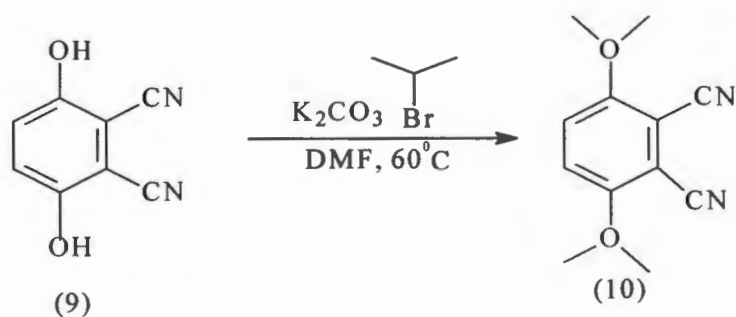


Figure 4.1.5 Figure showing synthesis of 3,6-bis(isopropoxy)-1,2-benzenedinitrile⁸⁷

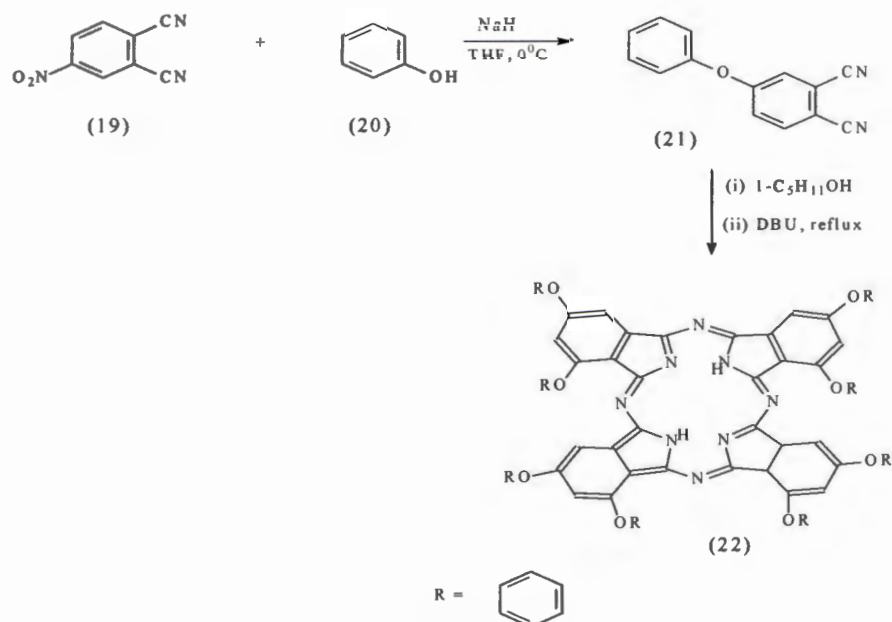


Figure 4.1.8 Figure showing synthetic route of 2,3,9,10,16,17,23,24-octa-substituted phthalocyanine¹⁰⁰

4.2 CHARACTERIZATION OF COMPOUNDS

4.2.1 ¹H and ¹³C NMR spectra

Tables 4.2.1-4.2.9 summarise the ¹H and ¹³C NMR chemical shifts of the compounds, while the corresponding spectra are shown in Figure 4.2.1-4.2.18

Table 4.2.1 Table showing proton and carbon chemical shifts of 4,5-dibromo-4E-octene

¹ H NMR (δ) (CDCl ₃)	¹³ C NMR (300 MHz) CDCl ₃
0.94 (t, 4H, J = 7.4 Hz) 1.62 (m, 4H), 2.49 (t, 6H, J=7.5 Hz)	13.09, 21.23, 35,67 115.34, 129.10

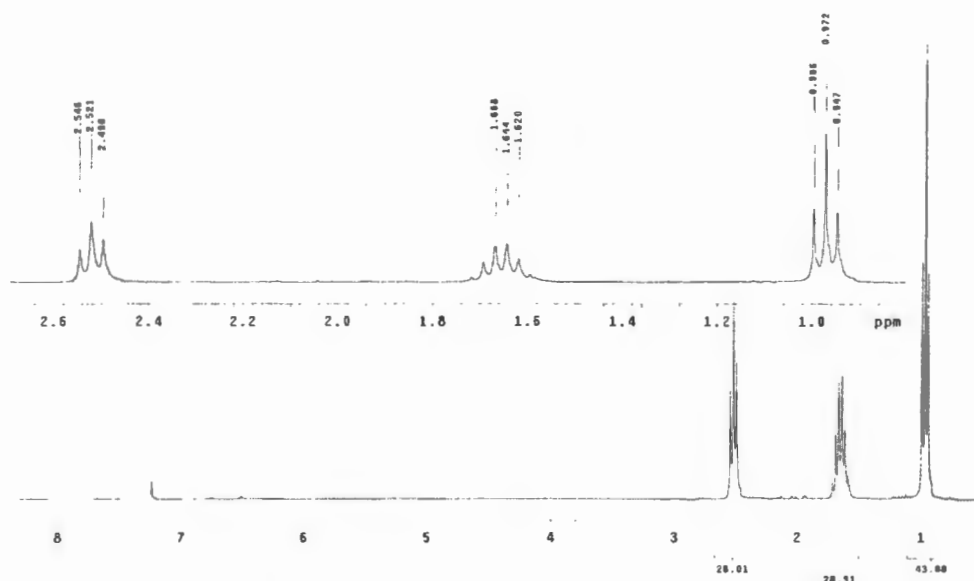


Figure 4.2.1 ¹H NMR spectrum of 4,5-dibromo-4E-octene in CDCl₃

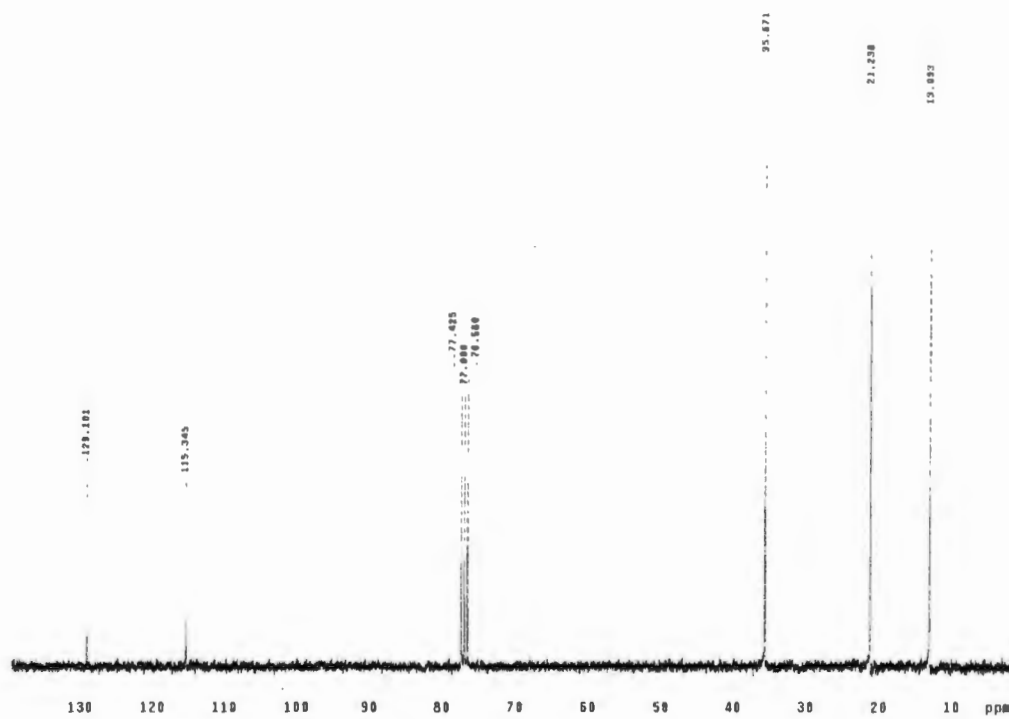
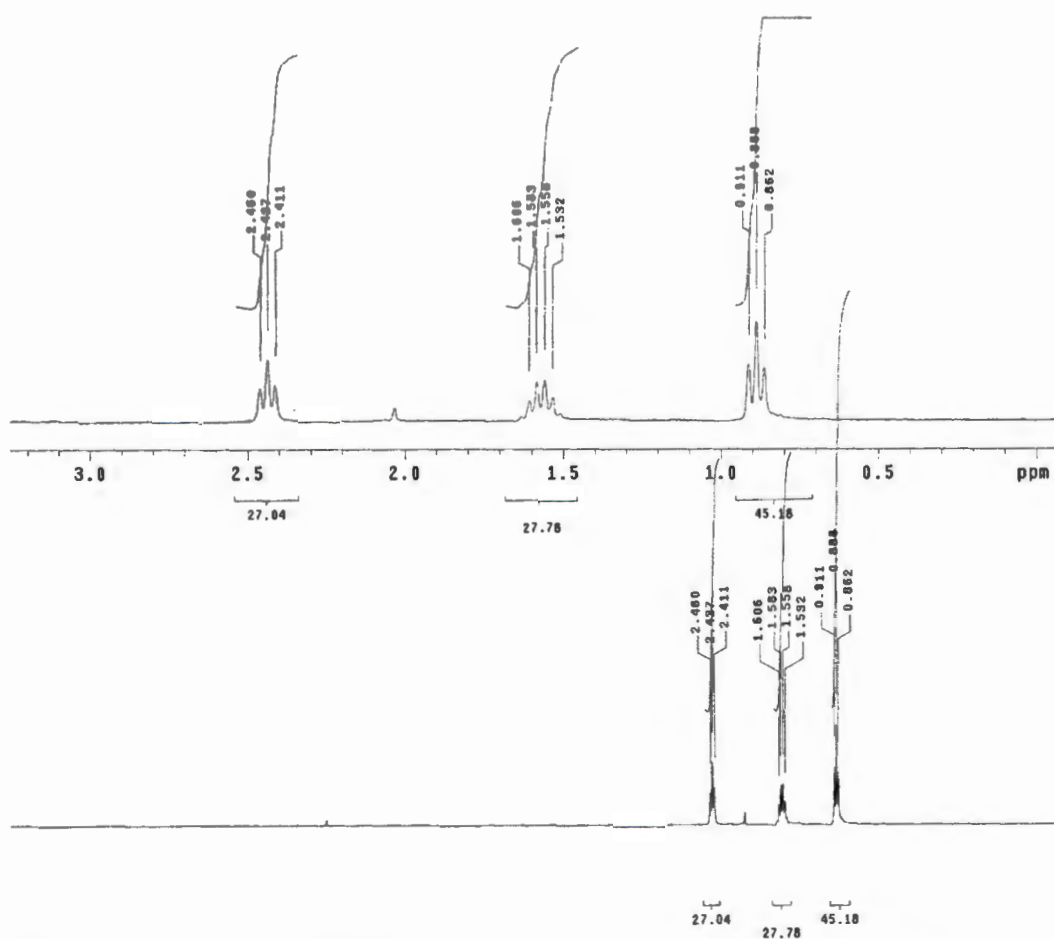


Figure 4.2.2 ¹³C NMR spectrum of 4,5-dibromo-4E-octene in CDCl₃

Table 4.2.2 Table showing proton and carbon chemical shifts of 2,3-dipropyl fumaronitrile

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
0.86 (t, 4H, $J = 7.5$ Hz), 1.53 (m, 4H), 2.41 (t, 6H, $J = 7.4$ Hz)	12.96, 20.72, 31.75, 116.02, 128.88

**Figure 4.2.3** ^1H NMR spectrum of 2,3-dipropyl fumaronitrile in CDCl_3

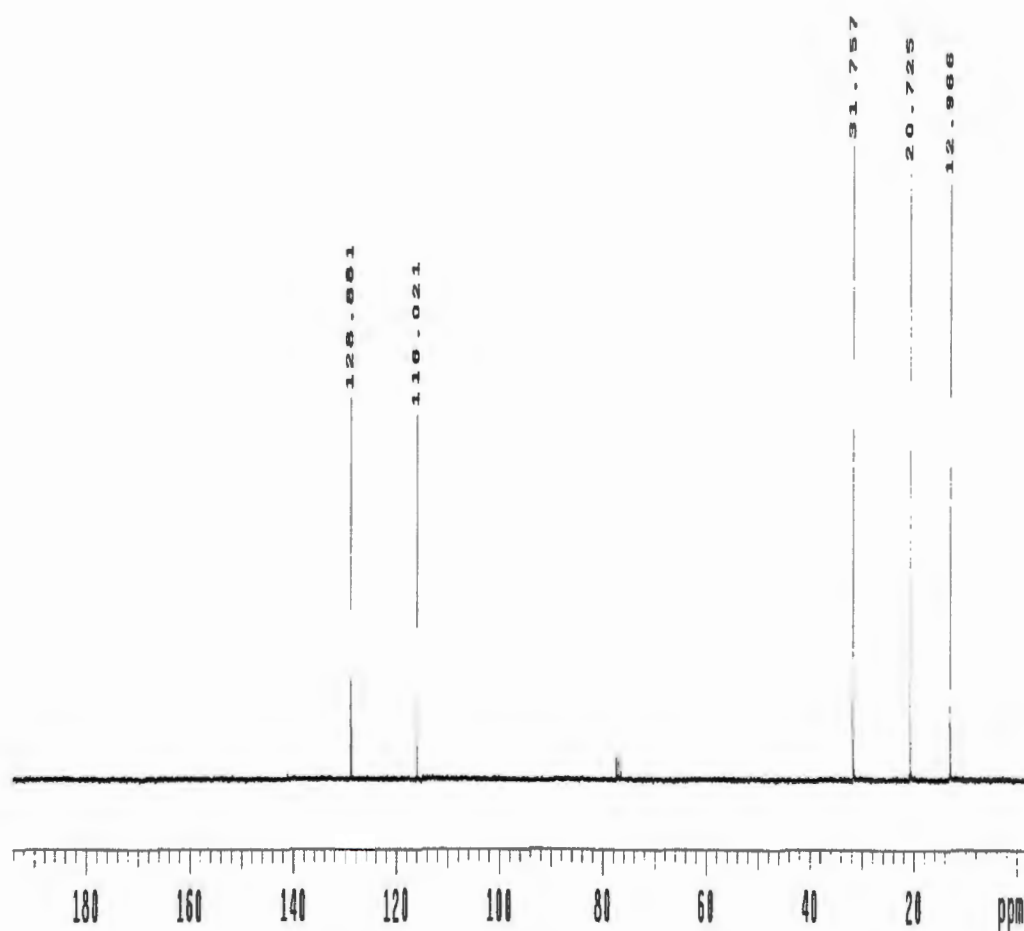


Figure 4.2.4 ^{13}C NMR spectrum of 2,3-dipropyl fumaronitrile in CDCl_3

Table 4.2.3 Table showing proton and carbon chemical shifts of 2,3-dipropyl maleonitrile

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
1.62 (t, 4H, $J = 7.5$ Hz), 2.27 (m, 4H), 3.00 (t, 6H, $J = 7.4$ Hz)	12.97, 20.73, 31.76, 116.02, 128.88

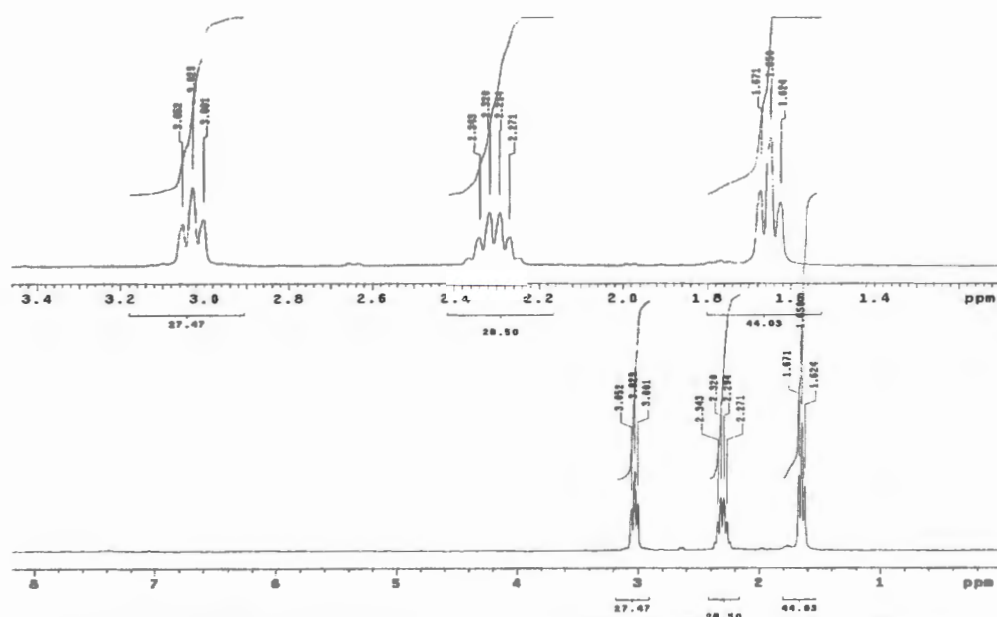


Figure 4.2.5 ¹H NMR spectrum of 2,3-dipropyl maleonitrile in CDCl₃

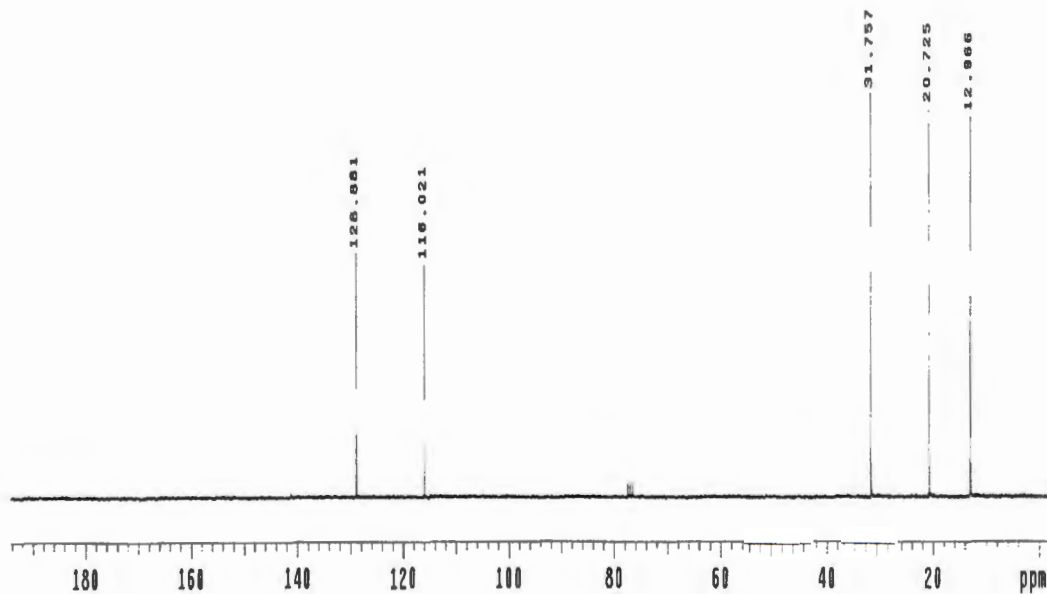


Figure 4.2.6 ¹³C NMR spectrum of 2,3-dipropyl maleonitrile in CDCl₃

Table 4.2.4 Table showing proton and carbon chemical shifts of bis (isopropoxy)-1,2-benzenedinitrile

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
1.37 (d, 12H, $J = 6.0$ Hz), 4.55 (hp, 2H, $J = 6.1$ Hz), 7.13 (s, 2H)	21.91, 73.69, 106.69, 113.20, 120.54, 154.33

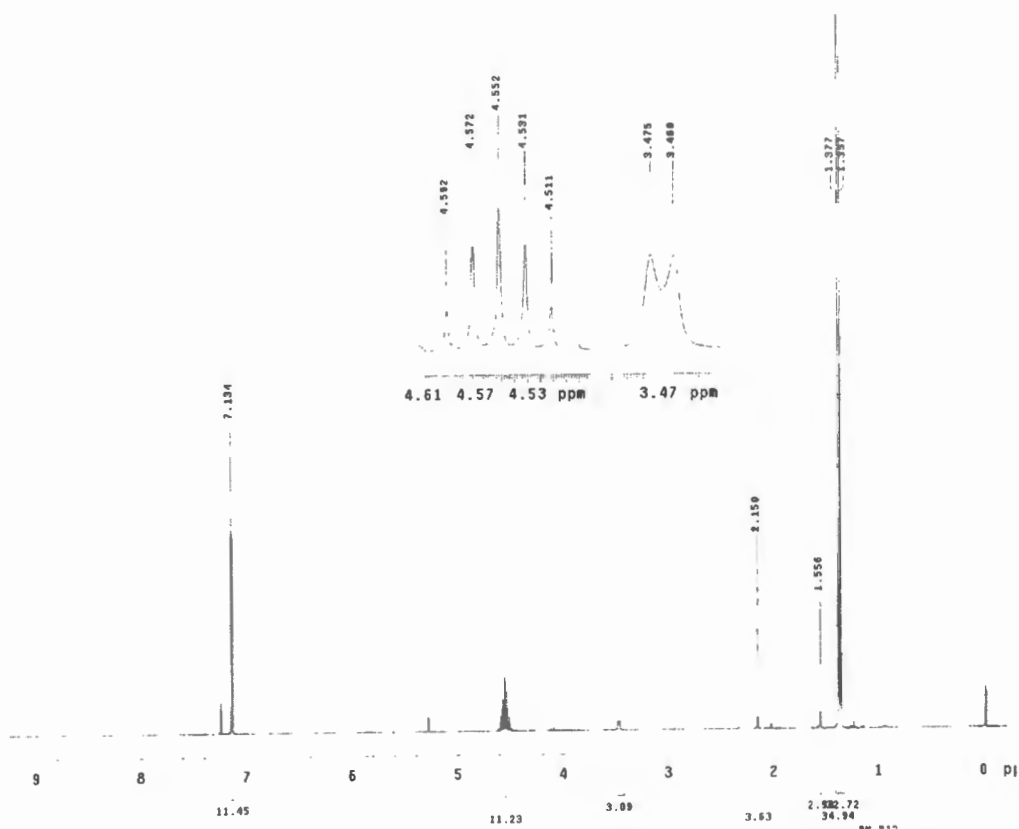


Figure 4.2.7 ^1H NMR spectrum of 3,6-bis(isopropoxy)-1,2-benzenedinitrile in CDCl_3

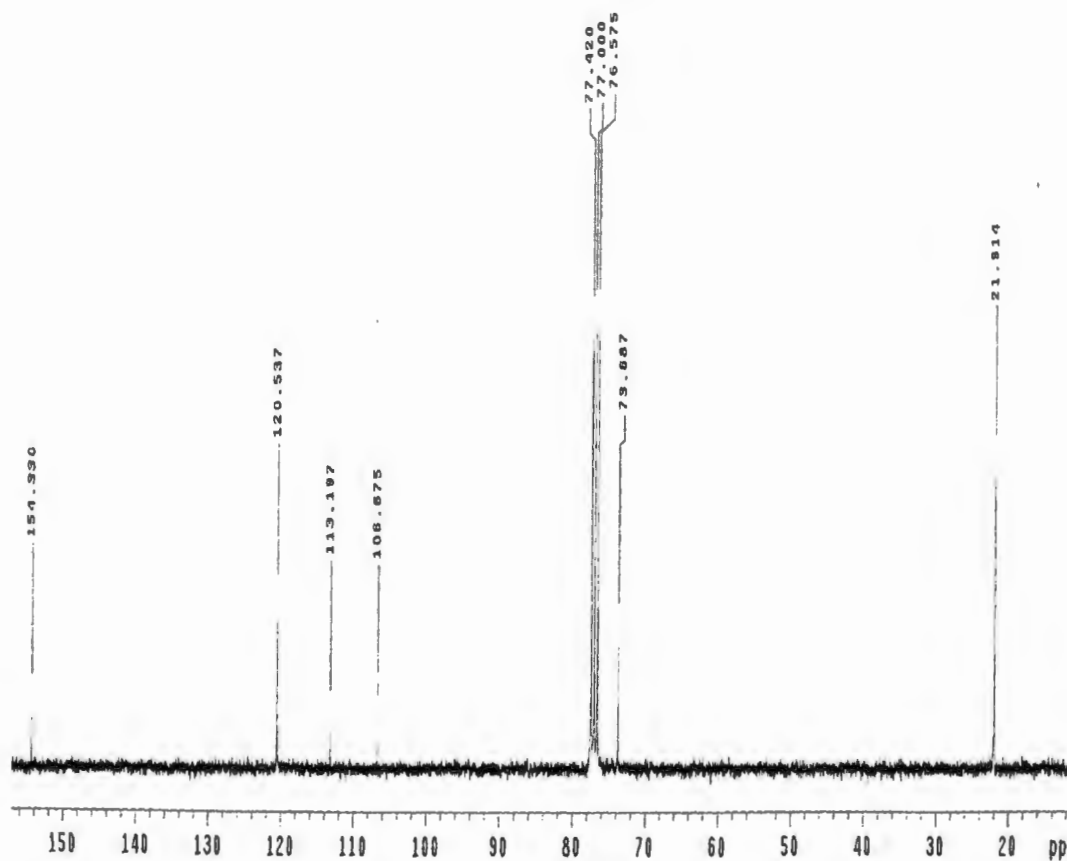


Figure 4.2.8 ^{13}C NMR spectrum of 3,6-bis(isopropoxy)-1,2-benzenenitrile in CDCl_3

Table 4.2.5 Table showing proton and carbon chemical shifts of 4,7-bis(isopropoxy)-1,3-diiminoisoindole

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
1.39 (d, 12H, $J = 6.2$ Hz), 4.63 (hp, 2H, 6.1 Hz), 6.93 (s, 2H)	22.20, 71.55, 117.51, 123.41, 148.10

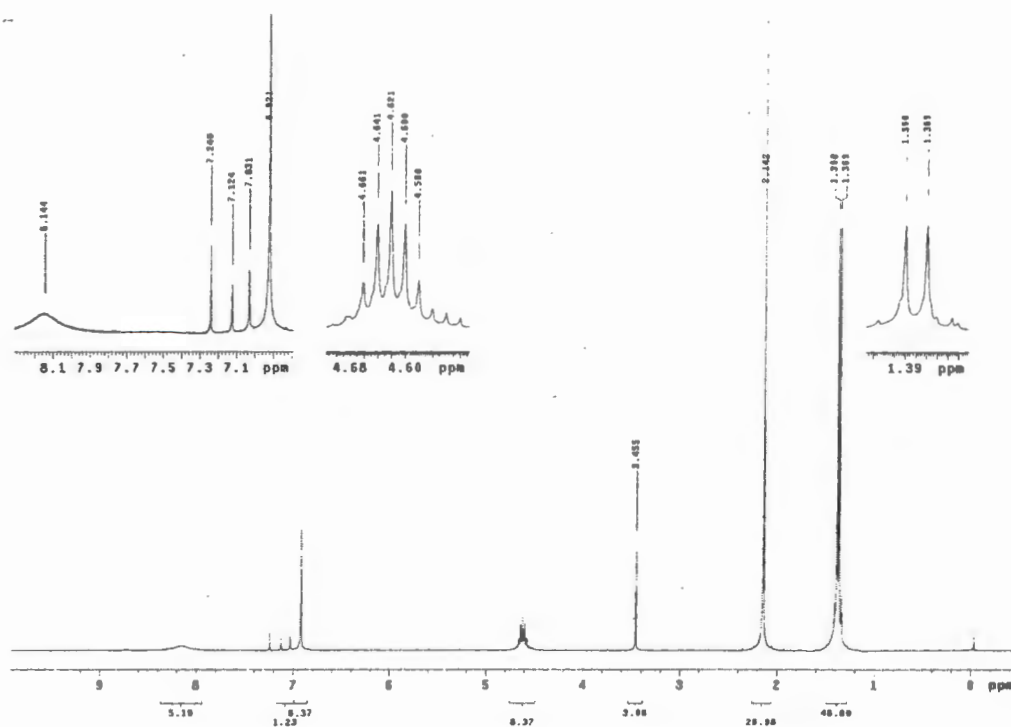


Figure 4.2.9 ¹H NMR spectrum of 4,7-bis(isopropoxy)-1,3-iminoisoindoline in CDCl₃

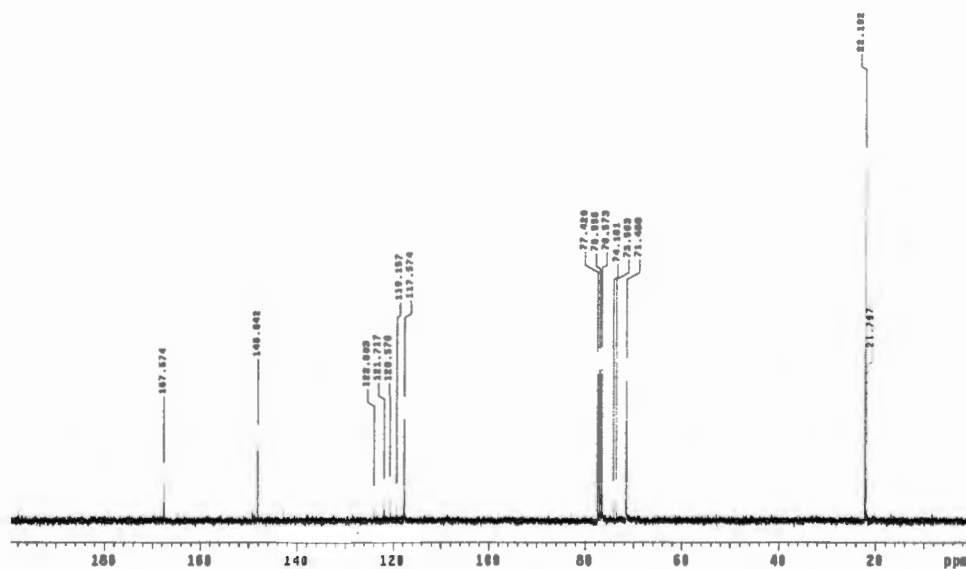


Figure 4.2.10 ¹³C NMR spectrum of 4,7-bis(isopropoxy)-1,3-iminoisoindoline in CDCl₃

Table 4.2.6 Table showing proton and carbon chemical shifts of bis (dimethylamino) maleonitrile

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
2.78 (s, 12H)	43.56, 113.53, 119.18

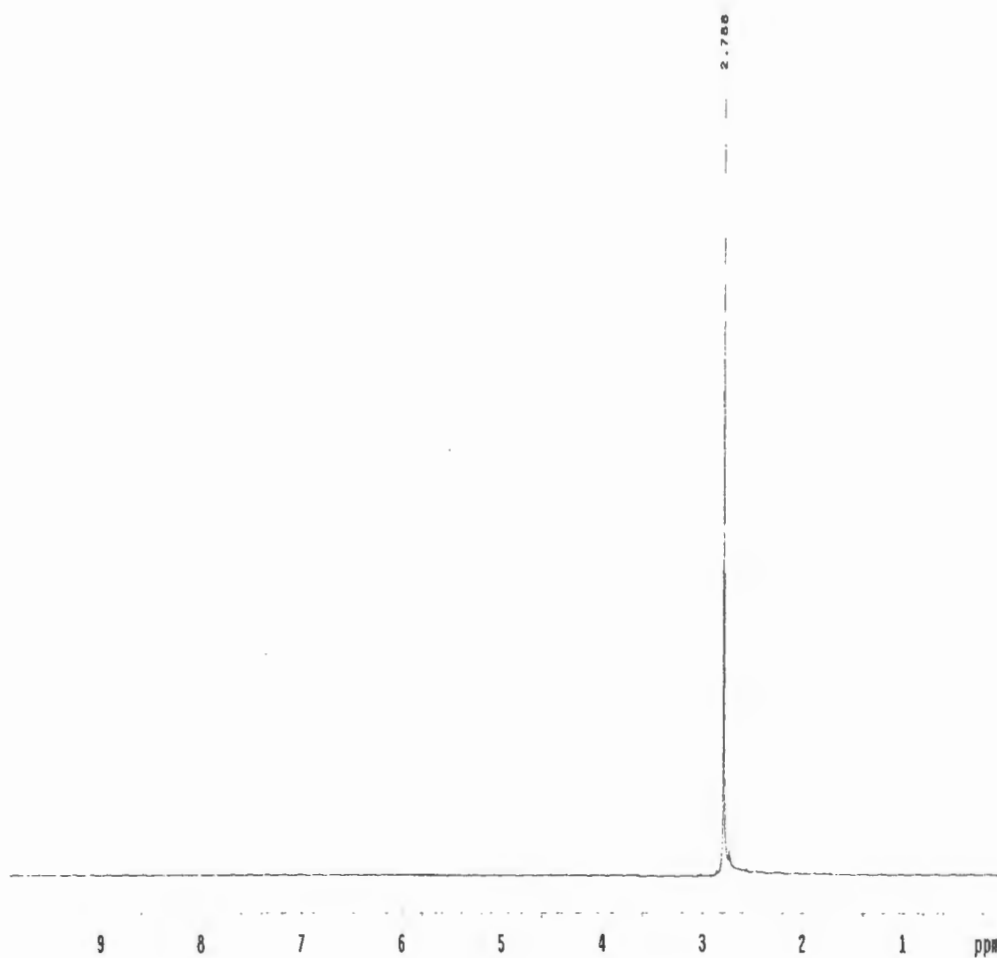


Figure 4.2.11 ^1H NMR spectrum of bis (dimethylamino) maleonitrile in CDCl_3

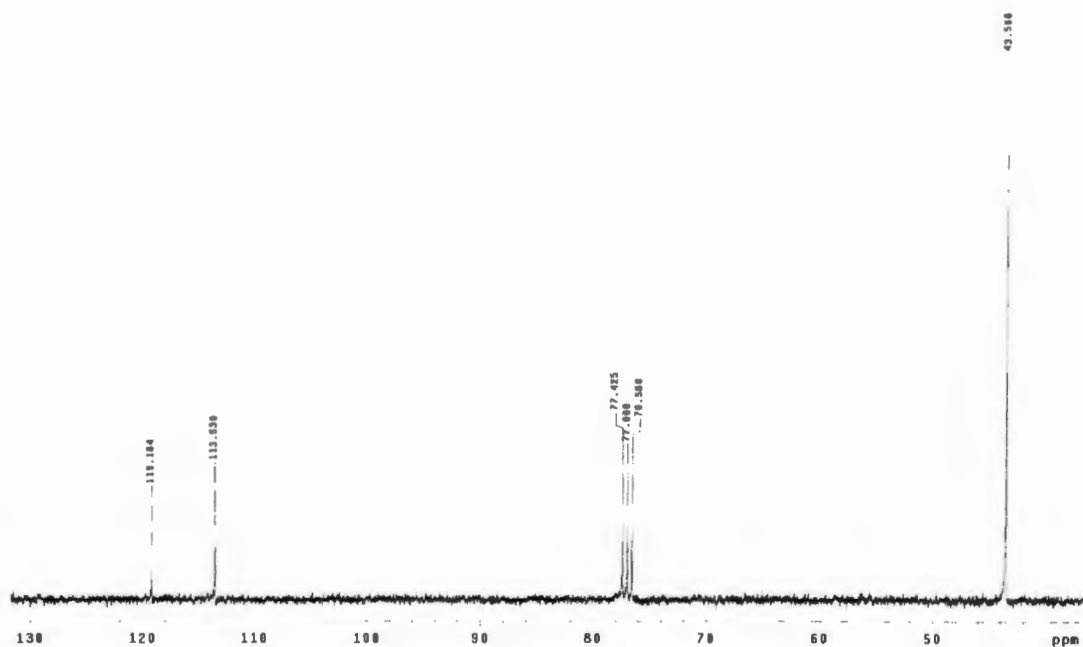


Figure 4.2.12 ^{13}C NMR spectrum of bis(dimethylamino) maleonitrile in CDCl_3

Table 4.2.7 Table showing proton and carbon chemical shifts of N,N,N',N'-tetramethylamino porphyrazine hybrid base

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
2.15 (s, 6H), 4.95 (m, 1H), 5.10 (m, 1H), 5.17 (m, 1H), 7.37 (d, 2H, J = 9 Hz), 7.46(d, 2H, J = 8.70 Hz)	11.03, 14.17, 19.236, 22.71, 22.778, 29.73, 30.96, 44.574, 53.43, 44.57, 53.43, 70.76, 75.24, 75.53, 114.50, 122.57, 124.26, 125.06, 128.54, 128.76, 130.84, 131.02, 135.05, 140.72, 140.79, 148.62, 150.47, 150.96, 155.08, 156.52, 206.87

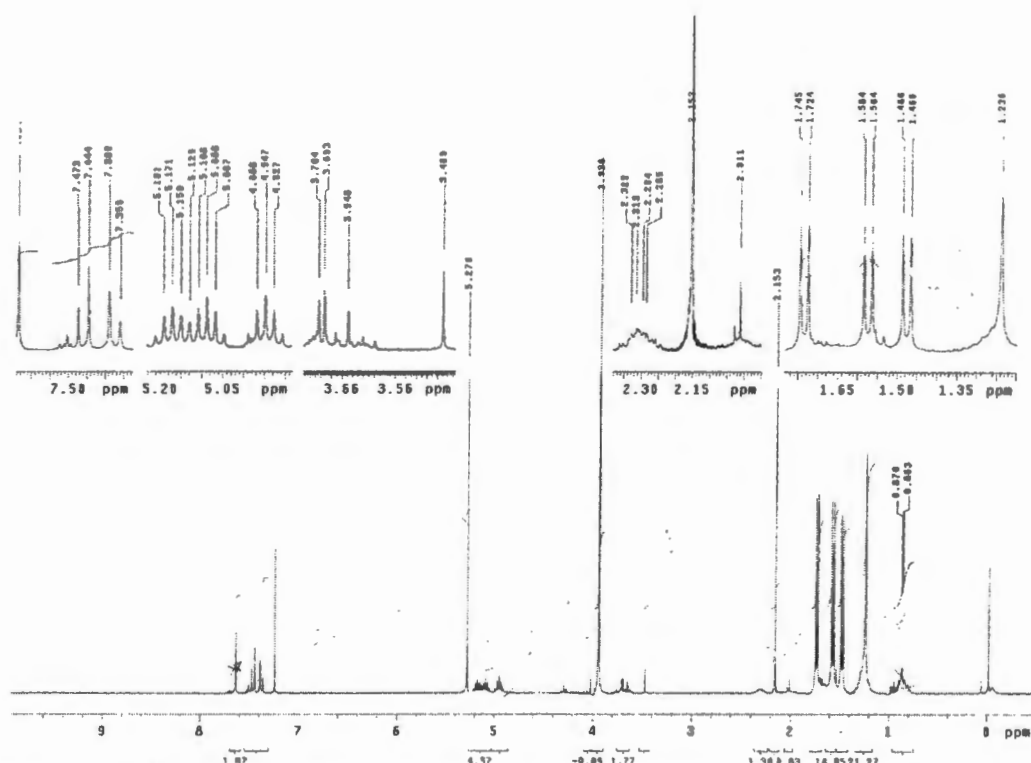


Figure 4.2.13 ¹H NMR spectrum of N,N,N',N'-tetramethylamino porphyrazine hybrid base in CDCl₃

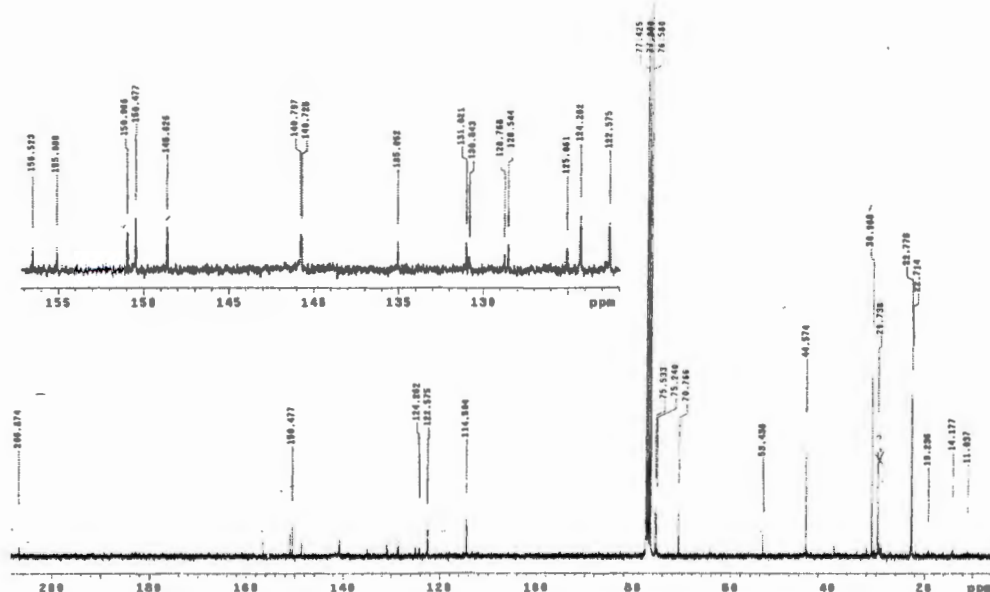


Figure 4.2.14 ¹³C NMR spectrum of N,N,N',N'-tetramethylamino porphyrazine hybrid base in CDCl₃

Table 4.2.8 Table showing proton and carbon chemical shifts of 1,2-diisocyano-4-phenoxybenzene

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
-0.90 (s, 2H), 3.46 (m, 5H, CH), 7.07 (m, 3H, ArH)	71.01, 117.45, 119.69, 119.92, 126.95, 127.34, 134.43, 135.20

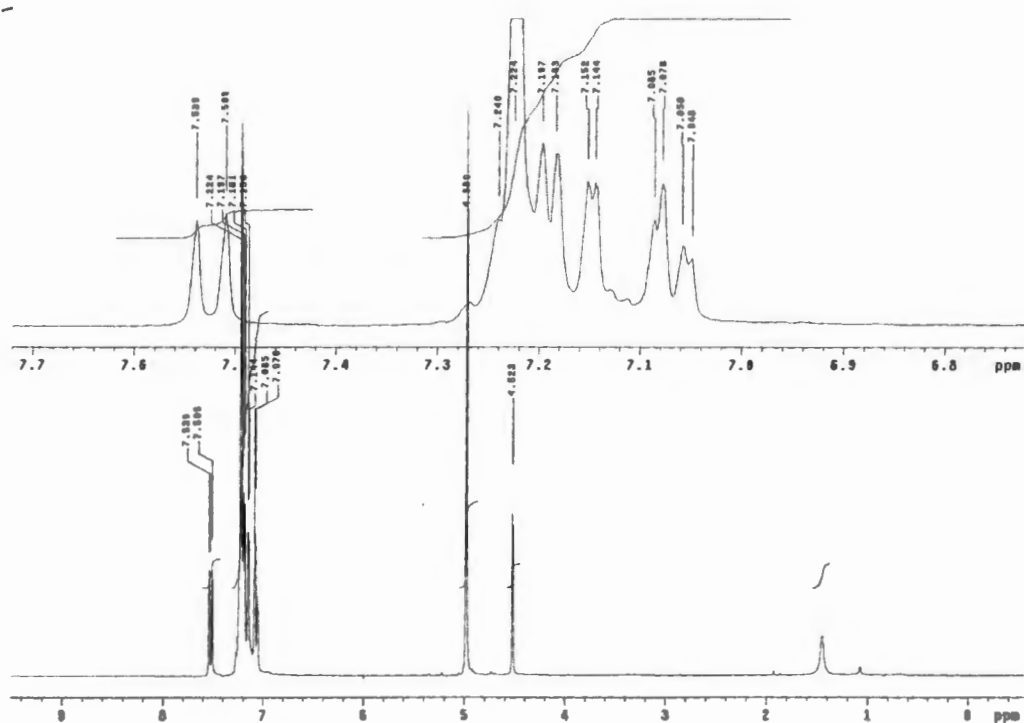


Figure 4.2.15 ^1H NMR spectrum of 1,2-diisocyano-4-phenoxybenzene in CDCl_3

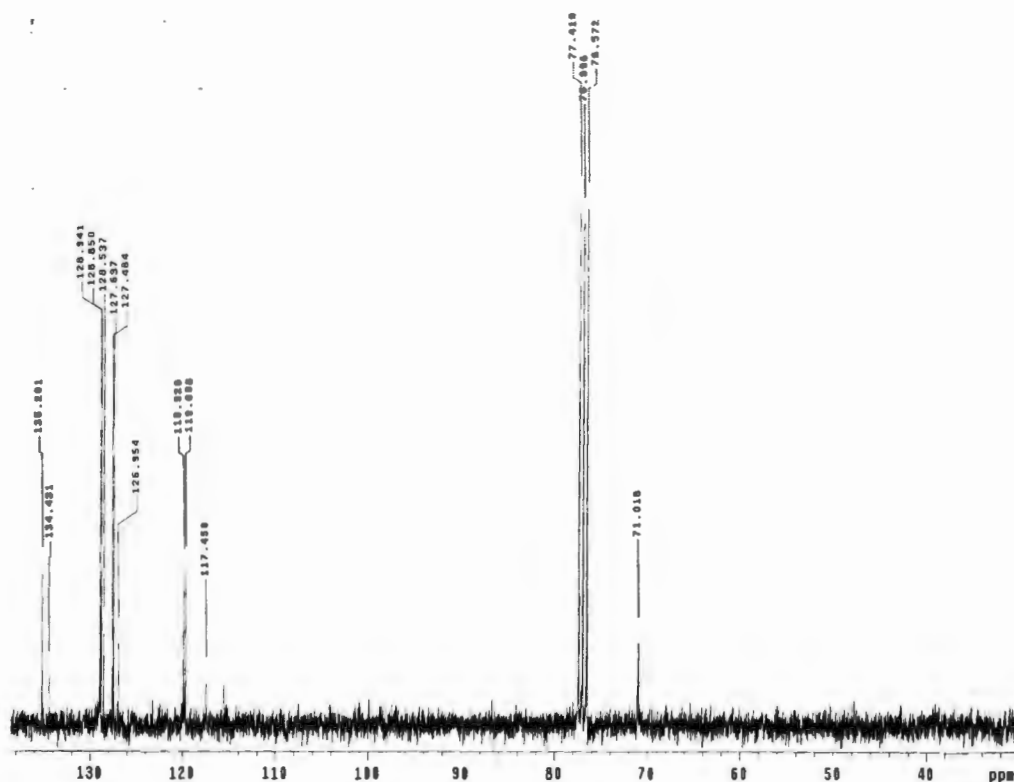


Figure 4.2.16 ^{13}C NMR spectrum of 1,2-diisocyno-4-phenoxybenzene in CDCl_3

Table 4.2.9 Table showing proton and carbon chemical shifts of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine

^1H NMR (δ) CDCl_3	^{13}C NMR (300 MHz) CDCl_3
-2.016 (s, 2H, NH), 3.66 (m, 4H, CH), 6.99 (m, 4H, ArH), 7.23 (m, 4H, ArH), 7.50 (m, 4H, ArH), 8.036 (m, 4H, ArH), 8.99 (m, 4H, ArH), 9.23 (m, 4H, ArH)	71.01, 76.57, 76.99, 77.41, 117.45, 119.69, 119.92, 126.95, 127.48, 127.63, 128.53, 128.85, 128.94, 134.43, 135.20

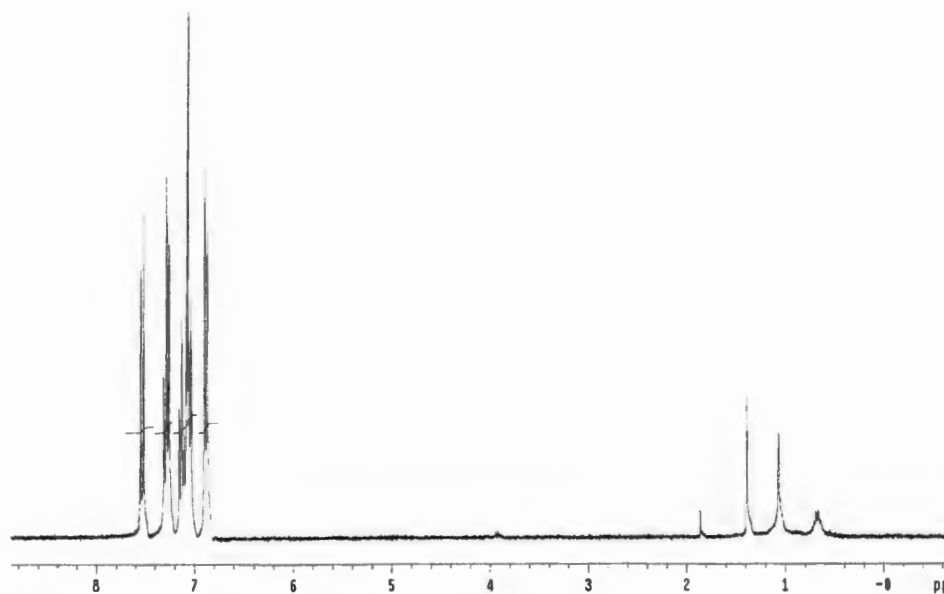


Figure 4.2.17 ^1H NMR spectrum of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine in CDCl_3

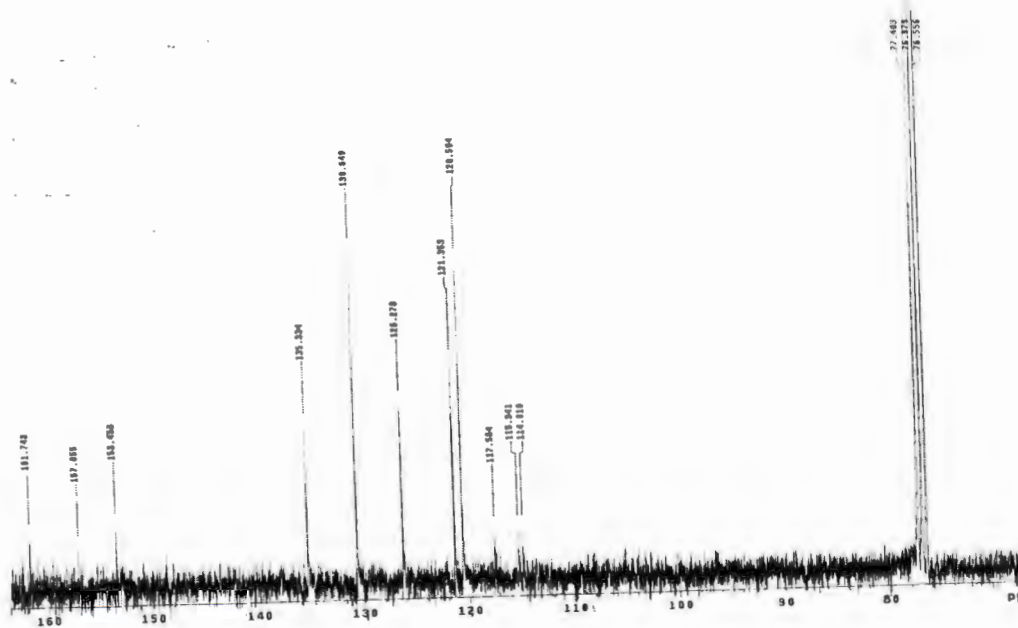


Figure 4.2.18 ^{13}C NMR spectrum of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine in CDCl_3

4.3 ULTRAVIOLET-VISIBLE SPECTRA

Ultraviolet-visible spectra of different porphyrazines are compiled in Figure 4.3.1 - 4.3.8 and a summary of the wavelengths of maximum absorption and absorbances at these wavelengths for the compounds are summarized in Table 4.3.1

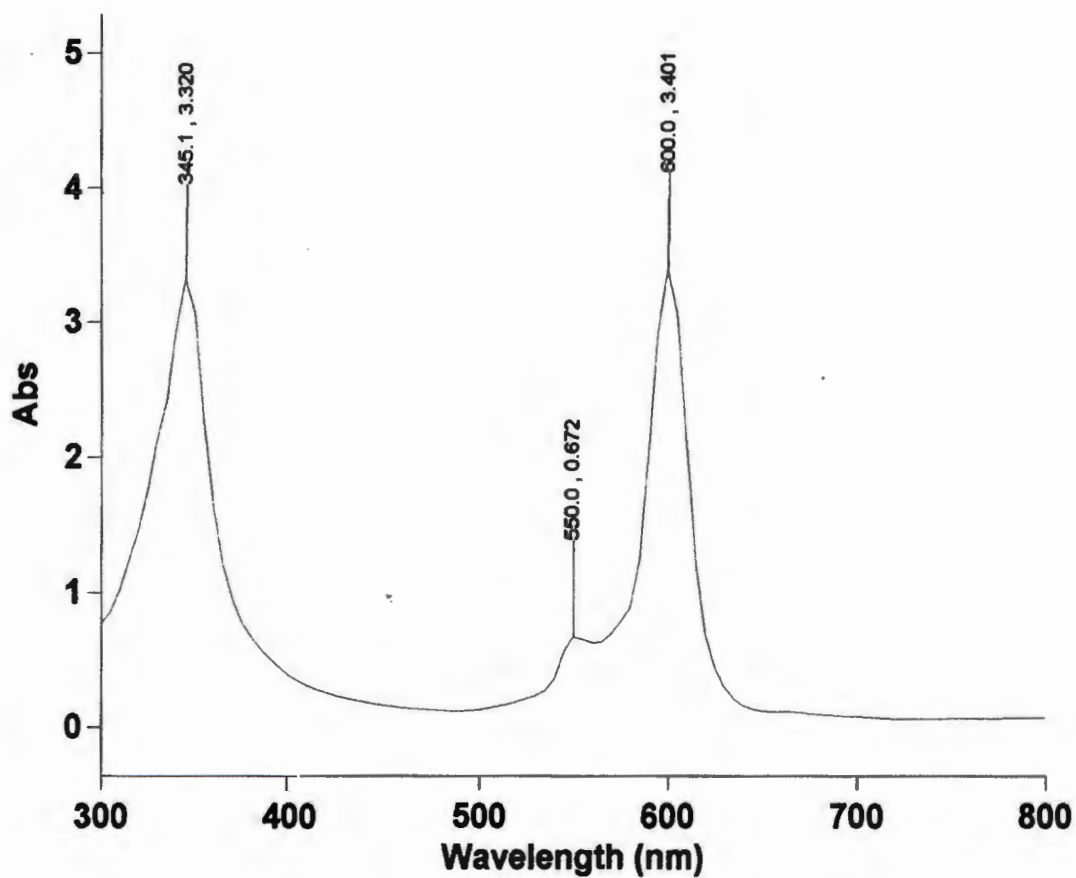


Figure 4.3.1 Ultraviolet-visible spectrum of 2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine magnesium

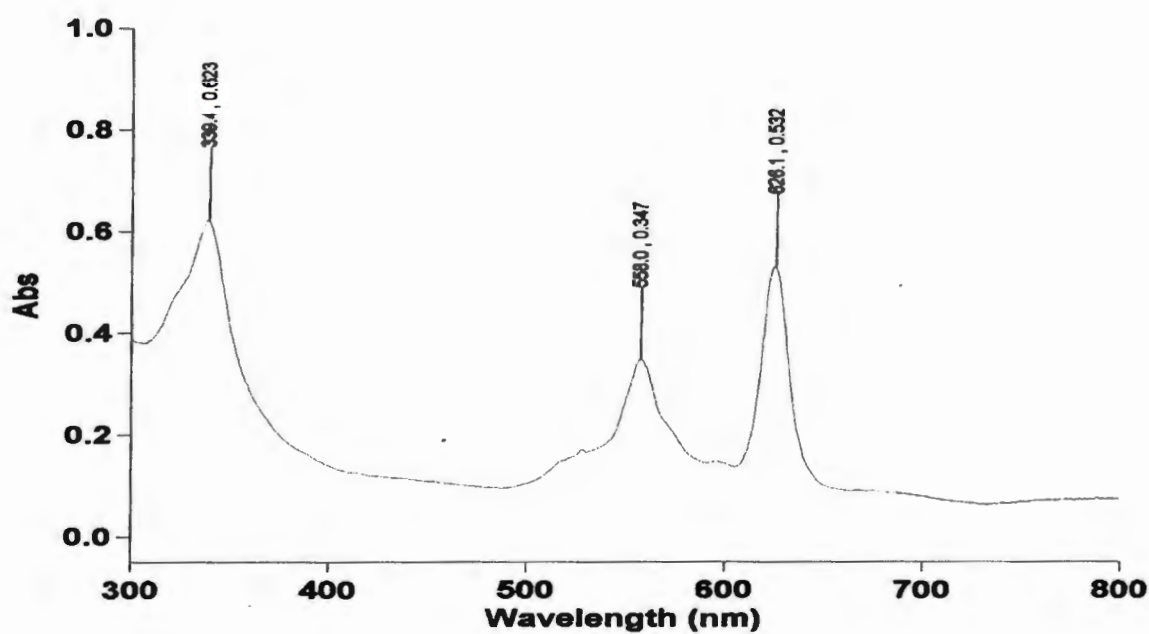


Figure 4.3.2 Ultraviolet-visible spectrum of 2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine base

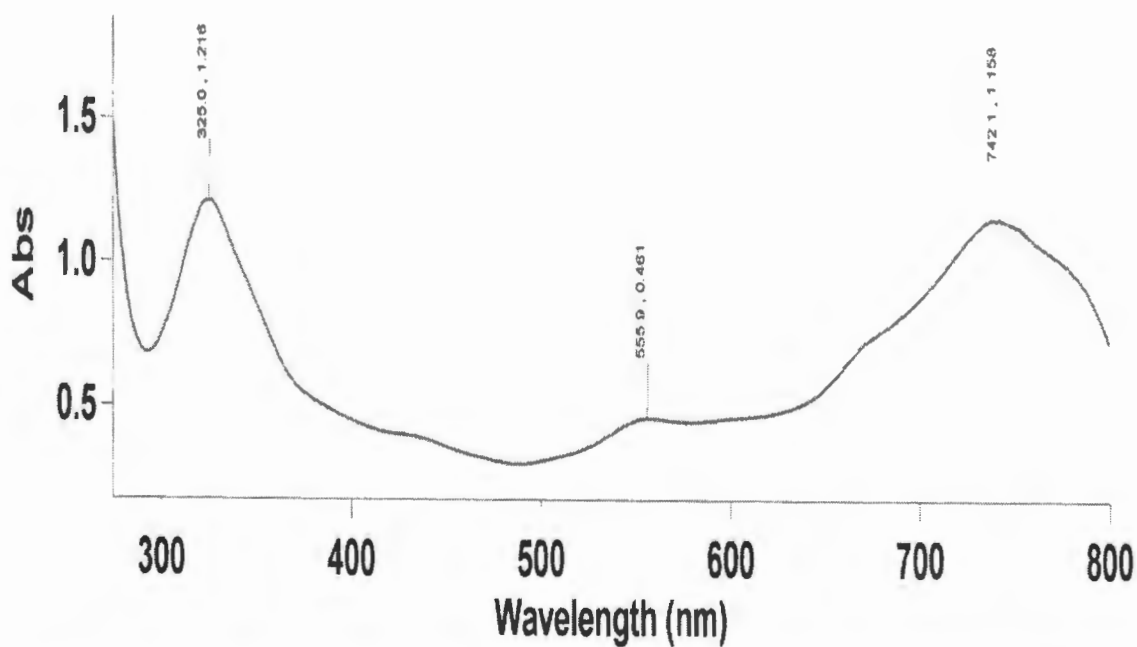


Figure 4.3.3 Ultraviolet-visible spectrum of N,N,N',N'-tetramethylamino-porphyrazine hybrid base

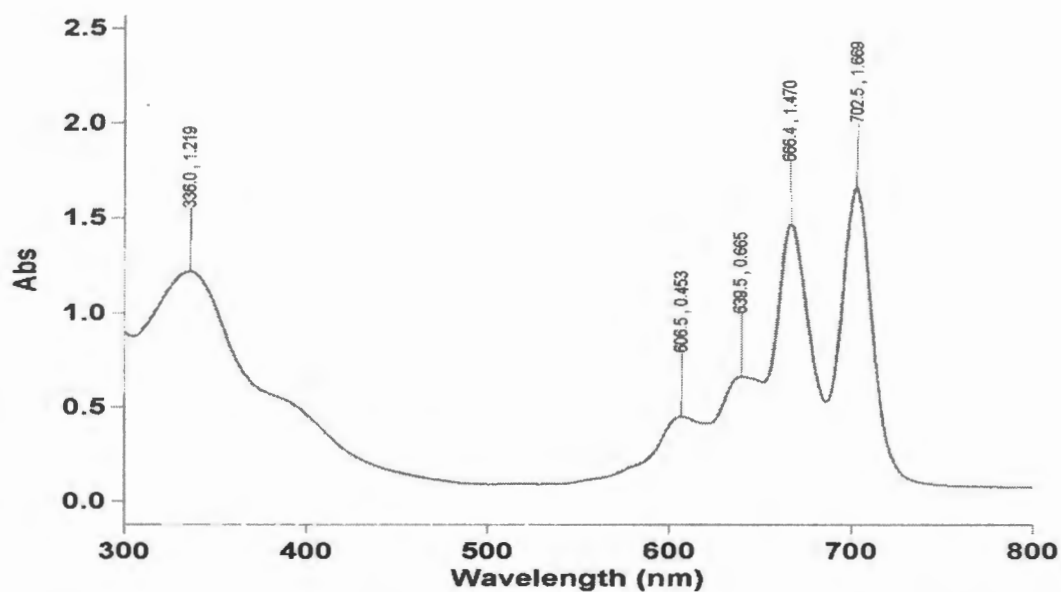


Figure 4.3.4 Ultraviolet-visible spectrum of 2,3,9,10,16,17,23,24-octa-substituted phthalocyanine

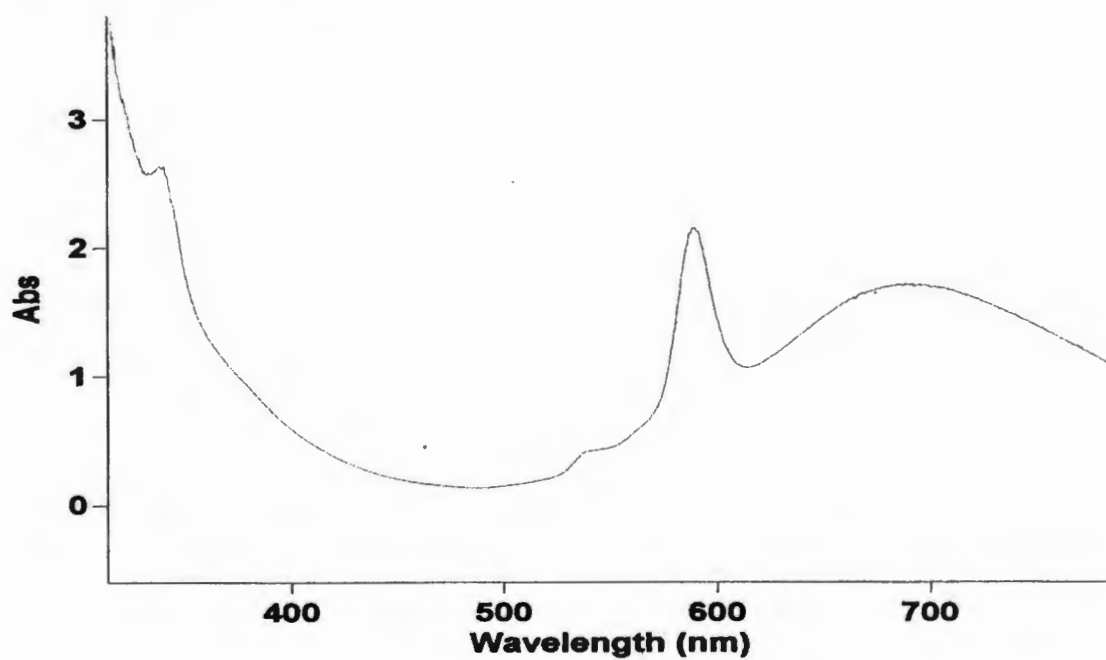


Figure 4.3.5 Ultraviolet-visible spectrum of 2,3,7,8,12,13,17,18-octakis(propyl) porphyrazine copper(II)

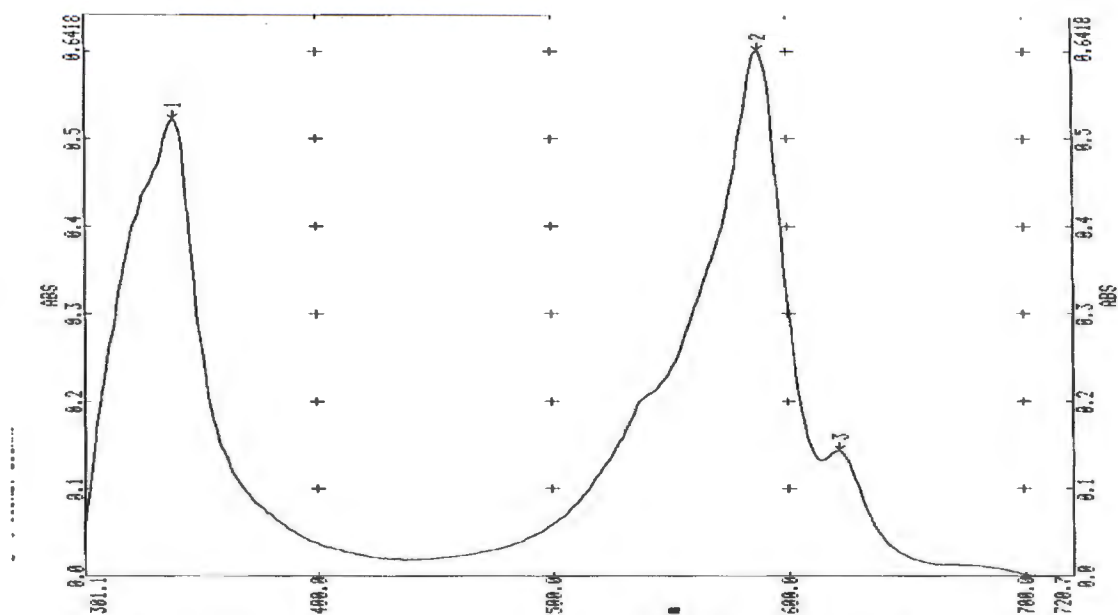
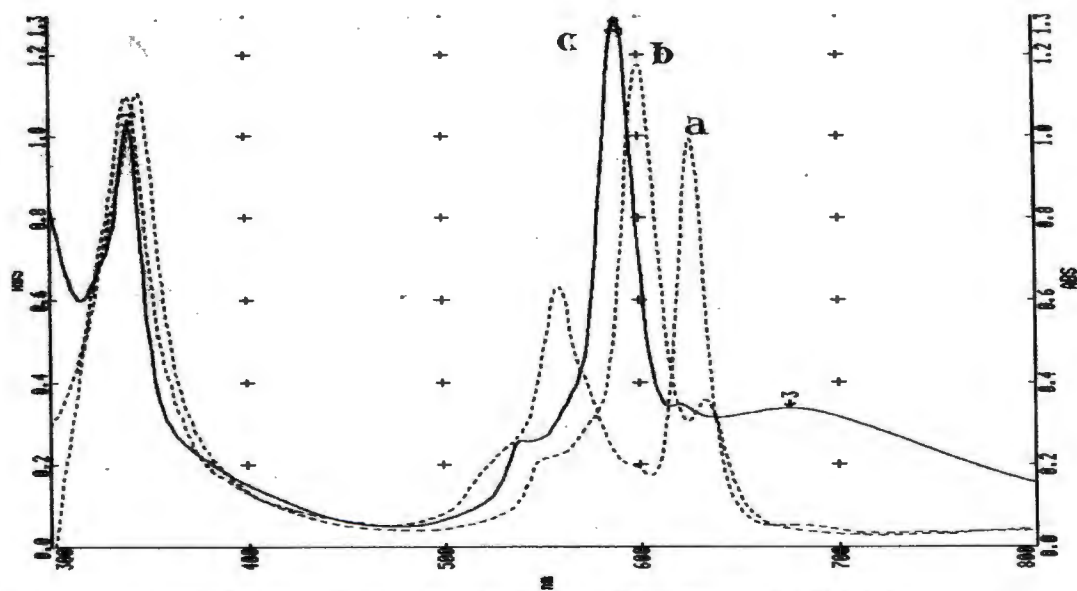
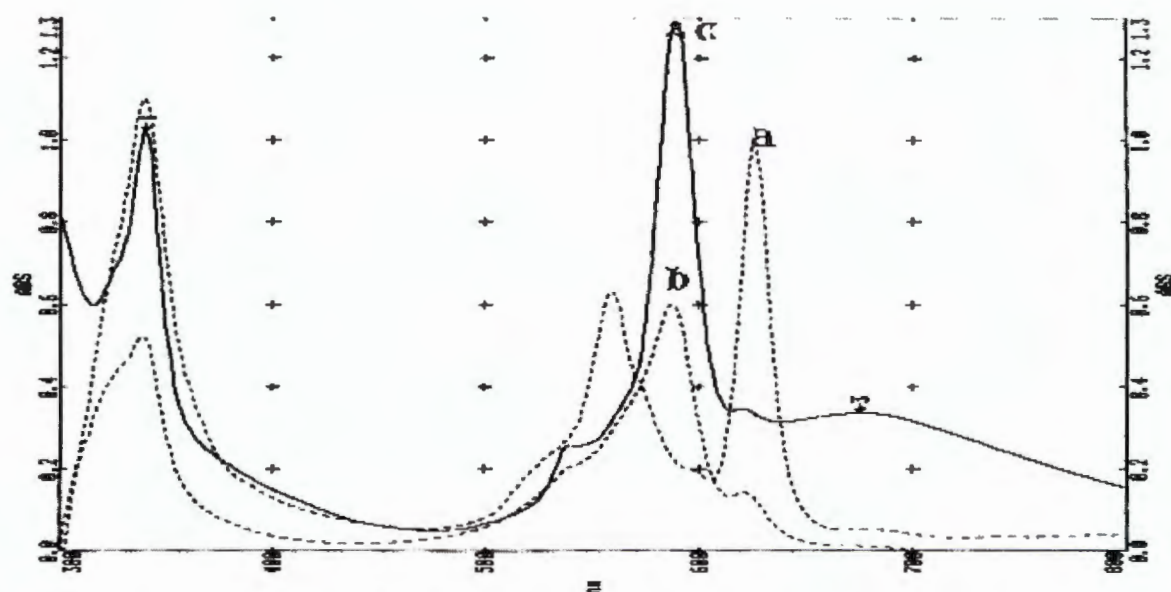


Figure 4.3.6 Ultraviolet-visible spectrum of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II)



Comparison between porphyrzine with magnesium as central metal (b) and when the central metal is removed (a) and when copper is the central metal (c)

Figure 4.3.7 Ultraviolet-visible spectrum of copper, magnesium and free base 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzines



a = Magnesium removed b = Cobalt ion inserted c = Magnesium present
 Figure 4.3.8 Ultraviolet-visible spectrum of cobalt, magnesium and free base 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines

Table 4.3.1 Table showing the summary of the maximum absorbances at a particular wavelength for different porphyrazines

Complex	$\lambda_{\max}$ (ϵ , $\text{L mol}^{-1} \text{cm}^{-1}$)	Solvent
Mg(II)-pz ¹	345 (3.3×10^7); 550 (5.3×10^7); 600 (5.8×10^7)	CH ₂ Cl ₂
Pz ¹ -base	339 (3.0×10^7); 558 (4.9×10^7); 626 (5.5×10^7)	CH ₂ Cl ₂
Cu(II)-pz ¹	336 (1.0×10^8); 581 (1.8×10^8); 665 (2.0×10^8)	CH ₂ Cl ₂
Co(II)-pz ¹	340 (3.4×10^5); 589 (5.89×10^5); 629 (6.29×10^5)	CH ₂ Cl ₂
Pz ² -base	325 (3.9×10^7); 556 (6.7×10^7); 742 (9.0×10^7)	CH ₂ Cl ₂
Cu(II)-pz ²	320 (2.3×10^6); 556 (4.1×10^6); 745 (5.5×10^6)	CH ₂ Cl ₂
Co(II)-pz ²	322 (4.4×10^8); 557 (7.7×10^8); 743 (1.0×10^9)	CH ₂ Cl ₂
Pc-base	337 (5.3×10^8); 606 (9.6×10^8); 640 (1.0×10^9); 661 (1.0×10^9); 702 (1.1×10^9)	CH ₂ Cl ₂
Cu(II)-pc	332 (1.5×10^8); 607 (2.7×10^8); 642 (2.9×10^8); 667 (3.0×10^8); 699 (3.1×10^8)	CH ₂ Cl ₂
Co(II)-pc	330 (1.9×10^8); 608 (3.5×10^8); 645 (3.7×10^8); 669 (3.9×10^8); 700 (4.1×10^8)	CH ₂ Cl ₂

4.4 INFRARED SPECTRA OF COMPOUNDS

Infrared spectra of the prepared porphyrazines are given in Figure 4.4.1 - 4.4.4 and the summary of the frequencies of the prominent absorption bands of the porphyrazines is given in Table 4.4.1

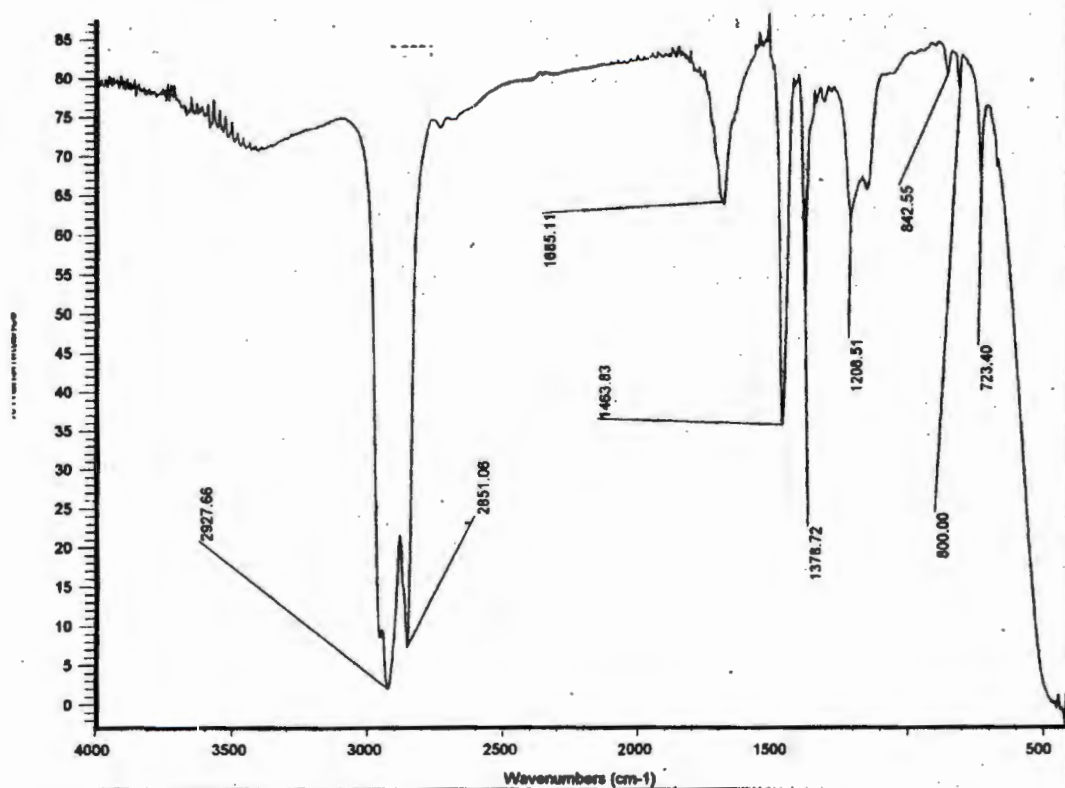


Figure 4.4.1 Infrared spectrum of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium

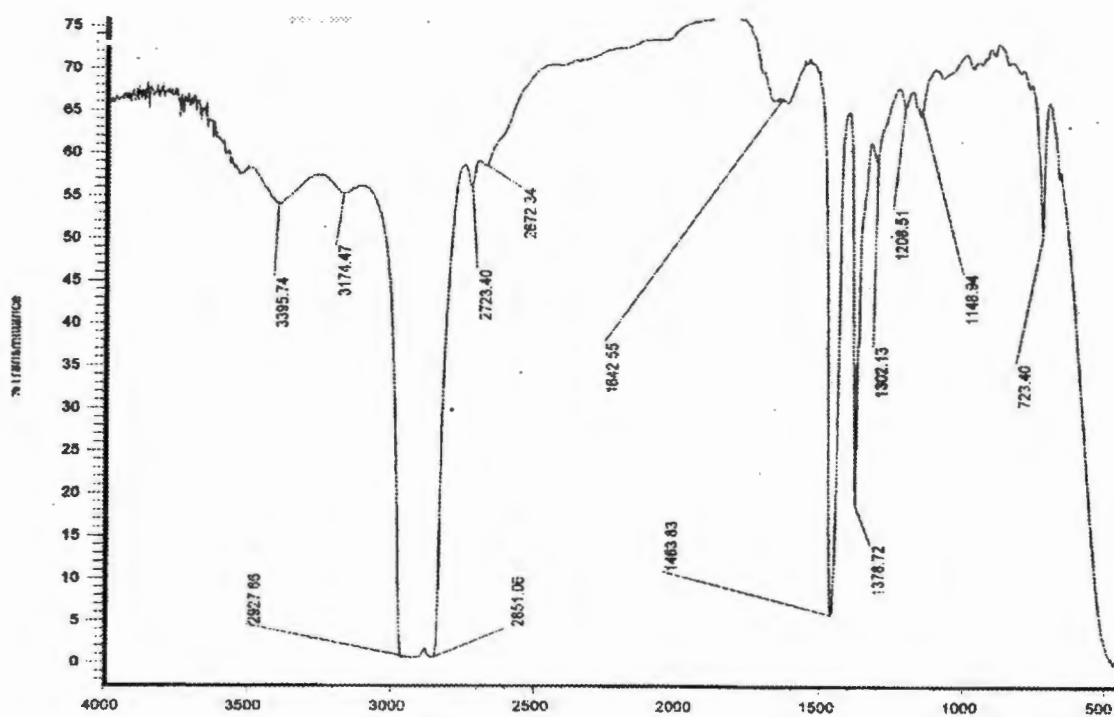


Figure 4.4.2 Infrared spectrum of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine free base

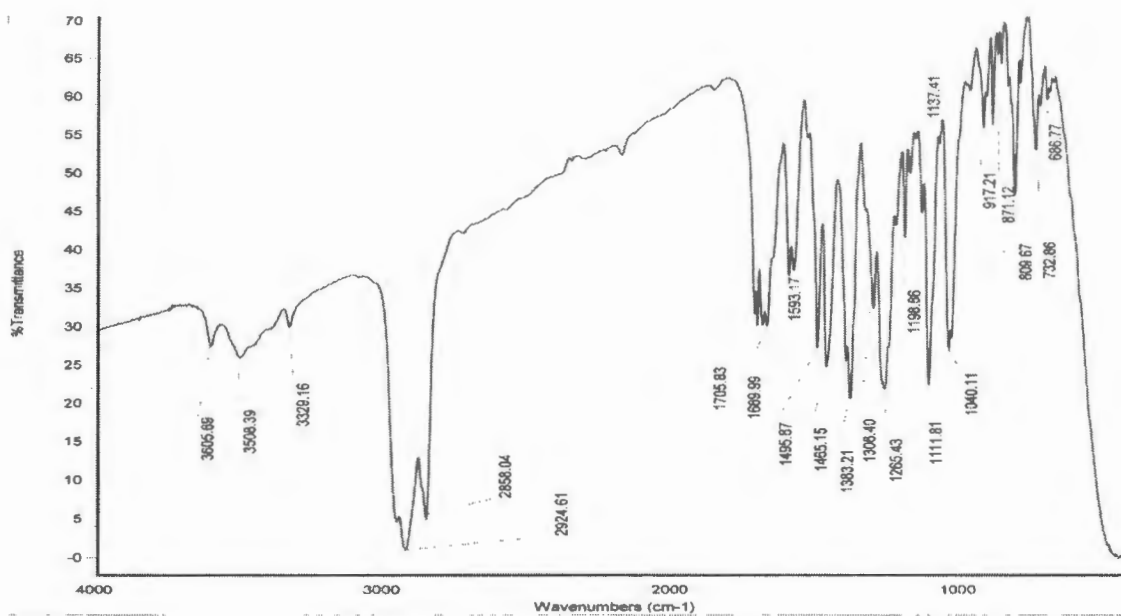


Figure 4.4.3 Infrared spectrum of N,N,N',N'-tetramethylamino porphyrazine hybrid base

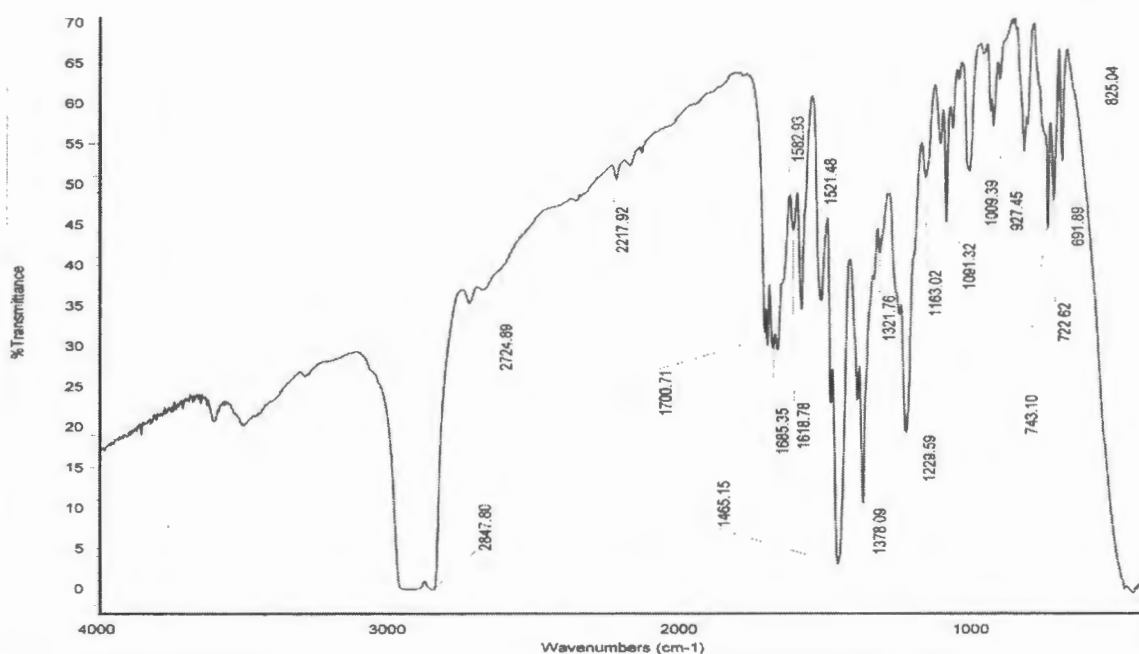


Figure 4.4.4 Infrared spectrum of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine

Table 4.4.1 Table showing the summary of the frequencies of prominent absorption bands of the synthesized porphyrazines

Complex	Band (cm ⁻¹)	Assignment
Pz^I-base	3021	$\nu(\text{N-H})$
	2928-2851	$\nu(\text{CH}_2, \text{CH}_3)$
	1464	$\nu(\text{C-H})$
	1209	$\nu(\text{C=C})$
	723	$\nu(\text{C-H})$
Mg(II)-pz^I	3396	$\nu(\text{C-H})$ aromatic
	2928-2851	$\nu(\text{CH}_2, \text{CH}_3)$
	1643	$\nu(\text{N-Mg})$
Cu(II) pz^I	1379	$\nu(\text{C-H})$
	3055	$\nu(\text{C-H})$ aromatic
	2925-2854	$\nu(\text{CH}_2, \text{CH}_3)$
	1640	$\nu(\text{C=C})$
Co(II)-pz^I	1522	$\nu(\text{N-Cu})$
	3051	$\nu(\text{C-H})$ aromatic
	2824-2897	$\nu(\text{CH}_2, \text{CH}_3)$
	1644	$\nu(\text{C=C})$

	1518	$\nu(\text{N-Co})$
Pz²-base	3508	$\nu(\text{N-H})$
	1593	$\nu(\text{C=C})$
	1265 and 1040	$\nu(\text{C-H})$
Co(II)-pz²	1112	$\nu(\text{C-O})$
	733	$\nu(\text{C-H})$
	2997	$\nu(\text{C-H})$ aromatic
	1574	$\nu(\text{N-Co})$
Cu(II)-pz²	1473	$\nu(\text{C=C})$
	3001	$\nu(\text{C-H})$ aromatic
	1660	$\nu(\text{C=C})$
	1521	$\nu(\text{N-Cu})$
	1013	$\nu(\text{C-C})$
Pc-base	3620	$\nu(\text{N-H})$
	2848	$\nu(\text{C-H})$ aromatic
	1685	$\nu(\text{C=C})$
	1163	$\nu(\text{C-H})$
	743	$\nu(\text{C-H})$
Cu(II)-pc	2986	$\nu(\text{C-H})$ aromatic
	2856-2746	$\nu(\text{CH}_2, \text{CH}_3)$
	2340 and 1580	$\nu(\text{C=C})$
	1579	$\nu(\text{N-Cu})$
Co(II)-pc	2999	$\nu(\text{C-H})$ aromatic
	2770-2897	$\nu(\text{CH}_2, \text{CH}_3)$
	1586	$\nu(\text{C=C})$
	1565	$\nu(\text{N-Co})$

4.5 ELEMENTAL ANALYSIS

Elemental analysis of the synthesized porphyrazine complexes produced results that are in close agreement with the calculated percentages of carbons, hydrogens and nitrogens and the results are summarized in Tables 4.5.1 to 4.5.10

Table 4.5.1 2,3,9,10,16,17,23,24-octakis (propyl) porphyrazine magnesium

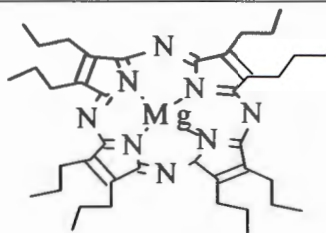
Formula	C₃₃H₄₂N₈Mg(II)		
MW (g/mol)	574.30		
Structure			
Elemental analysis			
	C	H	N
Found	68.93	7.28	20.0
Calculated	68.95	7.31	19.50

Table 4.5.2 2,3,9,10,16,17,23,24-octakis (propyl) porphyrazines base

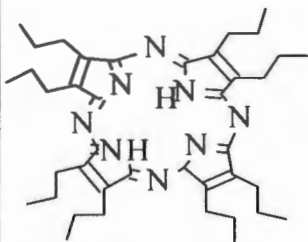
Formula	C₃₃H₄₄N₈		
MW (g/mol)	552.00		
Structure			
Elemental analysis			
	C	H	N
Found	71.68	8.01	20.28
Calculated	71.74	7.97	20.29

Table 4.5.3 2,3,9,10,16,17,23,24-octakis(propyl) porphyrazine copper(II)

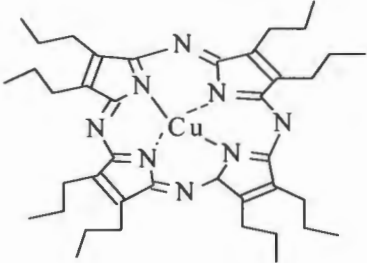
Formula	C₃₃H₄₂N₈Cu(II)		
MW (g/mol)	613.54		
Structure			
Elemental analysis			
	C	H	N
Found	64.50	6.81	18.00
Calculated	64.54	6.85	18.25

Table 4.5.4 2,3,9,10,16,17,23,24-octakis (propyl) porphyrazine cobalt(II)

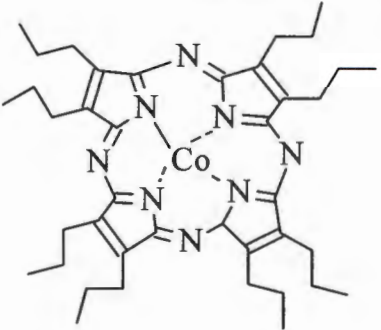
Formula	C₃₃H₄₂N₈Co(II)		
MW (g/mol)	608.93		
Structure			
Elemental analysis			
	C	H	N
Found	65.00	6.86	18.32
Calculated	65.03	6.90	18.39

Table 4.5.5 N,N,N',N'-tetramethylamino porphyrazine hybrid base

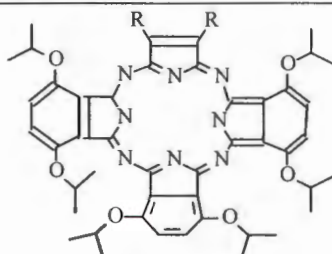
Formula	C₄₆H₆₀N₁₀O₆		
MW (g/mol)	850.23		
Structure			
Elemental analysis			
	C	H	N
Found	65.63	7.88	6.73
Calculated	64.49	7.29	6.47

Table 4.5.6 N,N,N',N'-tetramethyl amino porphyrazine hybrid copper(II)

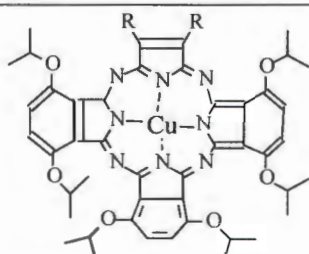
Formula	C₄₆H₆₀N₁₀O₆Cu(II)		
MW (g/mol)	913.77		
Structure			
Elemental analysis			
	C	H	N
Found	61.11	6.54	14.98
Calculated	60.40	6.56	15.32



Table 4.5.7 N,N,N',N'-tetramethylamino porphyrazine hybrid cobalt(II)

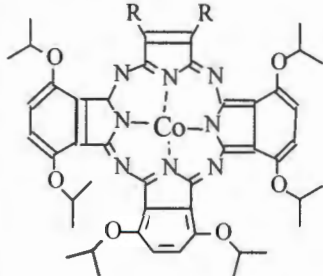
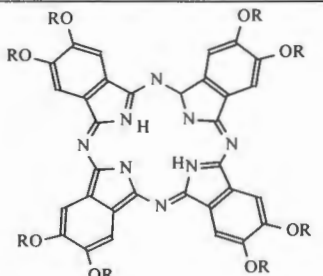
Formula	C₄₆H₆₀N₁₀O₆Co(II)		
MW (g/mol)	909.16		
Structure			
Elemental analysis			
	C	H	N
Found	61.27	6.33	15.02
Calculated	60.74	6.59	15.39

Table 4.5.8 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base

Formula	C₇₉H₅₂N₈O₈		
MW (g/mol)	1240.032		
Structure			
Elemental analysis			
	C	H	N
Found	76.21	4.18	9.11
Calculated	76.45	4.19	9.03

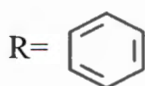


Table 4.5.9 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II)

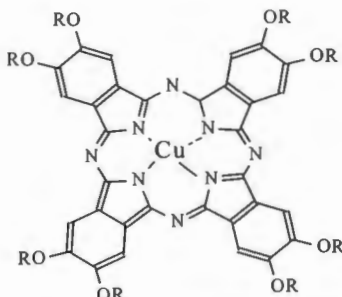
Formula	C₇₉H₅₀N₈O₈Cu(II)		
MW (g/mol)	1303.572		
Structure			
Elemental analysis			
	C	H	N
Found	72.68	3.86	8.45
Calculated	72.72	3.83	8.59

Table 4.5.10 2,3,9,10,16,17,23,24-octa substituted phthalocyanine cobalt(II)

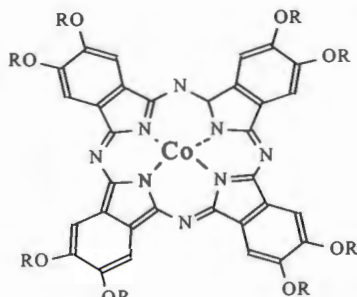
Formula	C₇₉H₅₀N₈O₈Co(II)		
MW (g/mol)	1298.962		
Structure			
Elemental analysis			
	C	H	N
Found	72.88	3.80	8.48
Calculated	72.98	3.84	8.62

Table 4.5.11 2,3-Benzo[3,6-bis(isopropoxy)]-7,8,12,13,17,18-hexapropyl porphyrazines base

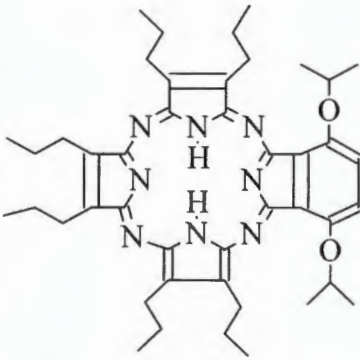
Formula	C₄₂H₆₂N₇O₂		
MW (g/mol)	710.00		
Structure			
Elemental analysis			
	C	H	N
Found	70.80	8.69	15.70
Calculated	71.00	8.73	15.77

Table 4.5.12 2,3-Benzo[3,6-bis(isopropoxy)]-7,8,12,13,17,18-hexapropyl porphyrazine copper(II)

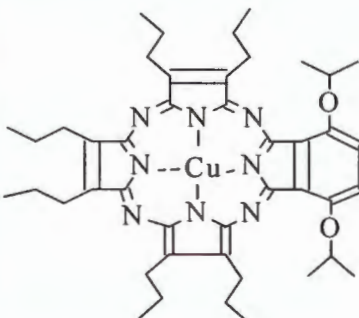
Formula	C₄₂H₆₂N₇O₂Cu(II)		
MW (g/mol)	773.54		
Structure			
Elemental analysis			
	C	H	N
Found	65.08	8.07	14.33
Calculated	65.16	8.02	14.48

Table 4.5.13 2,3-Benzo[3,6-bis(isopropoxy)]-7,8,12,13,17,18-hexapropyl porphyrazine cobalt(II)

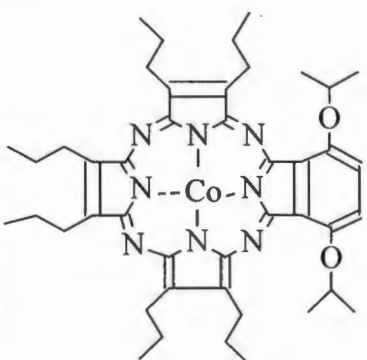
Formula	$\text{C}_{42}\text{H}_{62}\text{N}_7\text{O}_2\text{Co(II)}$		
MW (g/mol)	768.93		
Structure			
Elemental analysis			
	C	H	N
Found	65.00	8.01	14.53
Calculated	65.55	8.06	14.57

Table 4.5.14 Tetranitro phthalocyanine base

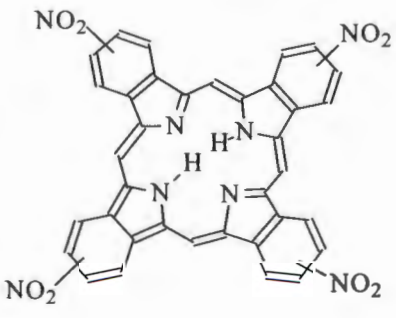
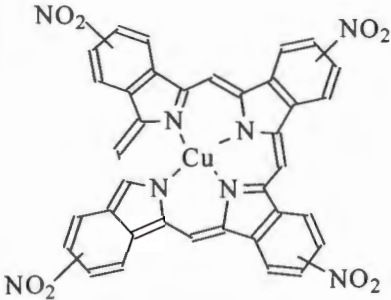
Formula	$\text{C}_{32}\text{H}_{14}\text{N}_{12}\text{O}_8$		
MW (g/mol)	638.00		
Structure			
Elemental analysis			
	C	H	N
Found	60.09	2.16	17.51
Calculated	60.19	2.19	17.55

Table 4.5.15 Tetranitro phthalocyanine copper(II)

Formula	C₃₂H₁₄N₁₂O₈Cu(II)		
MW (g/mol)	701.54		
Structure			
Elemental analysis			
	C	H	N
Found	54.70	1.98	15.77
Calculated	54.74	2.00	15.96

4.6 KINETIC STUDIES

4.6.1 KINETICS OF METALLATION OF COMPOUNDS

Preliminary repetitive scanning of the ultraviolet-visible spectral region during the insertion of Cu(II) and Co(II) in 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base, 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II), N,N,N',N'-tetramethylamino porphyrazine hybrid base and 2,3,9,10,16,17,23,24-octa substituted phthalocyanine gave well defined isosbestic points for over two half-lives of various reactions. Typical spectral changes for these reactions are compiled in Figure 4.6.1 – 4.6.7 while the corresponding graphs are Figure 4.6.8 – 4.6.46

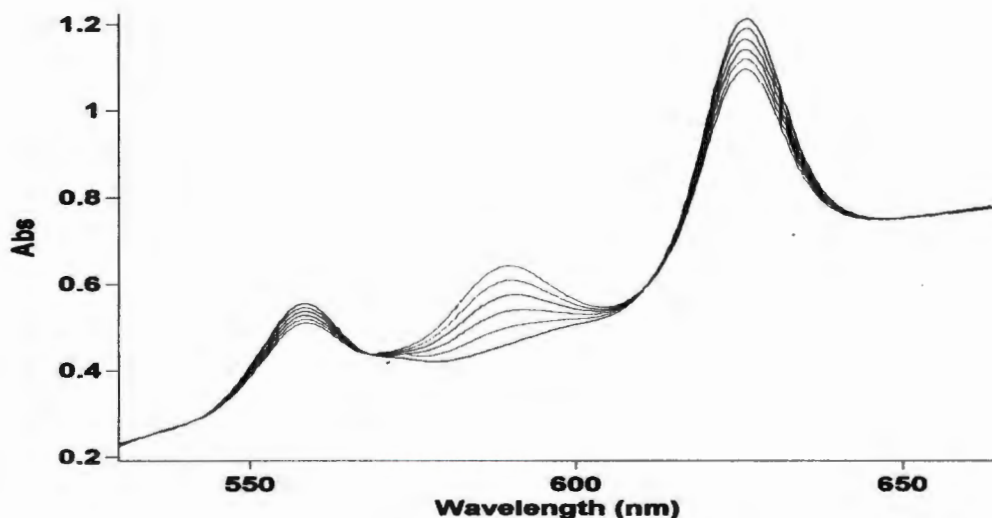


Figure 4.6.1 Spectral change during the reaction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base (5×10^{-6} M) and copper acetate (5×10^{-6} M) in acetic acid at 20°C at 5-minutes intervals.

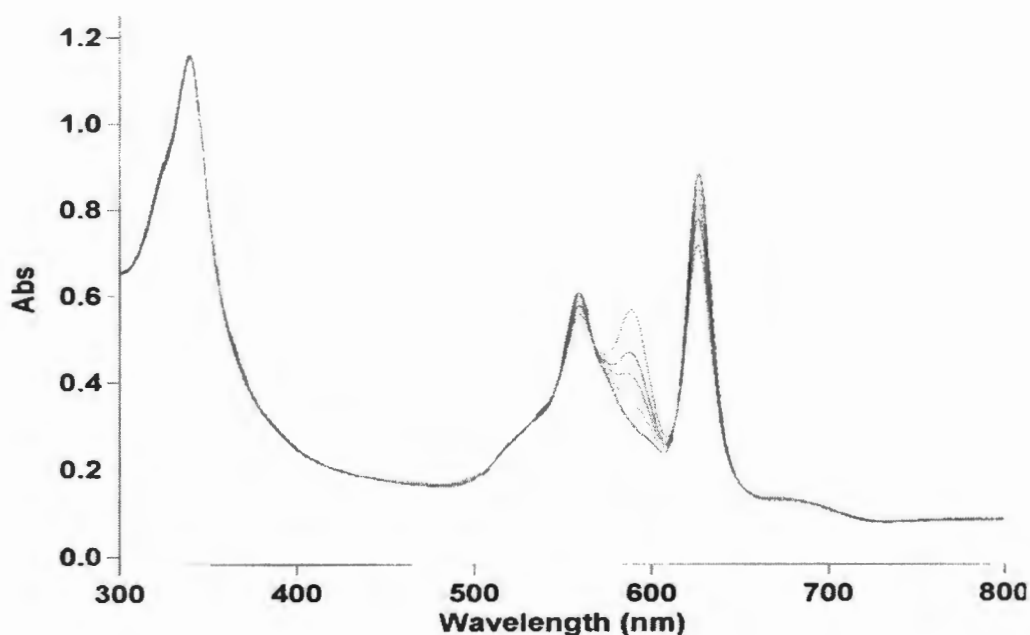


Figure 4.6.2 Spectral change during the reaction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base (1.1×10^{-5} M) and cobalt acetate (1.1×10^{-5} M) in acetic acid at 55°C at 5-minutes intervals.

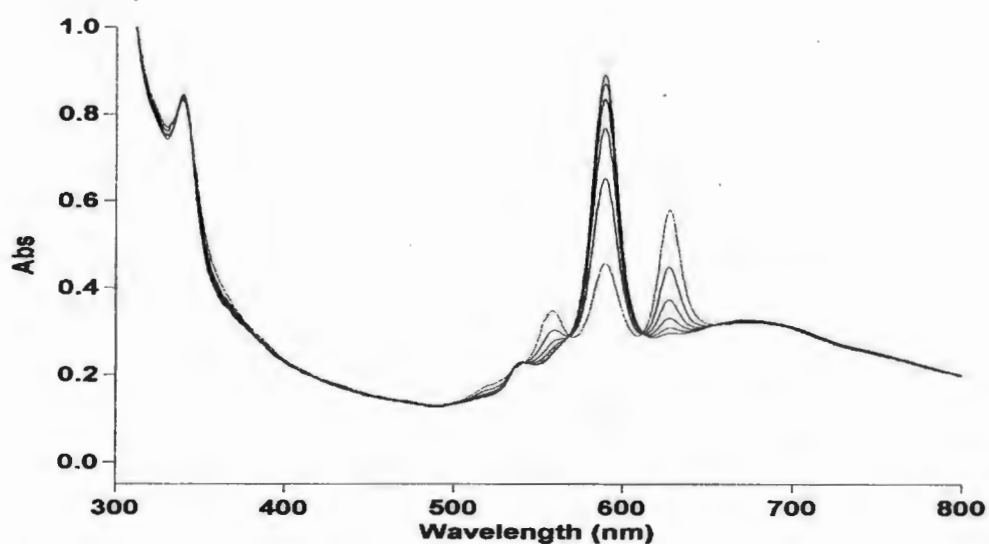


Figure 4.6.3 Spectral change during the reaction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine magnesium ($1.6 \times 10^{-5} \text{ M}$) and copper(II) acetate ($1.6 \times 10^{-5} \text{ M}$) in acetic acid at 40°C at 5-minutes intervals.

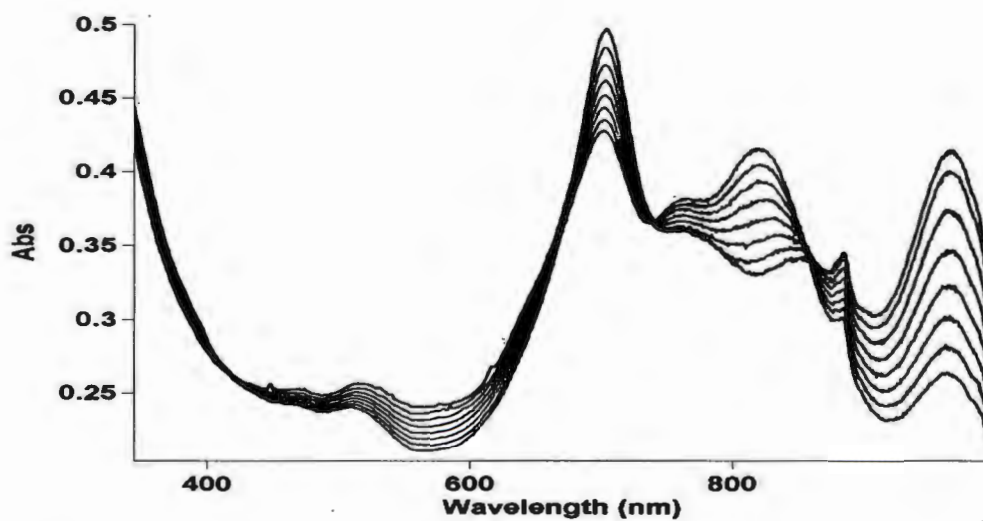


Figure 4.6.4 Spectral change during reaction of cobalt acetate ($0.72 \times 10^{-6} \text{ M}$) and N,N,N',N'-tetramethylaminoporphyrizine hybrid base ($0.72 \times 10^{-6} \text{ M}$) in acetic acid at 15°C at 5-minutes intervals.

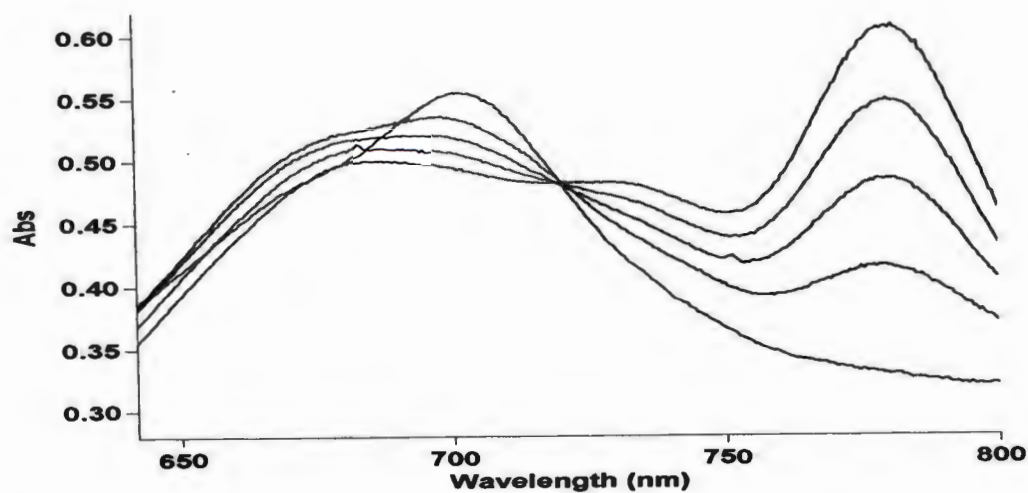


Figure 4.6.5 Spectral change during reaction of copper acetate (0.82×10^{-5} M) and N,N,N',N'-tetramethylamino porphyrazine hybrid base (0.82×10^{-5} M) in acetic acid at 40°C at 5 minutes intervals.

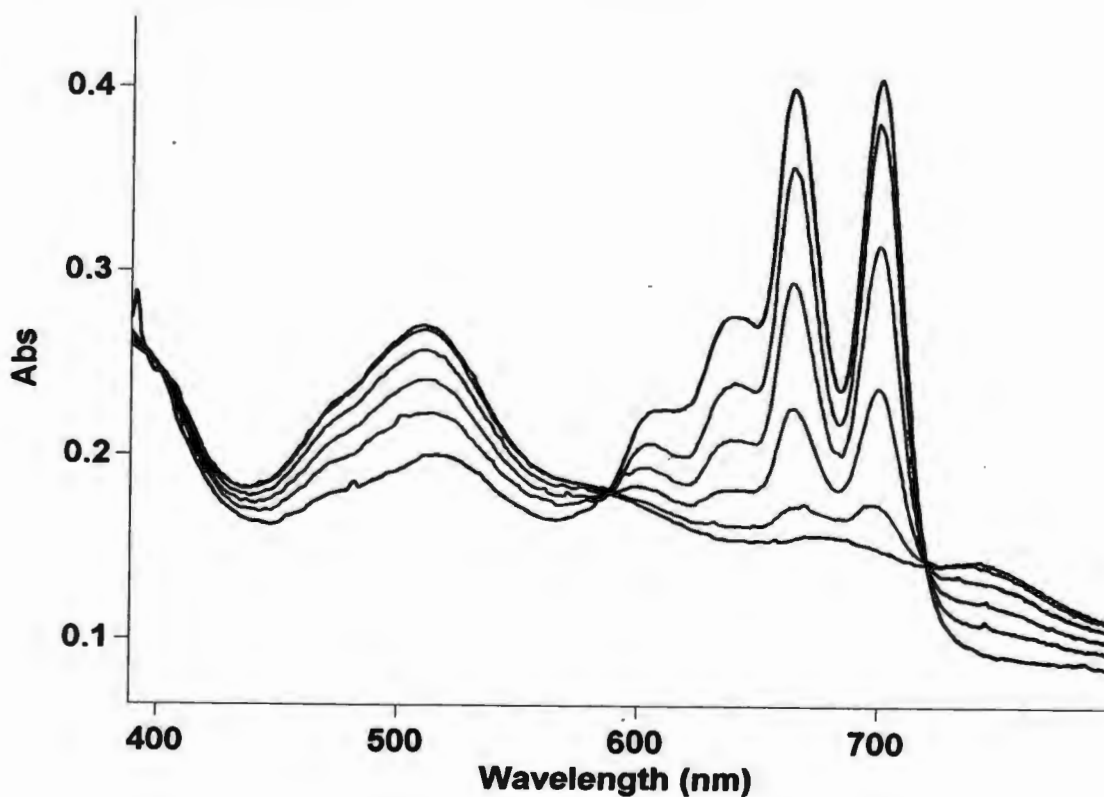


Figure 4.6.6 Spectral change during reaction of cobalt acetate (0.32×10^{-6} M) and 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (0.32×10^{-6} M) in acetic acid at 45°C at 5 minutes intervals.

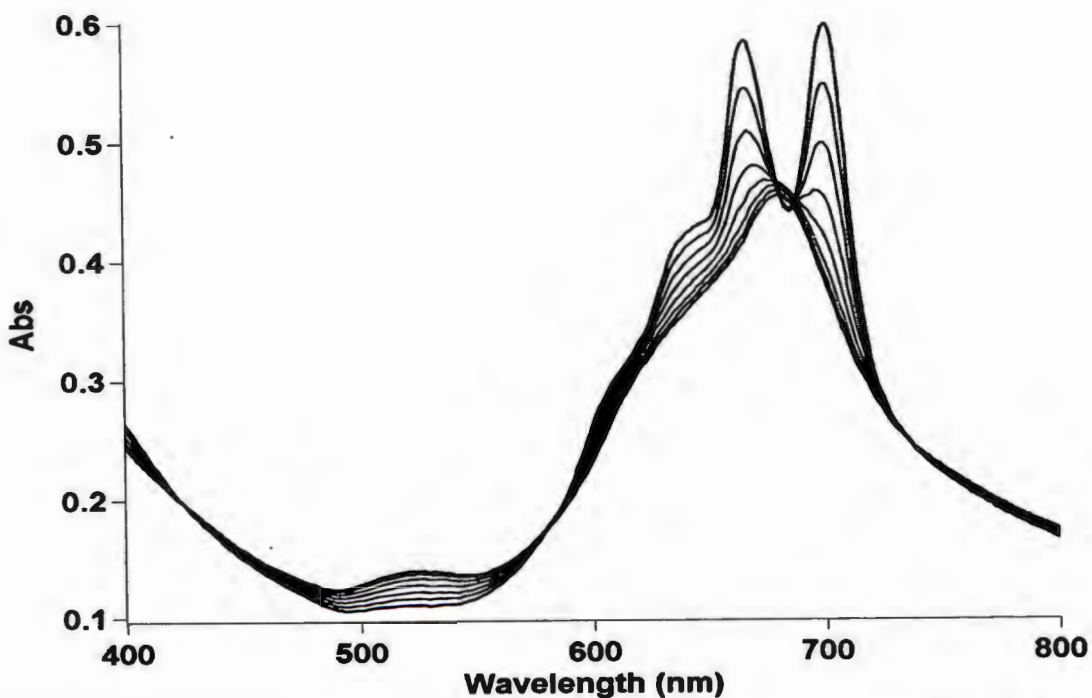
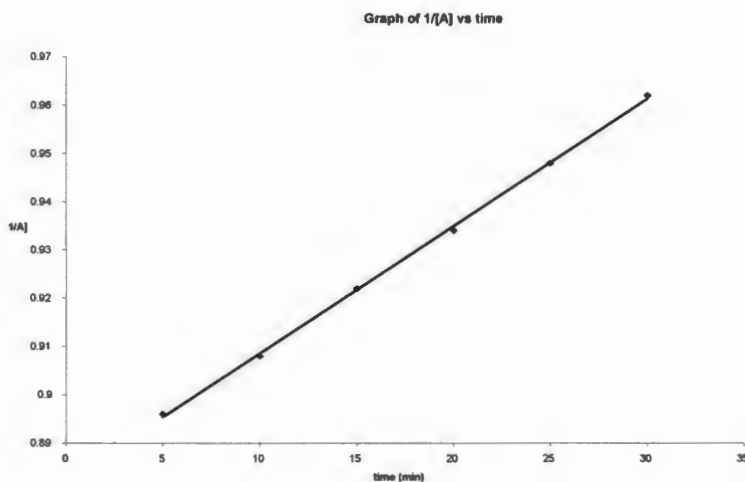
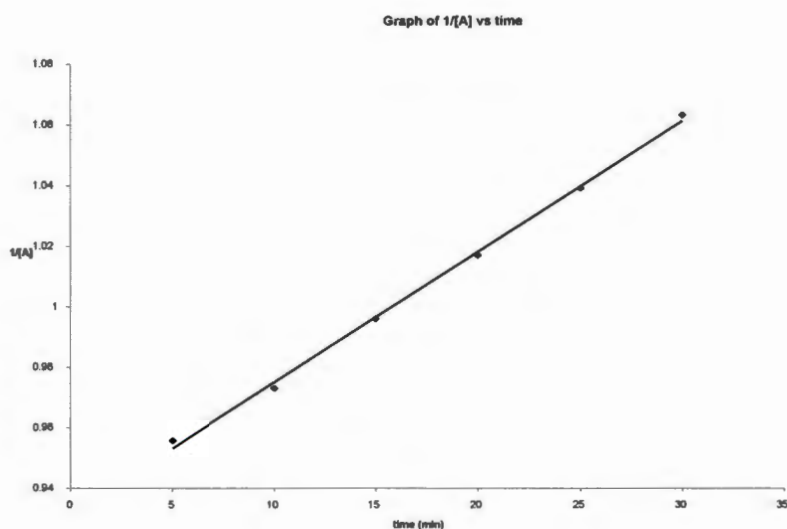


Figure 4.6.7 Spectral change during reaction of copper acetate (0.45×10^{-6} M) and 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (0.45×10^{-6} M) in acetic acid at 25°C at 2 minutes intervals.



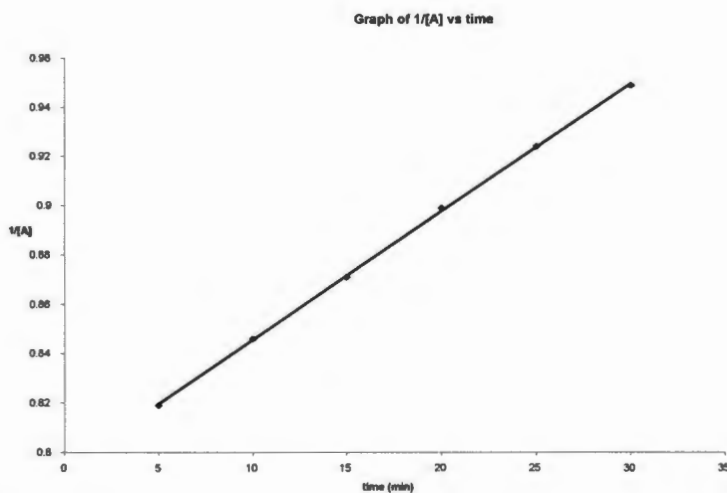
Rate constant = $2.6 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.8 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base (5×10^{-6} M) with copper(II) ion (5×10^{-6} M) in acetic acid at 20°C ($\lambda = 588 \text{ nm}$)



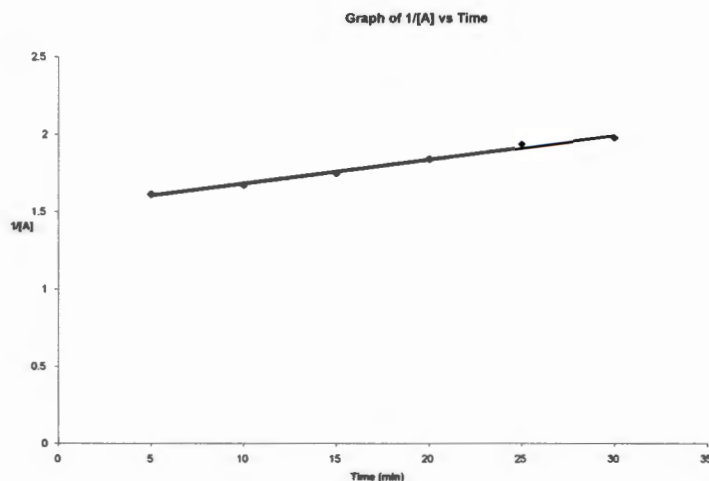
Rate constant = $4.30 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.9 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base ($5 \times 10^{-6} \text{ M}$) with copper(II) ion ($5 \times 10^{-6} \text{ M}$) in acetic acid at 25°C ($\lambda = 588 \text{ nm}$).



Rate constant = $5.20 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.10 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base ($5 \times 10^{-6} \text{ M}$) with copper(II) ion ($5 \times 10^{-6} \text{ M}$) in acetic acid at 30°C ($\lambda = 588 \text{ nm}$)



Rate constant = $15.30 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.11 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base ($5 \times 10^{-6} \text{ M}$) with copper(II) ion ($5 \times 10^{-6} \text{ M}$) in acetic acid at 40°C ($\lambda = 588 \text{ nm}$)

Table 4.6.1 Table of kinetic results of $\ln k$ vs $1/T$ of the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base ($5 \times 10^{-6} \text{ M}$) with copper (II) ion ($5 \times 10^{-6} \text{ M}$) in acetic acid ($\lambda = 588 \text{ nm}$)

Temp. (K)	$1/T \times 10^{-3}$ (K^{-1})	$k \times 10^{-3}$ ($\text{M}^{-1} \cdot \text{s}^{-1}$)	$\ln k$	$\ln (k/T)$	$t_{1/2}$ (min^{-1})
293	3.41	2.70	-5.95	-11.63	341.21
298	3.36	3.20	-5.44	-11.14	216.92
303	3.30	3.90	-5.25	-10.82	152.62
313	3.19	5.80	-4.17	-9.92	100.0

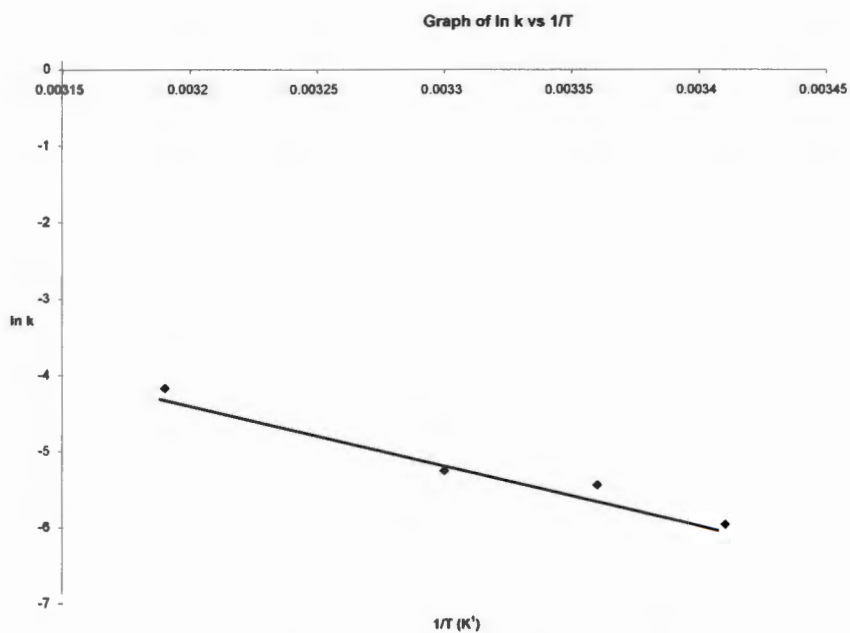


Figure 4.6.12 A typical plot of $\ln k$ vs $1/T$ for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base (5×10^{-6} M) with copper(II) ion (5×10^{-6} M) in acetic acid ($\lambda = 588$ nm)

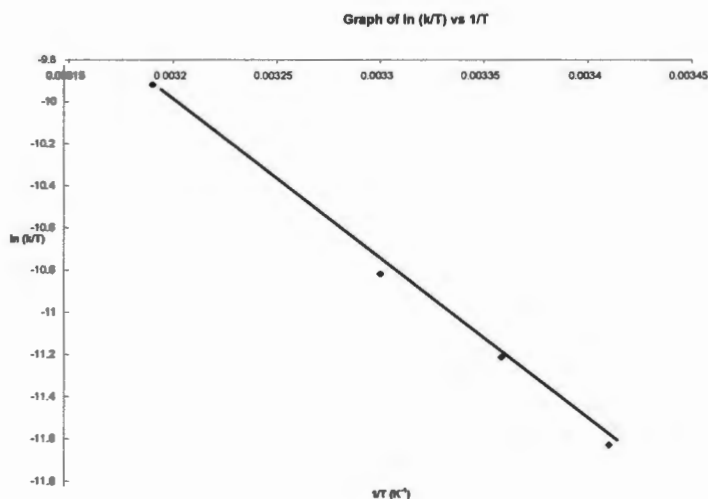
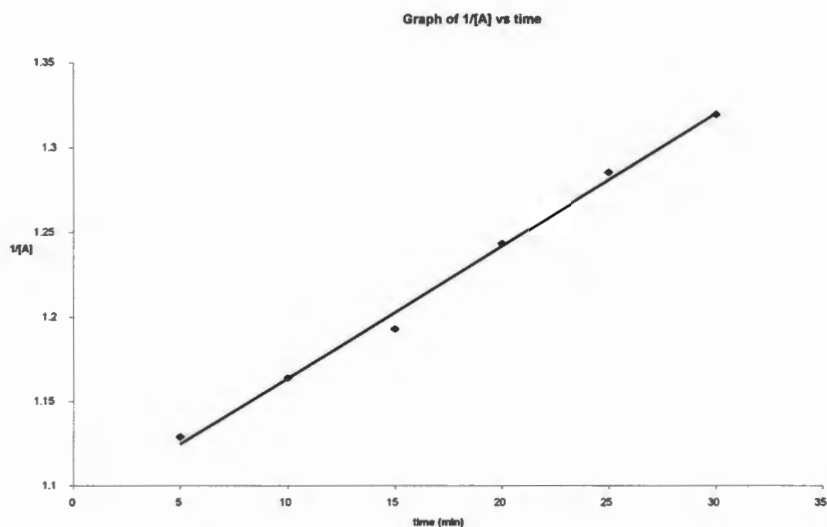
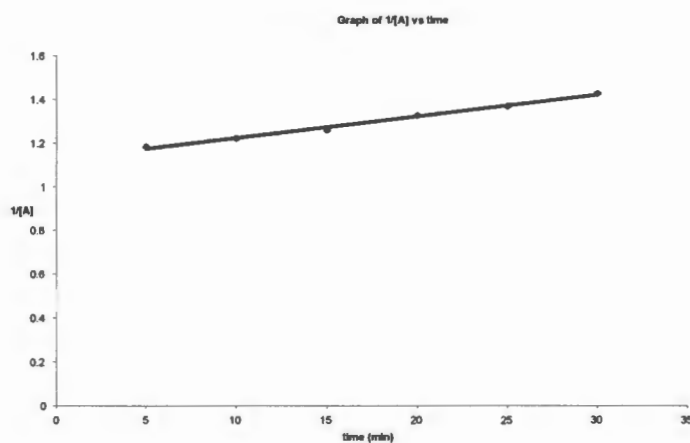


Figure 4.6.13 A typical plot of $\ln (k/T)$ vs $1/T$ for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base (5×10^{-6} M) with copper(II) ion (5×10^{-6} M) in acetic acid ($\lambda = 588$ nm)



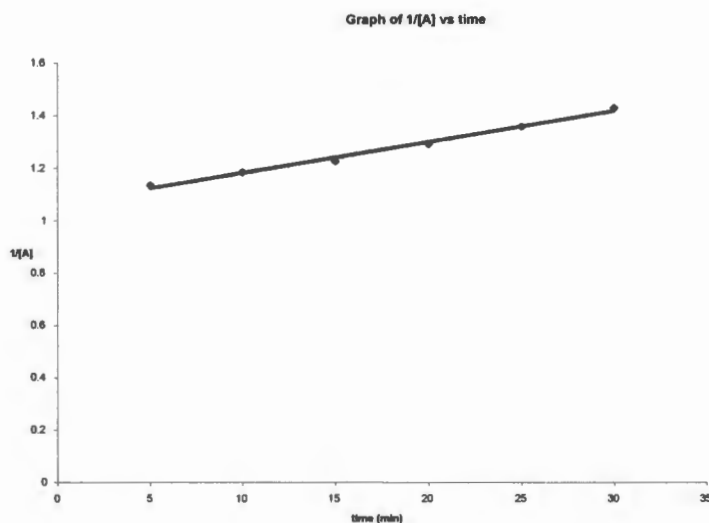
Rate constant = $7.80 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.14 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base ($1.1 \times 10^{-5} \text{ M}$) with cobalt(II) ion ($1.1 \times 10^{-5} \text{ M}$) in acetic acid at 50°C at 5 minutes intervals ($\lambda = 588 \text{ nm}$).



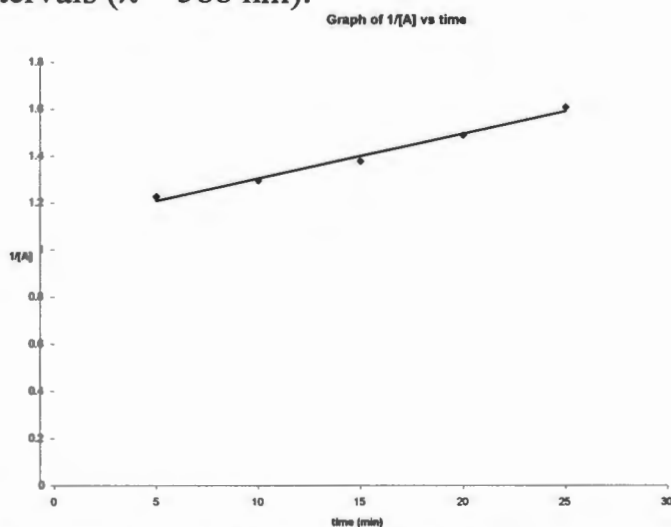
Rate constant = $9.90 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.15 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base ($1.1 \times 10^{-5} \text{ M}$) with cobalt(II) ion ($1.1 \times 10^{-5} \text{ M}$) in acetic acid at 55°C at 5 minutes intervals ($\lambda = 588 \text{ nm}$).



Rate constant = $11.60 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.16 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine base ($1.1 \times 10^{-5} \text{ M}$) with cobalt(II) ion ($1.1 \times 10^{-5} \text{ M}$) in acetic acid at 60°C at 5 minutes intervals ($\lambda = 588 \text{ nm}$).



Rate constant = $16.70 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.17 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine base ($1.1 \times 10^{-5} \text{ M}$) with cobalt(II) ion ($1.1 \times 10^{-5} \text{ M}$) in acetic acid at 65°C at 5 minutes intervals ($\lambda = 588 \text{ nm}$).

Table 4.6.2 Table of kinetic results of $\ln k$ vs $1/T$ of the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base (1.1×10^{-5} M) with cobalt(II) ion (1.1×10^{-5} M) in acetic acid ($\lambda = 588$ nm).

Temp (K)	$1/T \times 10^3$ (K^{-1})	$k \times 10^3$ ($M^{-1}.s^{-1}$)	$\ln k$	$\ln (k/T)$	$t_{1/2}$ (min^{-1})
323	3.09	7.80	-4.85	-10.63	111.10
328	3.04	9.90	-4.61	-10.41	75.18
333	3.00	11.60	-4.45	-10.26	68.02
338	2.95	12.90	-4.35	-10.17	52.63
343	2.91	16.70	-4.09	-9.93	50.01

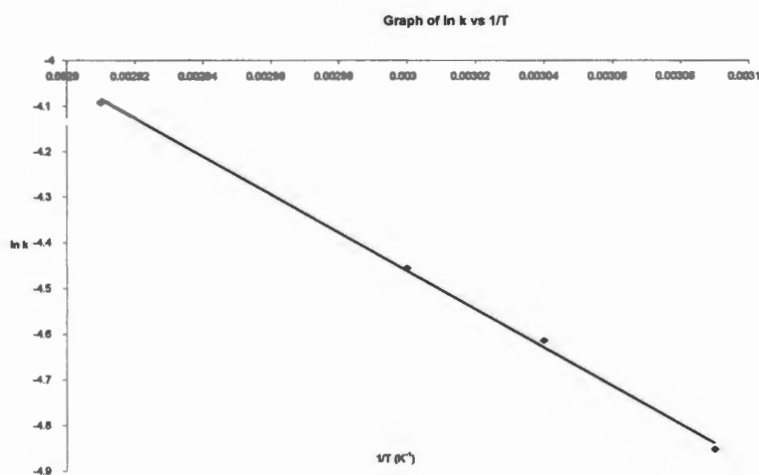


Figure 4.6.18 A typical plot of $\ln k$ vs $1/T$ for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base (1.1×10^{-5} M) with cobalt(II) ion (1.1×10^{-5} M) in acetic acid ($\lambda = 588$ nm).

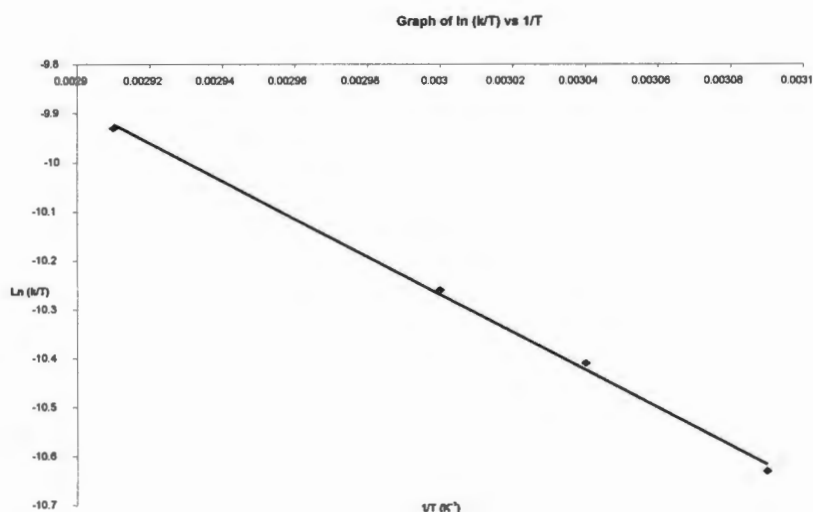
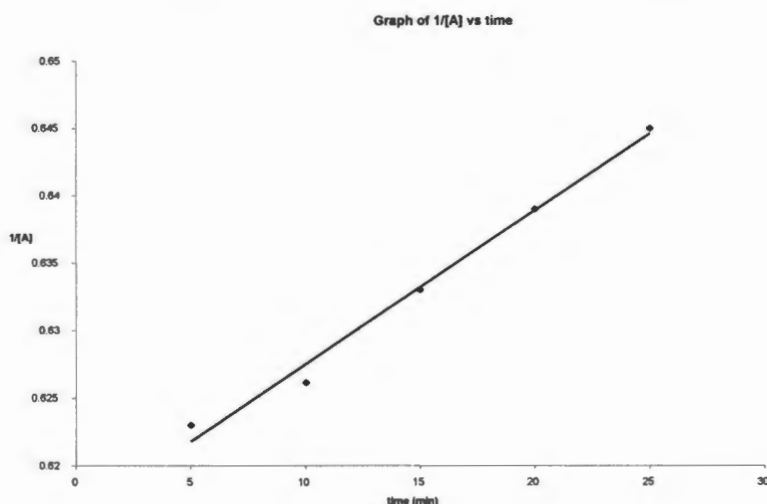
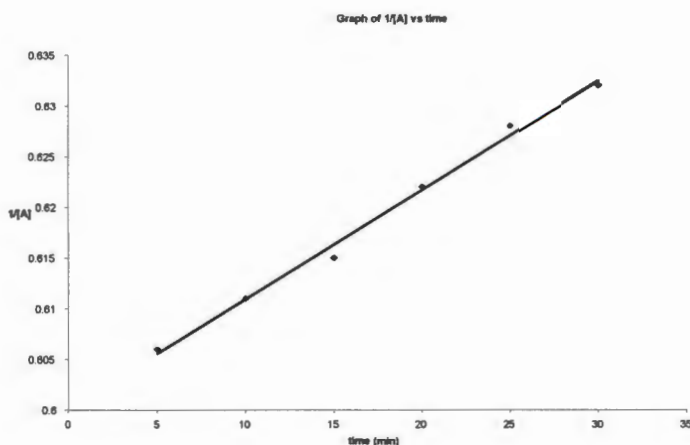


Figure 4.6.19 A typical plot of $\ln(k/T)$ vs $1/T$ for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine base (1.1×10^{-5} M) with cobalt(II) ion (1.1×10^{-5} M) in acetic acid ($\lambda = 588$ nm)



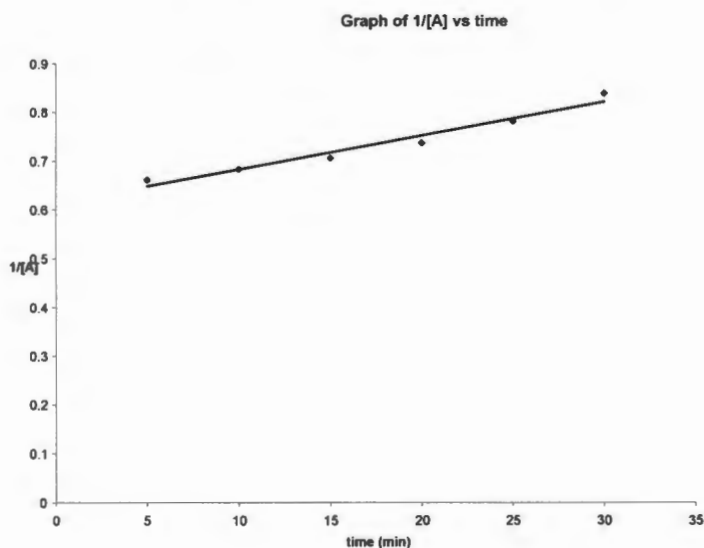
Rate constant = $0.98 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.20 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine magnesium(II) (1.6×10^{-5} M) with copper(II) ion (1.6×10^{-5} M) in acetic acid at 30°C at 5 minutes intervals ($\lambda = 588$ nm).



Rate constant = $1.10 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.21 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine magnesium ($1.6 \times 10^{-5} \text{ M}$) with copper(II) ion ($1.6 \times 10^{-5} \text{ M}$) in acetic acid at 30°C at 5 minutes intervals ($\lambda = 588 \text{ nm}$).



Rate constant = $6.90 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.22 A typical kinetic plot for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine magnesium ($1.6 \times 10^{-5} \text{ M}$) with copper(II) ion ($1.6 \times 10^{-5} \text{ M}$) in acetic acid at 30°C at 5 minutes intervals ($\lambda = 588 \text{ nm}$).

Table 4.6.3 Table of kinetic results of $\ln k$ vs $1/T$ of the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine magnesium (1.6×10^{-5} M) with copper(II) ion (1.6×10^{-5} M) in acetic acid ($\lambda = 588$ nm)

Temp (K)	$1/T \times 10^3$ (K^{-1})	$k \times 10^{-3}$ ($M^{-1}.s^{-1}$)	$\ln k$	$\ln (k/T)$	$t_{1/2}$ (min^{-1})
303.0	3.24	0.90	-6.92	-12.72	452.32
308.0	3.20	1.10	-5.60	-11.25	368.71
313.0	3.19	6.90	-4.97	-10.72	298.20

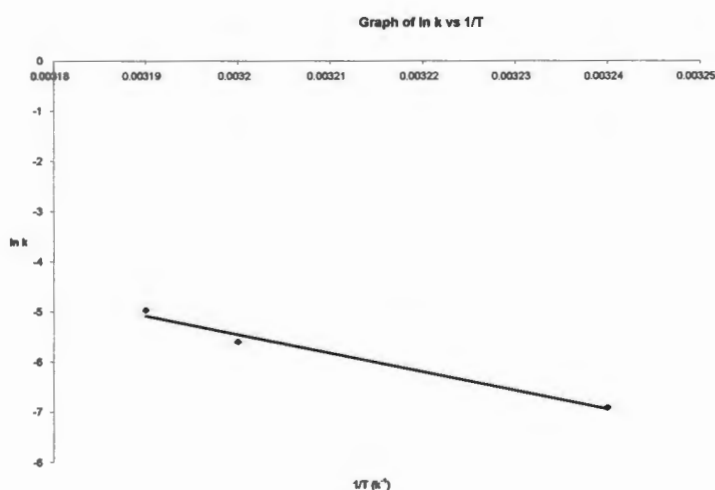


Figure 4.6.23 A typical plot of $\ln k$ vs $1/T$ for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine magnesium (1.6×10^{-5} M) with copper(II) ion (1.6×10^{-5} M) in acetic acid ($\lambda = 588$ nm)

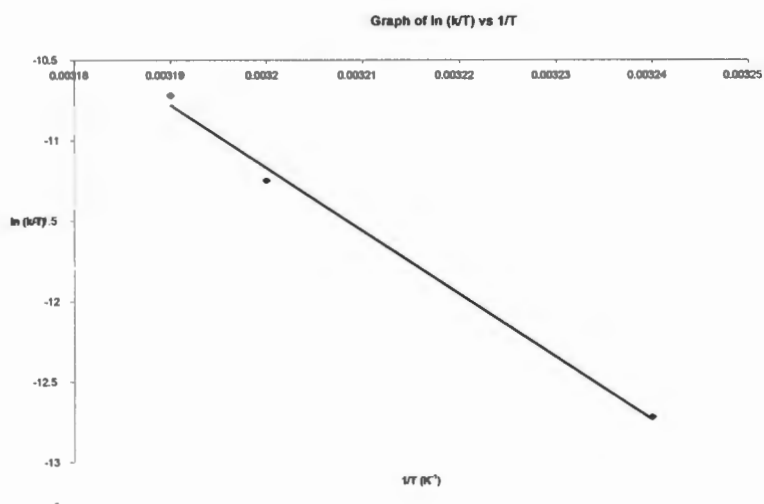
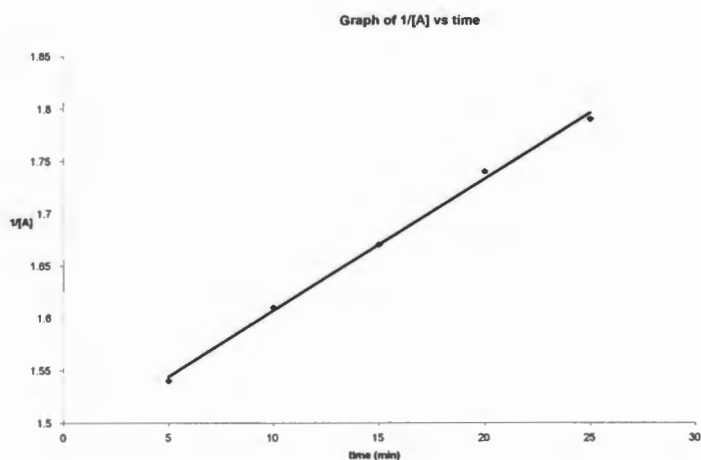
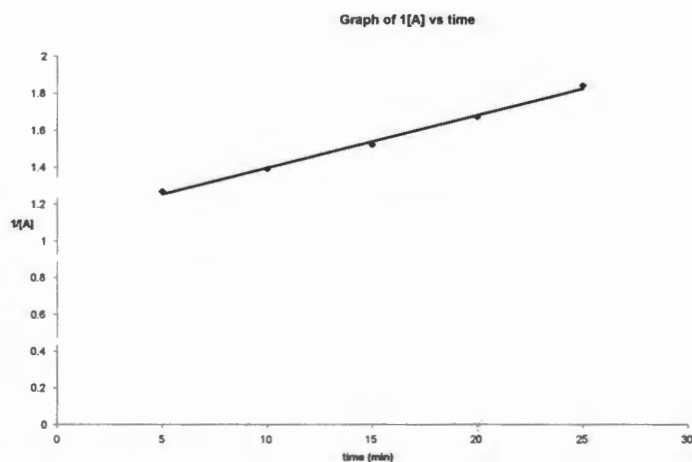


Figure 4.6.24 A typical plot of $\ln(k/T)$ vs $1/T$ for the metallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine magnesium (1.6×10^{-5} M) with copper(II) ion (1.6×10^{-5} M) in acetic acid ($\lambda = 588$ nm).



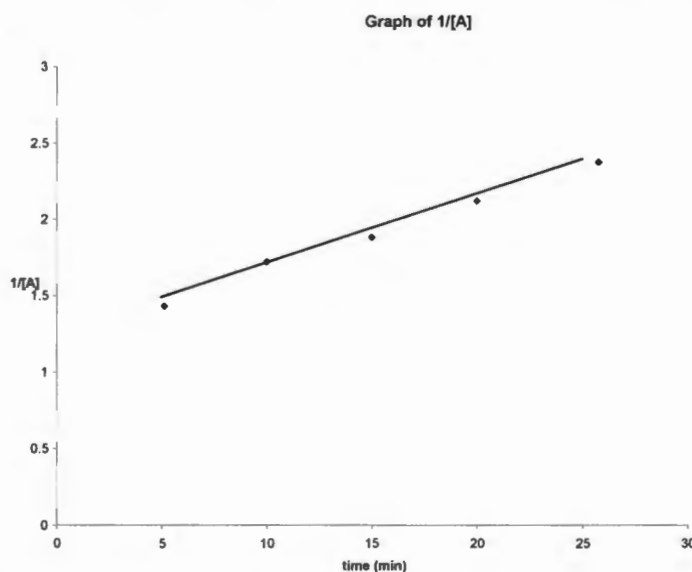
Rate constant = $0.0116 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.25 A typical kinetic plot for the metallation of N,N,N',N'-tetramethylamino porphyrizine hybrid base (0.72×10^{-6} M) with cobalt (II) ion (0.72×10^{-6} M) in acetic acid at 20°C at 5 minutes intervals ($\lambda = 779$ nm).



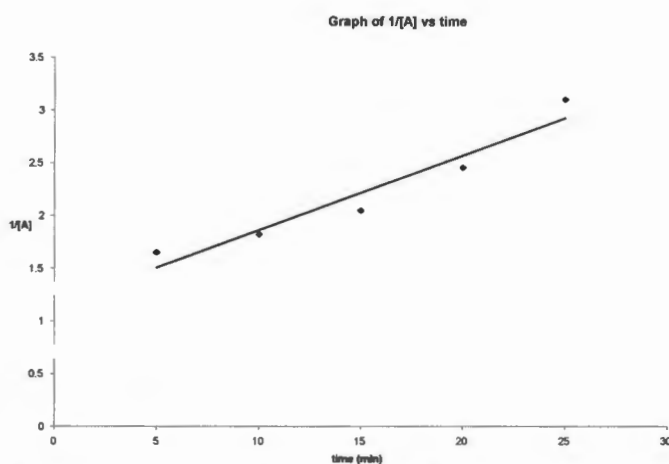
Rate constant = $0.028 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.26 A typical kinetic plot for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.72 \times 10^{-6} \text{ M}$) with cobalt (II) ion ($0.72 \times 10^{-6} \text{ M}$) in acetic acid at 25°C at 5 minutes intervals ($\lambda = 779 \text{ nm}$).



Rate constant = $0.0452 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.27 A typical kinetic plot for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.72 \times 10^{-6} \text{ M}$) with cobalt (II) ion ($0.72 \times 10^{-6} \text{ M}$) in acetic acid at 30°C at 5 minutes intervals ($\lambda = 779 \text{ nm}$).



Rate constant = $0.0712 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.28 A typical kinetic plot for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.72 \times 10^{-6} \text{ M}$) with cobalt (II) ion ($0.72 \times 10^{-6} \text{ M}$) in acetic acid at 35°C at 5 minutes intervals ($\lambda = 779 \text{ nm}$).

Table 4.6.4 Table of kinetic results of $\ln k$ vs $1/T$ of the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.72 \times 10^{-6} \text{ M}$) with cobalt(II) ion ($0.72 \times 10^{-6} \text{ M}$) in acetic acid ($\lambda = 779 \text{ nm}$).

Temp (K)	$1/T \times 10^{-3} (\text{K}^{-1})$	$k \times 10^{-3} (\text{M}^{-1} \cdot \text{s}^{-1})$	$\ln k$	$\ln (k/T)$
283	3.53	11.63	-4.45	-10.09
288	3.47	28.42	-3.56	-9.22
293	3.41	45.21	-3.09	-8.77
303	3.30	71.24	-2.64	-7.88

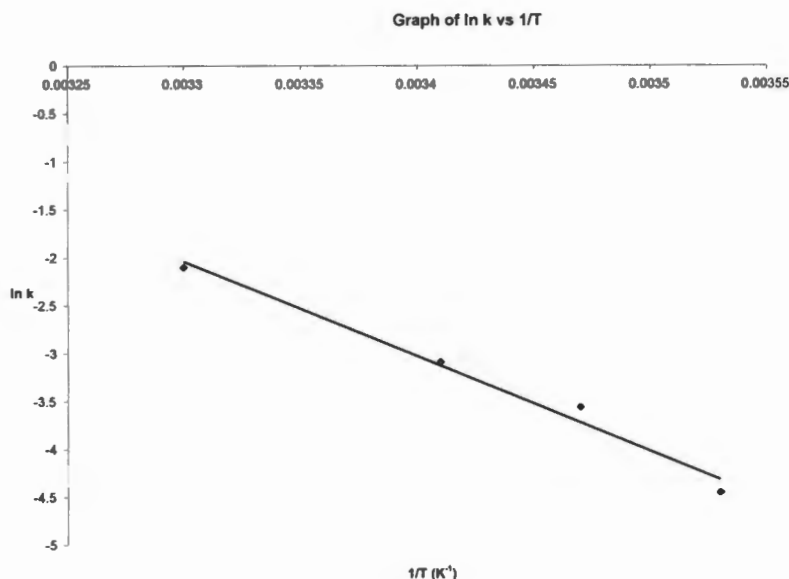


Figure 4.6.29 A typical plot of $\ln k$ vs $1/T$ for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base (0.72×10^{-6} M) with cobalt(II) ion (0.72×10^{-6} M) in acetic acid at 5 minutes intervals ($\lambda = 779$ nm).

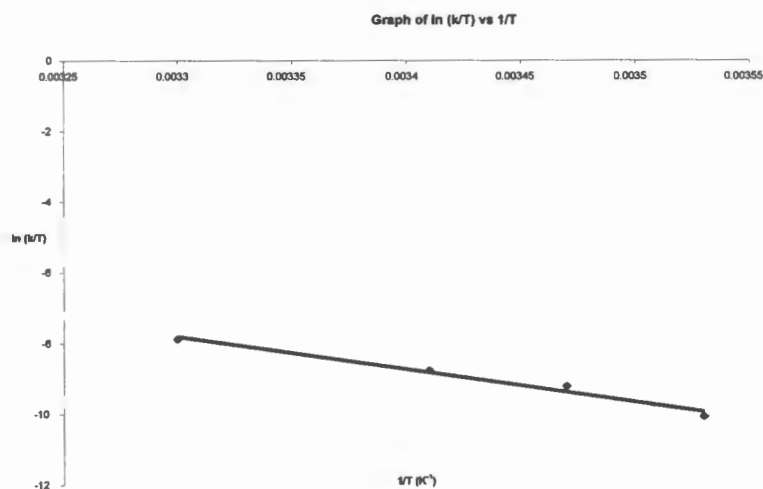
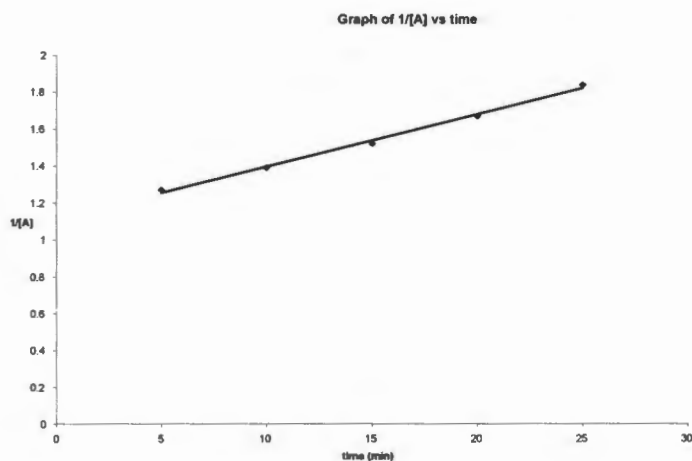
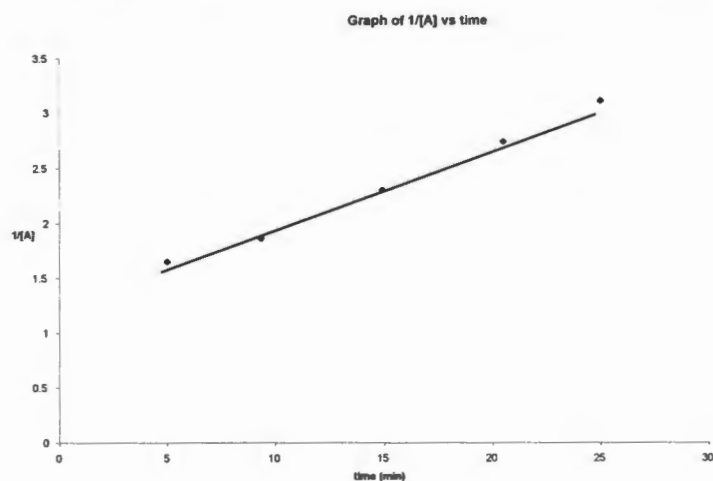


Figure 4.6.30 A typical plot of $\ln (k/T)$ vs $1/T$ for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base (0.72×10^{-6} M) with cobalt(II) ion (0.72×10^{-6} M) in acetic acid ($\lambda = 779$ nm).



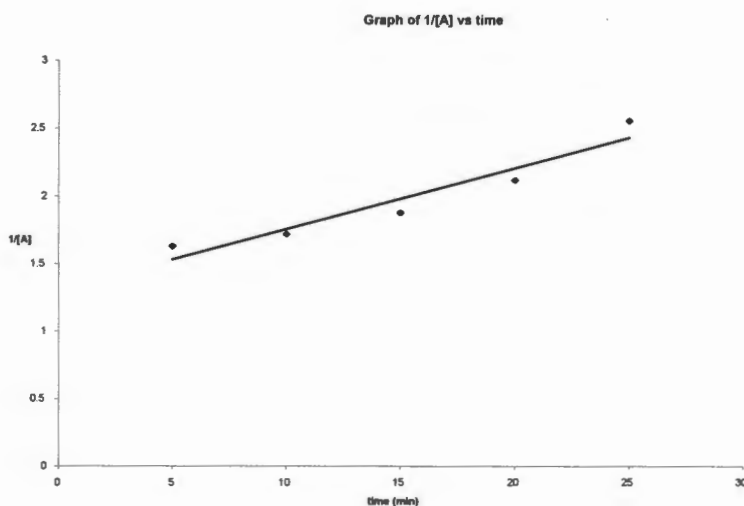
Rate constant = $0.0284 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.31 A typical kinetic plot for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.82 \times 10^{-5} \text{ M}$) with copper(II) ion ($0.82 \times 10^{-5} \text{ M}$) in acetic acid at 40°C at 5 minutes intervals ($\lambda = 779 \text{ nm}$).



Rate constant = $0.0452 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.32 A typical kinetic plot for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.82 \times 10^{-5} \text{ M}$) with copper (II) ion ($0.82 \times 10^{-5} \text{ M}$) in acetic acid at 45°C at 5 minutes intervals ($\lambda = 779 \text{ nm}$).



Rate constant $= 0.0712 \text{ M}^{-1}.\text{s}^{-1}$

Figure 4.6.33 A typical kinetic plot for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.82 \times 10^{-6} \text{ M}$) with copper (II) ion ($0.82 \times 10^{-6} \text{ M}$) in acetic acid at 50°C at 5 minutes intervals ($\lambda = 779 \text{ nm}$).

Table 4.6.5 Table of kinetic results of $\ln k$ vs $1/T$ of the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base ($0.82 \times 10^{-6} \text{ M}$) with copper(II) ion ($0.82 \times 10^{-6} \text{ M}$) in acetic acid ($\lambda = 779 \text{ nm}$).

Temp (K)	$1/T \times 10^{-3} (\text{K}^{-1})$	$k \times 10^{-3} (\text{M}^{-1}.\text{s}^{-1})$	$\ln k$	$\ln (k/T)$
313	3.19	28.41	-3.56	-9.30
318	3.14	45.20	-3.09	-8.85
323	3.09	71.23	-2.64	-8.41

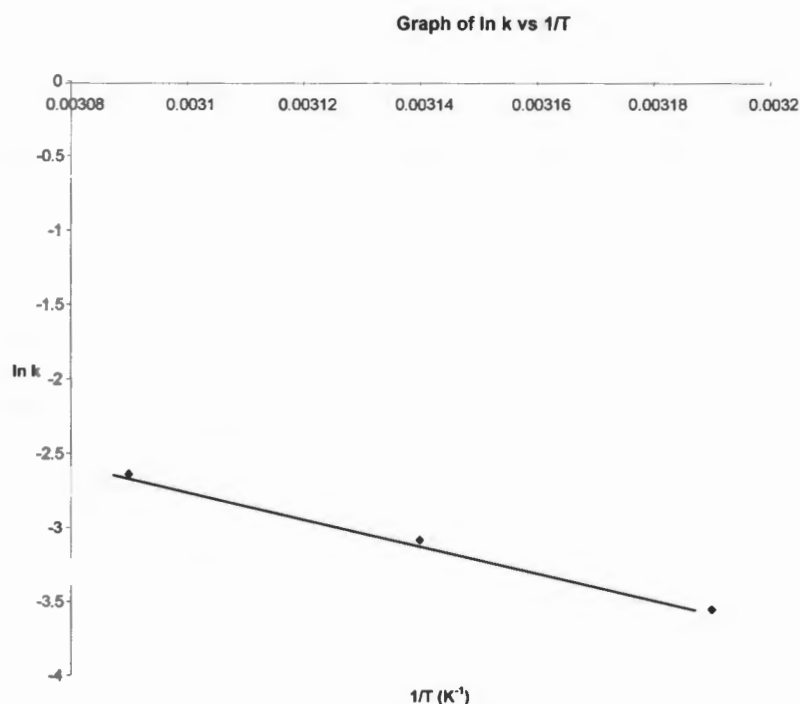


Figure 4.6.34 A typical plot of $\ln k$ vs $1/T$ for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base (0.82×10^{-6} M) with copper(II) ion (0.82×10^{-6} M) in acetic acid ($\lambda = 779$ nm).

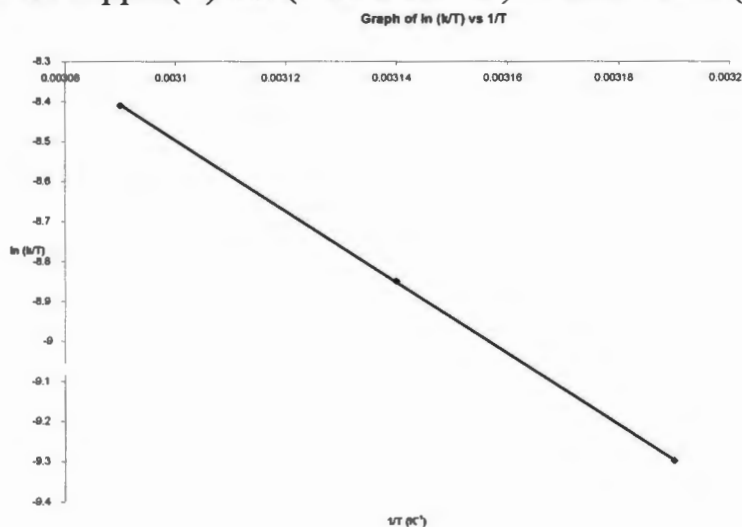
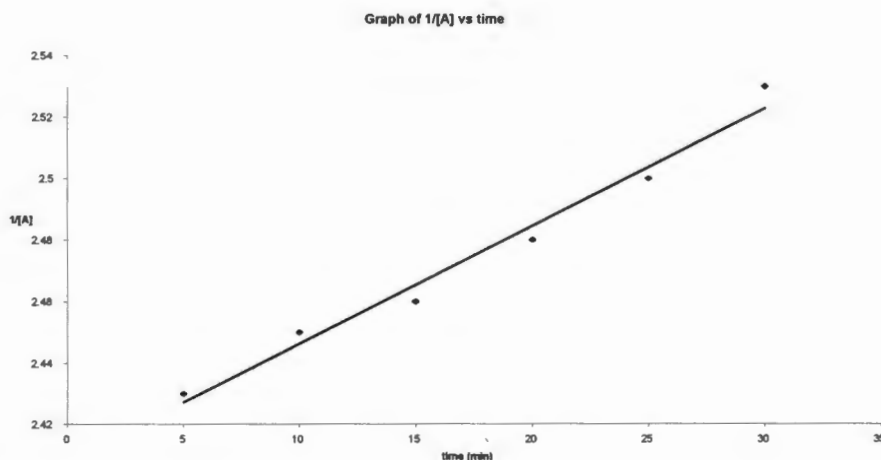
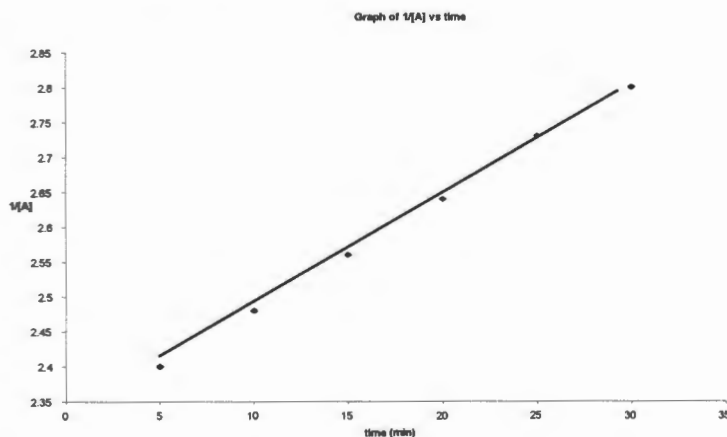


Figure 4.6.35 A typical plot of $\ln (k/T)$ vs $1/T$ for the metallation of N,N,N',N'-tetramethylamino porphyrazine hybrid base (0.82×10^{-6} M) with copper(II) ion (0.82×10^{-6} M) in acetic acid ($\lambda = 779$ nm).



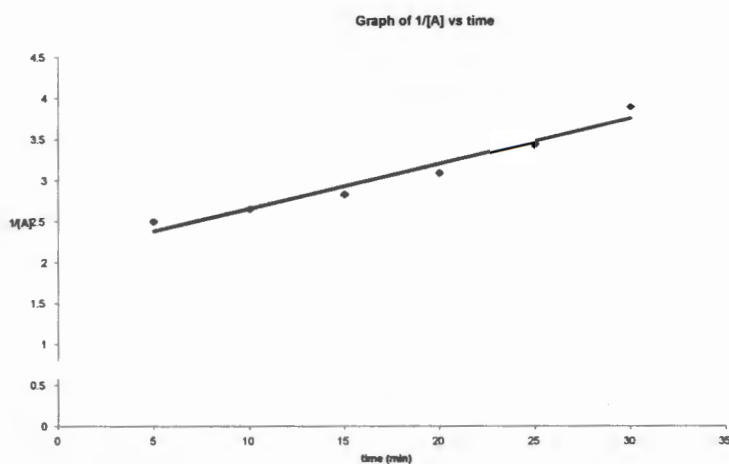
Rate constant = $0.0038 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.36 A typical kinetic plot for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.32 \times 10^{-6} \text{ M}$) with cobalt(II) ion ($0.32 \times 10^{-6} \text{ M}$) in acetic acid at 30°C at 5 minutes intervals ($\lambda = 700 \text{ nm}$).



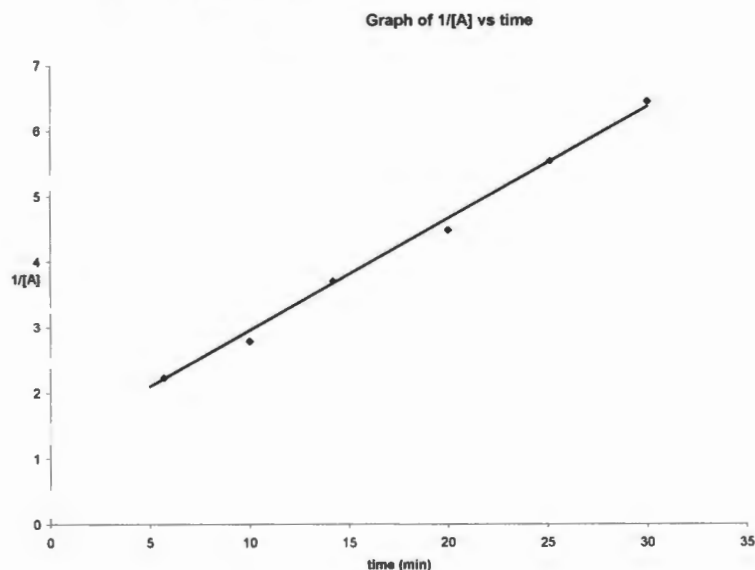
Rate constant = $0.0162 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.37 A typical kinetic plot for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.32 \times 10^{-6} \text{ M}$) with cobalt(II) ion ($0.32 \times 10^{-6} \text{ M}$) in acetic acid at 35°C at 5 minutes intervals ($\lambda = 700 \text{ nm}$).



Rate constant = $0.0547 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.38 A typical kinetic plot for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.32 \times 10^{-6} \text{ M}$) with cobalt(II) ion ($0.32 \times 10^{-6} \text{ M}$) in acetic acid at 40°C at 5 minutes intervals ($\lambda = 700 \text{ nm}$).



Rate constant = $0.170 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.39 A typical kinetic plot for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.32 \times 10^{-6} \text{ M}$) with cobalt(II) ion ($0.32 \times 10^{-6} \text{ M}$) in acetic acid at 45°C at 5 minutes intervals ($\lambda = 700 \text{ nm}$).

Table 4.6.6 Table of kinetic results of $\ln k$ vs $1/T$ of the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (0.32×10^{-6} M) with cobalt(II) ion (0.32×10^{-6} M) in acetic acid ($\lambda = 700$ nm).

Temp (K)	$1/T \times 10^3$ (K^{-1})	$k \times 10^3$ ($M^{-1}.s^{-1}$)	$\ln k$	$\ln (k/T)$	$t_{1/2}$
303	3.30	3.81	-5.57	-11.28	327.86
308	3.24	16.22	-4.12	-9.85	76.92
313	3.19	54.74	-2.90	-8.65	22.77
318	3.14	170.31	-1.77	-7.53	7.35

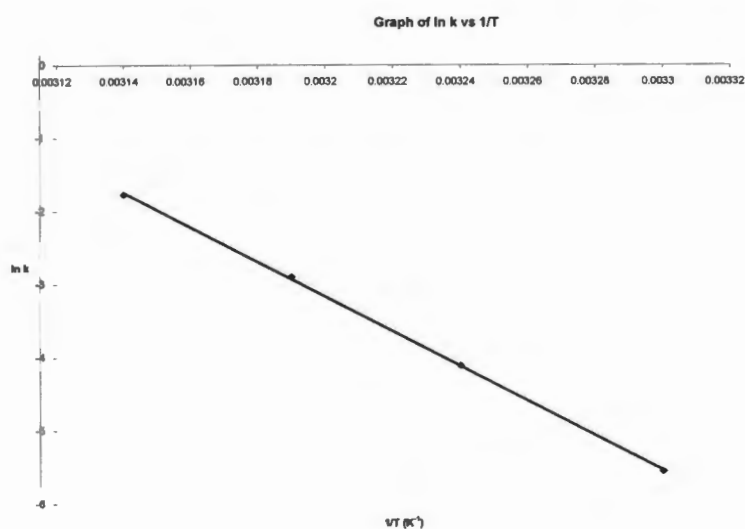


Figure 4.6.40 A typical plot of $\ln k$ vs $1/T$ for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (0.32×10^{-6} M) with cobalt(II) ion (0.32×10^{-6} M) in acetic acid ($\lambda = 700$ nm)

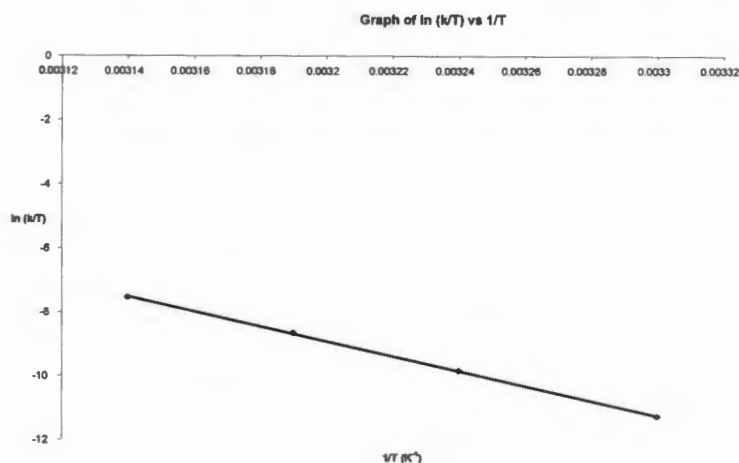
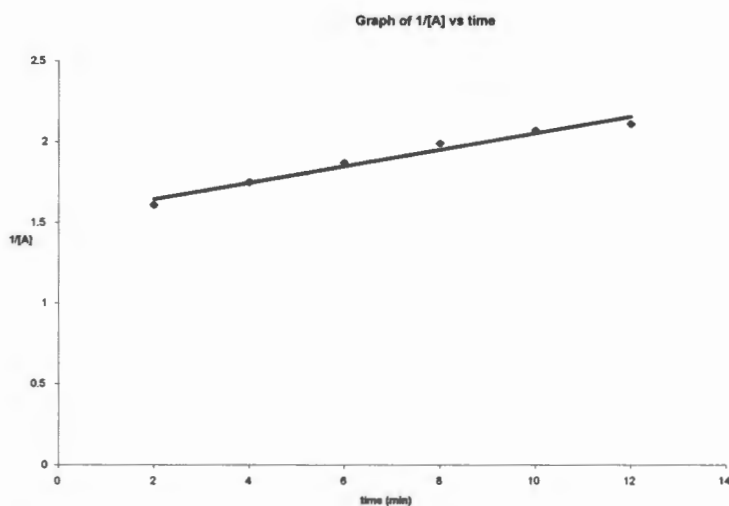
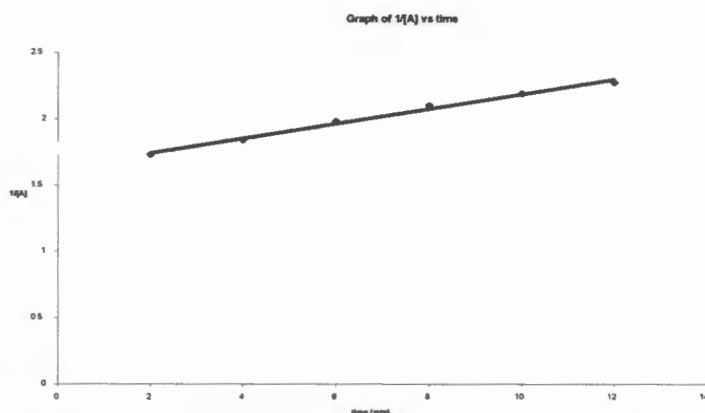


Figure 4.6.41 A typical plot of $\ln(k/T)$ vs $1/T$ for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.32 \times 10^{-6} \text{ M}$) with cobalt(II) ion ($0.32 \times 10^{-6} \text{ M}$) in acetic acid ($\lambda = 700 \text{ nm}$)



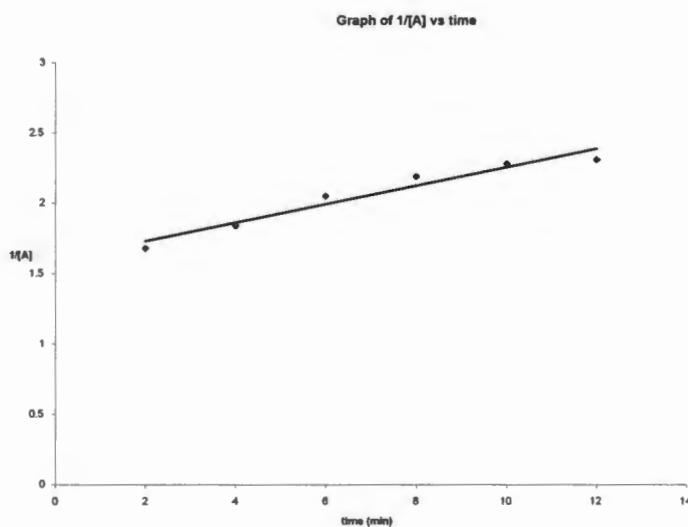
Rate constant = $0.511 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.42 A typical kinetic plot for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.45 \times 10^{-6} \text{ M}$) with copper(II) ion ($0.45 \times 10^{-6} \text{ M}$) in acetic acid at 20°C at 2 minutes intervals ($\lambda = 666 \text{ nm}$).



Rate constant = $0.552 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.43 A typical kinetic plot for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.45 \times 10^{-6} \text{ M}$) with copper(II) ion ($0.45 \times 10^{-6} \text{ M}$) in acetic acid at 25°C at 2 minutes intervals ($\lambda = 666 \text{ nm}$)



Rate constant = $0.658 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.6.44 A typical kinetic plot for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine ($0.45 \times 10^{-6} \text{ M}$) with copper(II) ion ($0.45 \times 10^{-6} \text{ M}$) in acetic acid at 30°C at 2 minutes intervals ($\lambda = 666 \text{ nm}$)

Table 4.6.7 Table of kinetic results of $\ln k$ vs $1/T$ of the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (0.45×10^{-6} M) with copper(II) ion (0.45×10^{-6} M) in acetic acid ($\lambda = 666$ nm)

Temp (K)	$1/T \times 10^3$ (K^{-1})	$k \times 10^{-3}$ ($M^{-1}.s^{-1}$)	$\ln k$	$\ln (k/T)$	$t_{1/2}$
293	3.41	0.511	-7.57	-13.25	3.19
298	3.35	0.552	-7.50	-13.19	2.95
303	3.30	0.658	-7.32	-13.04	2.48

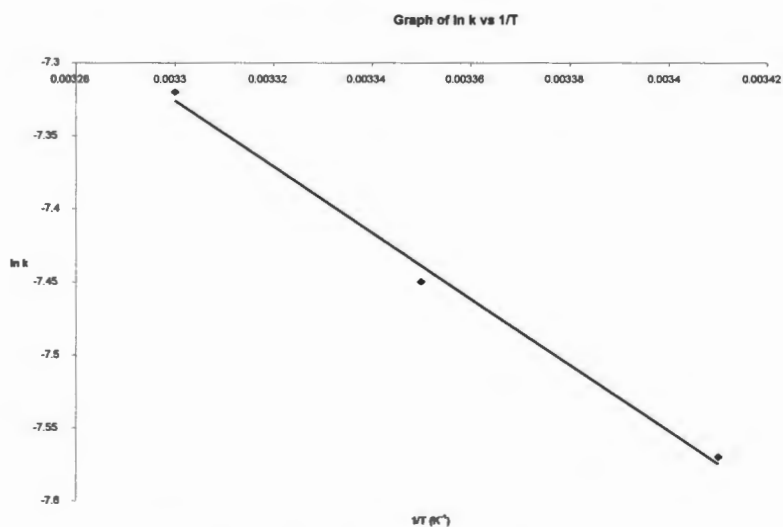


Figure 4.6.45 A typical plot of $\ln k$ vs $1/T$ for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (0.45×10^{-6} M) with copper(II) ion (0.45×10^{-6} M) in acetic acid ($\lambda = 666$ nm).

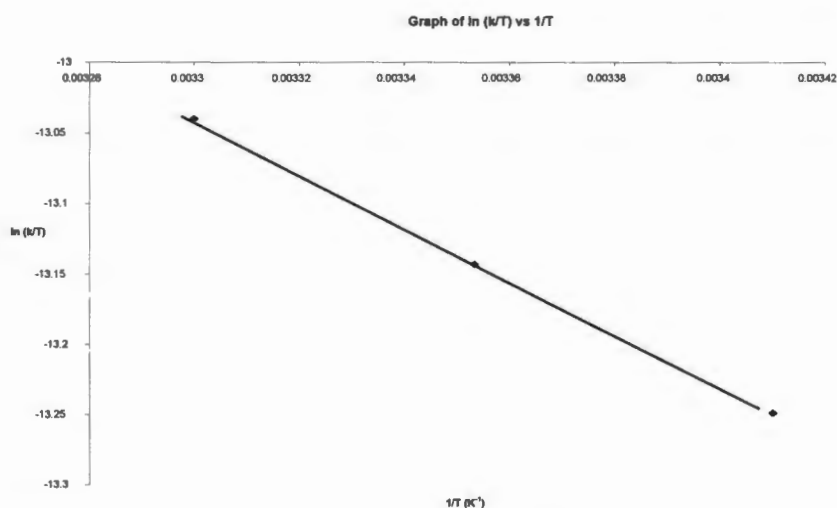


Figure 4.6.46 A typical plot of $\ln(k/T)$ vs $1/T$ for the metallation of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (0.45×10^{-6} M) with copper(II) ion (0.45×10^{-6} M) in acetic acid ($\lambda = 666$ nm)

4.7 KINETICS OF REDUCTION OF PORPHYRAZINE COPPER (II) COMPOUNDS BY 2,3,7,8,12,13,17,18-OCTAKIS (PROPYL) PORPHYRAZINE COBALT (II)

Preliminary repetitive scanning of the ultraviolet-visible spectral region during reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrine copper(II), N,N,N',N'-tetramethylamino porphyrine hybrid copper(II) and 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) in acetic acid and dichloromethane (1:1) gave well defined isosbestic points for more than 2 lives of the reactions. The spectral changes at different temperatures are shown in Figure 4.7.1 - 4.7.3 and the corresponding graphs in Figure 4.7.4 - 4.7.19

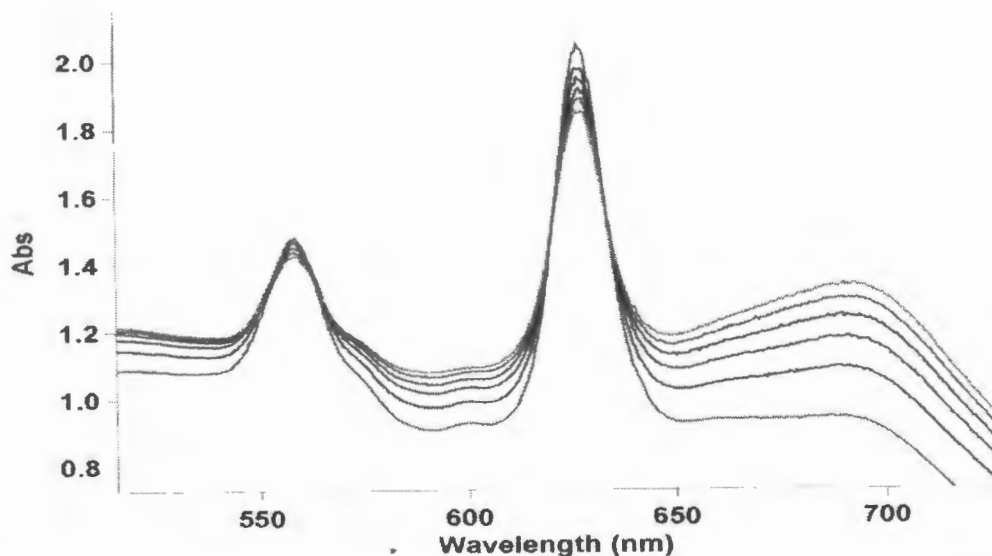


Figure 4.7.1 Spectral change during the reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine copper(II) (0.53×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) (0.53×10^{-5} M) at 25°C at 1 minute intervals ($\lambda = 588$ nm).

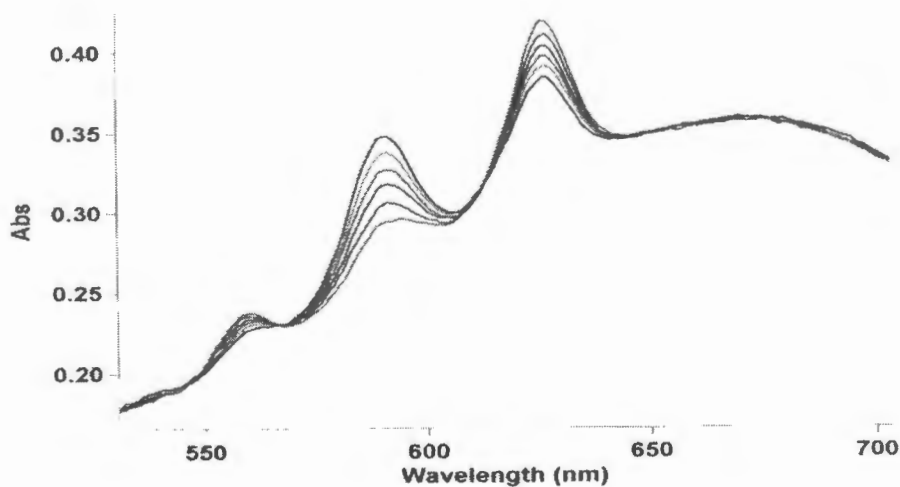


Figure 4.7.2 Spectral change during the reduction of N,N,N',N'-tetramethylamino porphyrzine hybrid copper(II) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) at 25°C at 2 minutes intervals ($\lambda = 640$ nm).

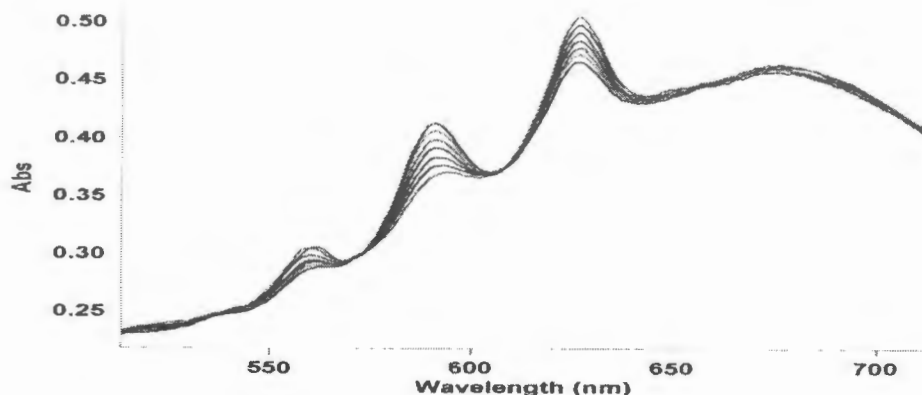
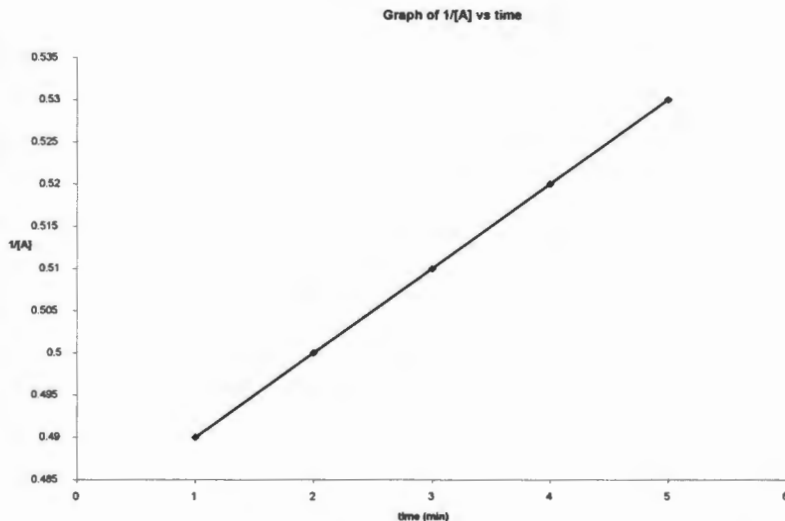
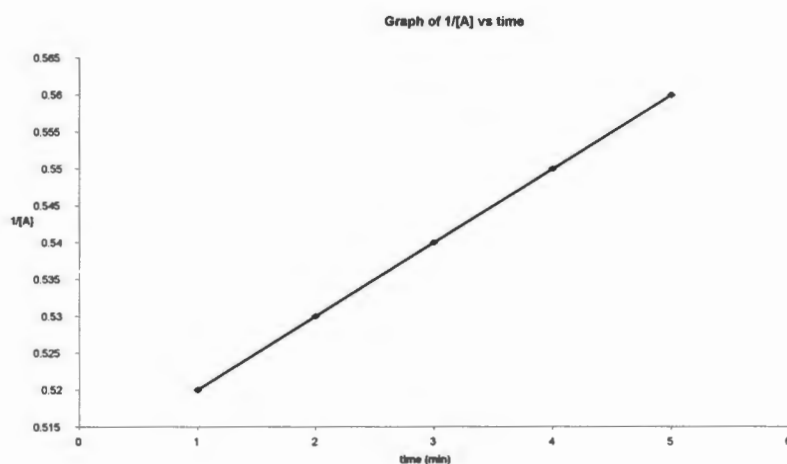


Figure 4.7.3 Spectral change during the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) at 25°C at 1 minute intervals ($\lambda = 640$ nm).



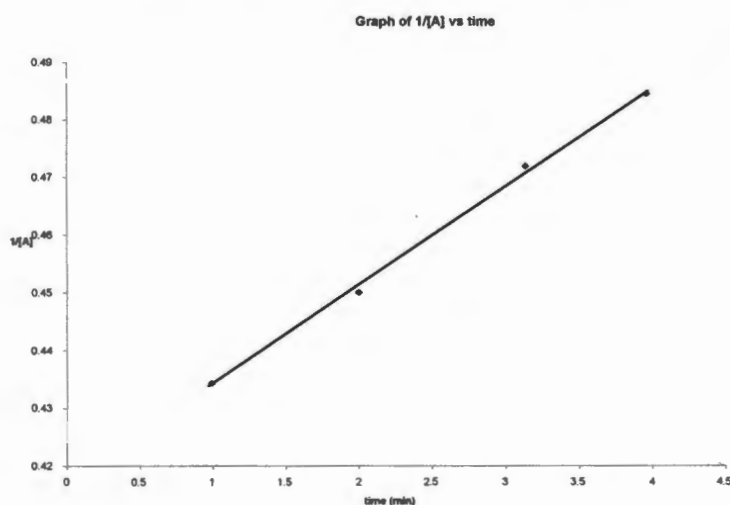
Rate constant = $0.010 \text{ L.M}^{-1}.\text{s}^{-1}$

Figure 4.7.4 A typical plot of $1/[A]$ vs time for the reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine copper(II) ($0.53 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) ($0.53 \times 10^{-5} \text{ M}$) at 25°C at 1 minute intervals in acetic acid ($\lambda = 588$ nm).



Rate constant = $0.014 \text{ L.M}^{-1}.\text{s}^{-1}$

Figure 4.7.5 A typical plot of $1/[A]$ vs time for the reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine copper(II) ($0.53 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) ($0.53 \times 10^{-5} \text{ M}$) at 30°C at 1 minute intervals in acetic acid ($\lambda = 588 \text{ nm}$).



Rate constant = $0.017 \text{ L.M}^{-1}.\text{s}^{-1}$

Figure 4.7.6 A typical plot of $1/[A]$ vs time for the reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine copper(II) ($0.53 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) ($0.53 \times 10^{-5} \text{ M}$) at 40°C at 1 minute intervals ($\lambda = 588 \text{ nm}$).

Table 4.7.1 Table of kinetic results of $\ln k$ vs $1/T$ of the reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine (0.53×10^{-5}) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.53×10^{-5} M) in acetic acid ($\lambda = 588$ nm)

Temp (K)	$1/T \times 10^{-3} (K^{-1})$	$k \times 10^{-3} (M^{-1}.s^{-1})$	$\ln k$	$\ln (k/T)$
298	3.35	10.0	-4.61	-10.30
303	3.30	14.0	-4.41	-10.13
313	3.19	17.0	-4.07	-9.82

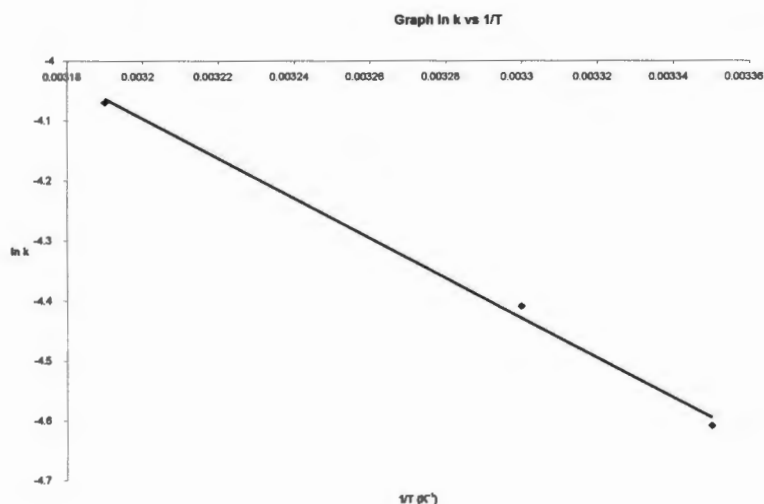


Figure 4.7.7 A typical plot of $\ln k$ vs $1/T$ for the reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine (0.53×10^{-5}) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.53×10^{-5} M) in acetic acid ($\lambda = 588$ nm).

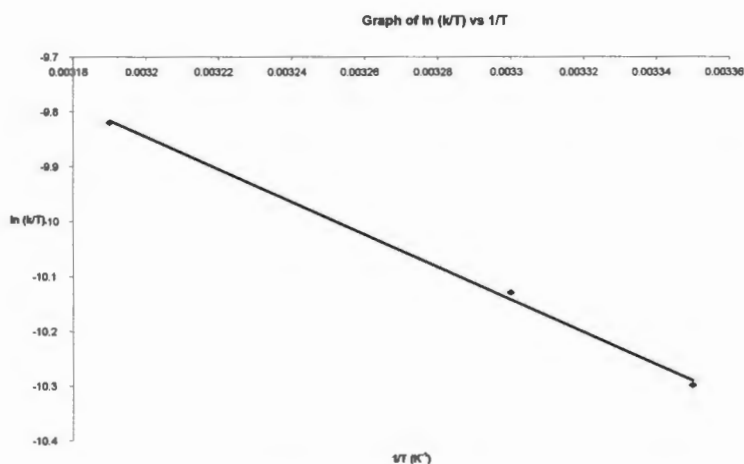
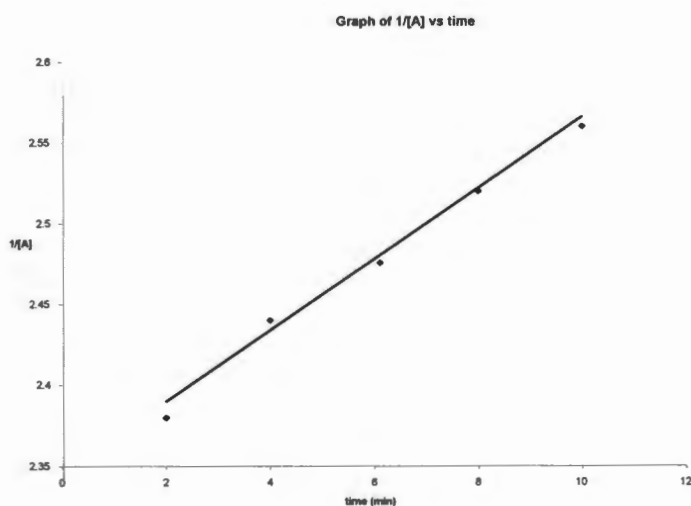
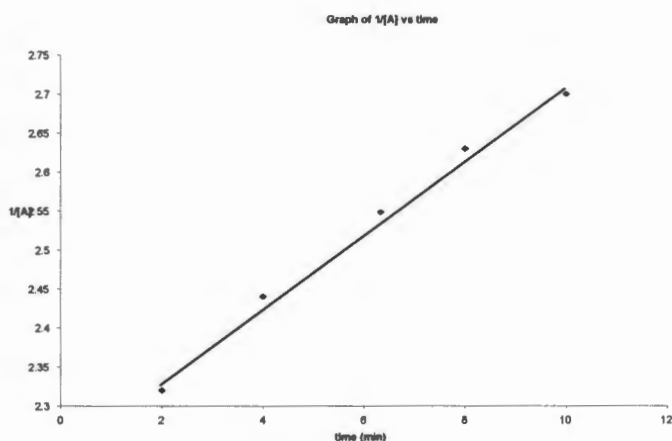


Figure 4.7.8 A typical plot of $\ln(k/T)$ vs $1/T$ for the reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines (0.53×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.53×10^{-5} M) in acetic acid ($\lambda = 588$ nm).



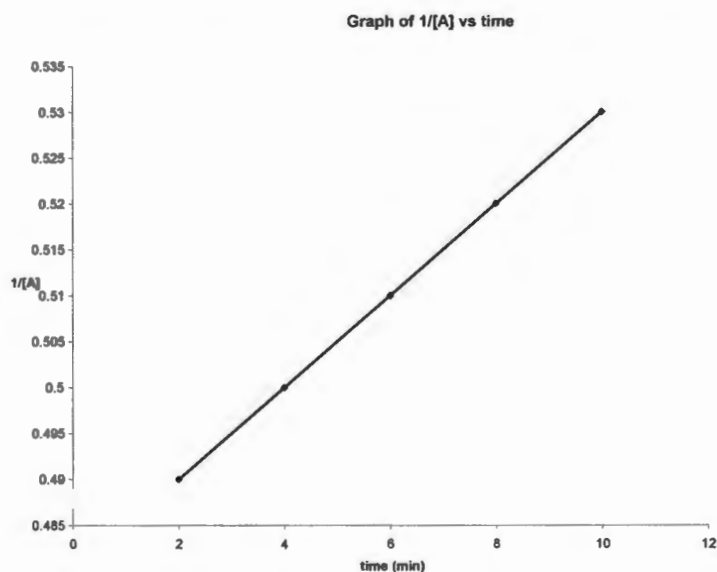
Rate constant = $0.022 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.7.9 A typical plot of $1/[A]$ vs time for the reduction of N,N,N',N'-tetramethylamino porphyrazine hybrid copper(II) (0.88×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.88×10^{-5} M) at 25°C at 2 minutes intervals ($\lambda = 640$ nm).



Rate constant = $0.048 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.7.10 A typical plot of $1/[A]$ vs time for the reduction of N,N,N',N'-tetramethylamino porphyrazine hybrid copper(II) ($0.88 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) ($0.88 \times 10^{-5} \text{ M}$) at 30°C at 2 minutes intervals ($\lambda = 640 \text{ nm}$).



Rate constant = $0.050 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.7.11 A typical plot of $1/[A]$ vs time for the reduction of N,N,N',N'-tetramethylamino porphyrazine hybrid copper(II) ($0.88 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) ($0.88 \times 10^{-5} \text{ M}$) at 35°C at 2 minutes intervals ($\lambda = 640 \text{ nm}$).

Table 4.7.2 Table of kinetic results of $\ln k$ vs $1/T$ of the reduction of N,N,N',N'-tetramethylamino porphyrazine hybrid copper(II) (0.88×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.88×10^{-5} M) ($\lambda = 640$ nm).

Temp (K)	$1/T \times 10^{-3}$ (K ⁻¹)	$k \times 10^{-3}$ (M ⁻¹ .s ⁻¹)	$\ln k$	$\ln (k/T)$
298	3.35	22.0	-3.82	-9.51
303	3.33	47.50	-3.04	-9.35
308	3.24	50.0	-2.99	-8.72

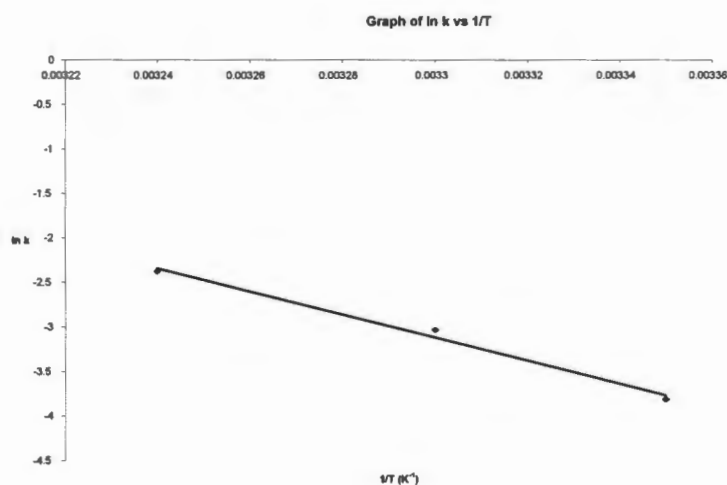


Figure 4.7.12 A typical plot of $\ln k$ vs $1/T$ for the reduction of N,N,N',N'-tetramethylamino porphyrazine hybrid copper(II) (0.88×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.88×10^{-5} M) in acetic acid ($\lambda = 640$ nm).

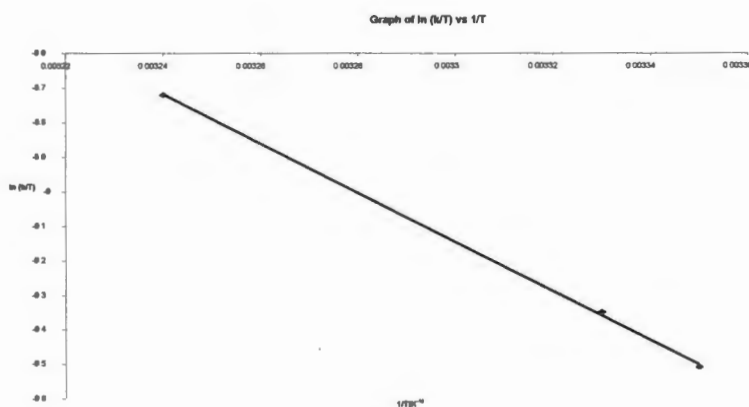
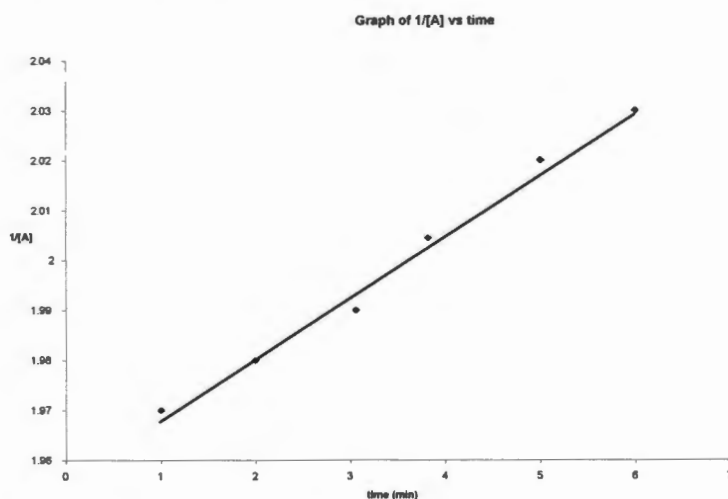
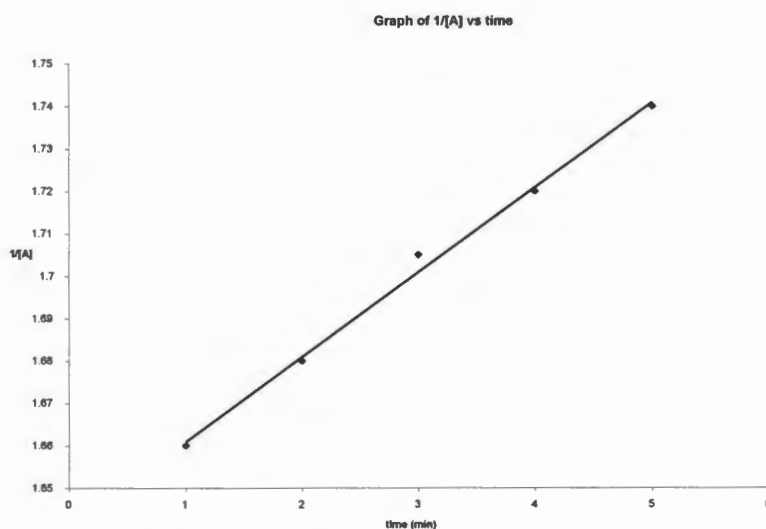


Figure 4.7.13 A typical plot of $\ln(k/T)$ vs $1/T$ for the reduction of N,N,N',N'-tetramethylamino porphyrazine hybrid copper(II) (0.88×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.88×10^{-5} M) in acetic acid ($\lambda = 640$ nm).



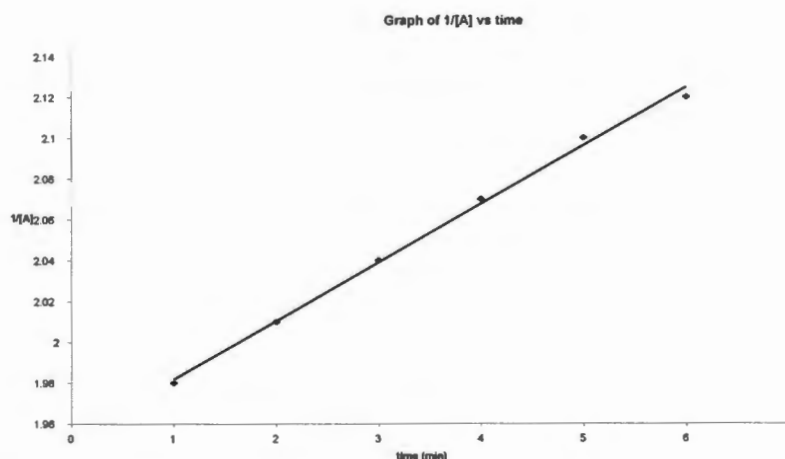
Rate constant = $0.0123 \text{ M}^{-1} \cdot \text{s}^{-1}$

Figure 4.7.14 A typical plot of $1/[A]$ vs time for the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) (0.53×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) (0.53×10^{-5} M) at 25°C at 1 minute intervals ($\lambda = 640$ nm).



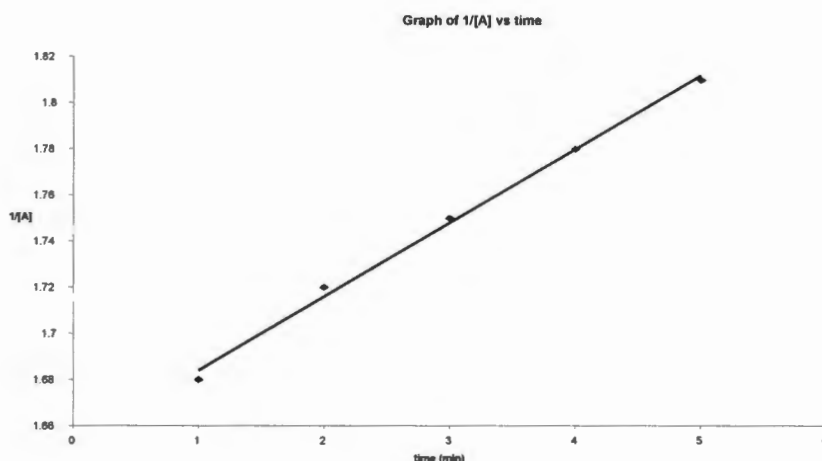
Rate constant = $0.020 \text{ L.M}^{-1}.\text{s}^{-1}$

Figure 4.7.15 A typical plot of $1/[A]$ vs time for the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine(II) ($0.53 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) ($0.53 \times 10^{-5} \text{ M}$) at 30°C at 1 minute intervals ($\lambda = 640 \text{ nm}$).



Rate constant = $0.029 \text{ L.M}^{-1}.\text{s}^{-1}$

Figure 4.7.16 A typical plot of $1/[A]$ vs time for the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (II) ($0.53 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) ($0.53 \times 10^{-5} \text{ M}$) at 35°C at 1 minute intervals ($\lambda = 640 \text{ nm}$).



Rate constant = $0.032 \text{ L.M}^{-1}.\text{s}^{-1}$

Figure 4.7.17 A typical plot of $1/[A]$ vs time for the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) ($0.53 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine cobalt(II) ($0.53 \times 10^{-5} \text{ M}$) at 40°C at 1 minute intervals ($\lambda = 640 \text{ nm}$).

Table 4.7.2 Table of kinetic results of $\ln k$ vs $1/T$ of the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) ($0.53 \times 10^{-5} \text{ M}$) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrizine cobalt(II) ($0.53 \times 10^{-5} \text{ M}$) ($\lambda = 640 \text{ nm}$).

Temp (K)	$1/T \times 10^{-3} (\text{K}^{-1})$	$k \times 10^{-3} (\text{M}^{-1}.\text{s}^{-1})$	$\ln k$	$\ln (k/T)$
298	3.41	12.30	-4.39	-10.09
303	3.30	20.0	-3.91	-9.63
308	3.24	28.60	-3.55	-9.32
313	3.19	32.0	-3.44	-9.19

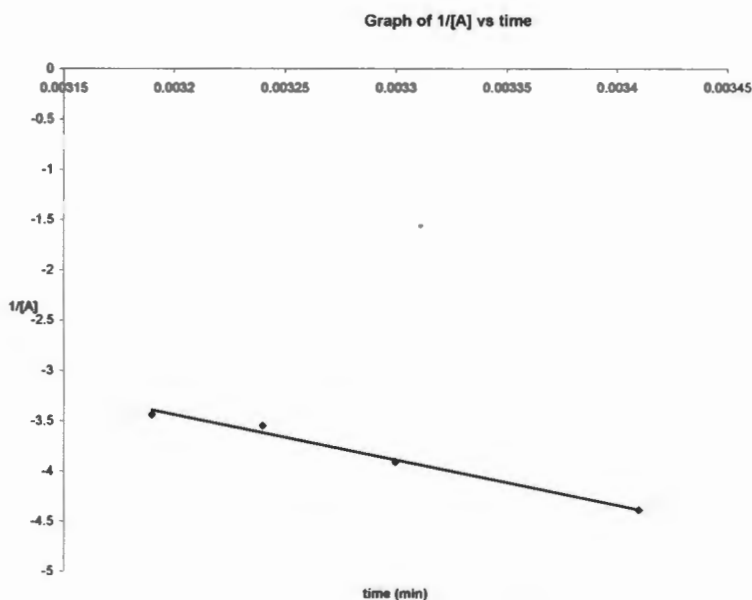


Figure 4.7.18 A typical plot of $\ln k$ vs $1/T$ for the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) (0.53×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) (0.53×10^{-5} M) ($\lambda = 640$ nm).

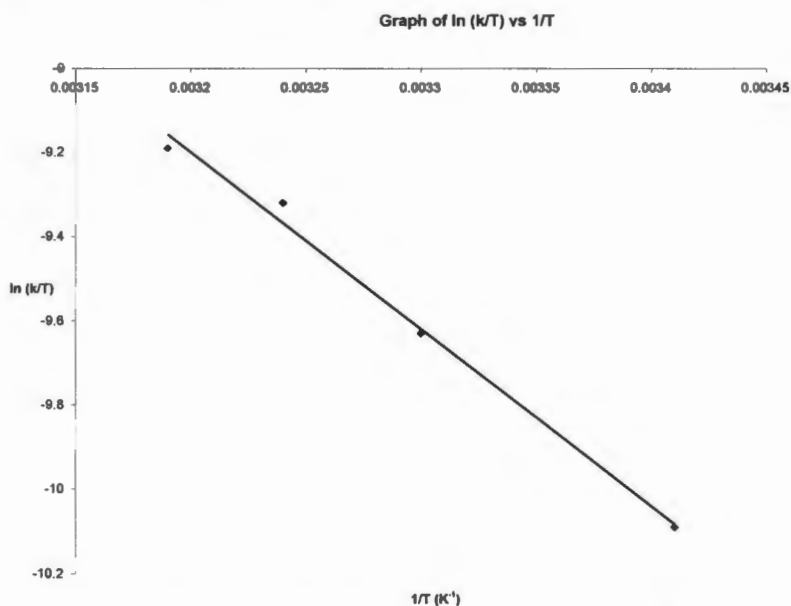


Figure 4.7.19 A typical plot of $\ln (k/T)$ vs $1/T$ for the reduction of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II) (0.53×10^{-5} M) by 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine cobalt(II) (0.53×10^{-5} M) ($\lambda = 640$ nm).

4.8 CALCULATIONS OF ACTIVATION PARAMETERS

From the graph of $\ln k$ vs $1/T$ for the insertion of Cu(II) ion to Pz^I-base

$$\frac{-E_a}{R} = -7808.6$$

$$E = 7808.6 \text{ K} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$E = 64916 \text{ J mol}^{-1}$$

$$E = 64.9 \text{ kJ mol}^{-1}$$

From the graph of $\ln (k/T)$ vs $1/T$ for the insertion of Cu(II) ion to Pz^I-base

$$\frac{-(\Delta H^*)}{RT} = -7578.1$$

$$\Delta H^* = 7578.1 \times 8.314 \text{ J K}^{-1} \times 273 \text{ K}$$

$$\Delta H^* = 17199953.32 \text{ J mol}^{-1}$$

$$\Delta H^* = 17.2 \times 10^{-3} \text{ kJ mol}^{-1}$$

$$\ln\left(\frac{K_B}{h}\right) + \frac{\Delta S^*}{R} = 14.3$$

$$\frac{\Delta S^*}{R} = 14.31 - \ln\left(\frac{K_B}{h}\right)$$

$$\Delta S^* = \left[14.31 - \ln\left(\frac{1.38 \times 10^{-23} \text{ J K}^{-1}}{6.62 \times 10^{-34} \text{ Js}}\right)\right] \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S^* = -78.56 \text{ J K}^{-1} \text{ mol}^{-1}$$

TABLE 4.8.1 Table showing the activation energies, enthalpies and entropies of the insertion of the of copper(II) metal ion to the different porphyrazines

Compound	E_a (kJ mol ⁻¹)	$\Delta H^\#$ (kJ mol ⁻¹)	$\Delta S^\#$ (J K ⁻¹ mol ⁻¹)
Pz ¹ -base	64.9	1.72×10^4	78.56
Mg(II)-pz ¹	309.0	8.87×10^4	1131.95
Pz ² -base	76.5	2.02×10^4	344.0
Pc-base	18.8	0.43×10^4	241.7

TABLE 4.8.2 Table showing the activation energies, enthalpies and entropies of the insertion of the of cobalt(II) metal ion to the different porphyrazines

Compound	E_a (kJ mol ⁻¹)	$\Delta H^\#$ (kJ mol ⁻¹)	$\Delta S^\#$ (J K ⁻¹ mol ⁻¹)
Pz ¹ -base	34.8	0.87×10^4	186.65
Pz ² -base	82.2	2.11×10^4	374.9
Pc-base	198.1	5.33×10^4	736.4

TABLE 4.8.3 Table showing the activation energies, enthalpies and entropies for the reduction of copper(II) metal ion to copper(I) in different porphyrazines

Reductions	E_a (kJ mol ⁻¹)	$\Delta H^\#$ (kJ mol ⁻¹)	$\Delta S^\#$ (J K ⁻¹ mol ⁻¹)
Pz ¹ [Cu(II)→Cu(I)]	27.7	0.67×10^4	188
Pz ² [Cu(II)→Cu(I)]	108.3	1.62×10^4	305
Pc [Cu(II)→Cu(I)]	37.3	0.96×10^4	22

CHAPTER FIVE

DISCUSSION

5.1 SYNTHESIS AND ISOLATION OF COMPOUNDS

5.1.1 Synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium

The 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines magnesium was successfully prepared in four major steps (Figure 4.1.1). First, the addition of bromine to 4-octyne (**1**) in the presence of acetic acid produced *trans*-dibromoalkene (**2**) with the yield of 55% and R_f value of 0.31 in pure hexane. Then these vinylic dibromides were converted to fumaronitriles (**3**) via a Rosenmund-von Braun reaction with the yield of 52% and R_f value of 0.51 in pure hexane. Subsequently, the fumaronitriles were photoisomerised to the corresponding maleonitriles (**4**) with the yield of 20% and R_f value of 0.48 in pure hexane. Finally, the mixed Lindsey macrocyclisation of the maleonitrile in the presence of magnesium butoxide yielded the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines magnesium(II) complex.

The yields obtained in all these reactions were moderate to good except the photoisomerization which was reaching photostationary state consisting of approximately equal amounts of *cis*- and *trans*-dinitriles. Separating the two isomers was very difficult since their R_f values were very close. When fractional vacuum distillation was used to separate them, it reduced the yield drastically. However, when column chromatography was used the yield was improved by about 30%.

It was observed that the yield of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium (II) was higher when maleonitrile was used as the starting material as opposed to fumaronitrile. This was expected since in order to cyclize, the two nitrile groups are supposed to be *cis* to each other. The reaction of the two dinitriles resulted in a mixture of six porphyrazines which were not easy to separate on the column due to the tendency of the product mixture to aggregate. The blue purple 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium (II) was fairly soluble in chloroform and dichloromethane respectively and was separated from other additional porphyrazines formed during the reaction by column chromatography.

The presence of the magnesium at the centre of the macrocycle affected the purity of the macrocycle in that the metal porphyrazine was tailing on the tlc plate, causing the purification by column chromatography to be difficult. Magnesium was therefore removed so as to get a pure compound hence the subsequent step.

5.1.2 Synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base

Demetallation of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium was accomplished by heating at reflux the metal porphyrazine in a $\text{CHCl}_3/\text{AcOH}$ (20:1) solution for about 20 minutes (Figure 4.1.2). After 20 minutes the solvent was slowly removed using the rotarvapour. Slow evaporation of the solvent was critical since it resulted into small microcrystalline solids of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base (**6**) which were recrystallized by slow diffusion of benzene into CHCl_3

solution. Fast evaporation of solvent resulted in aggregation of the products mixture.

The presence of nitrogen was critical since the reaction was very sensitive to oxygen. When slightest amount of oxygen entered the reaction system, one of the pyrrole rings opened to form a *seco*-porphyrazine. *Seco*-porphyrazine is characterized by opened pyrrole ring or rings at the periphery. The problem with the opening of the pyrrole ring was that when the macrocycle was metallated, metallation took place at the periphery instead of the centre of the macrocycle. It was also apparent that when trifluoroacetic acid was used to demetallate the metal porphyrazine, the yield was reduced, but when acetic acid was used to demetallate the metal porphyrazine, the yield was improved to about two folds of what was obtained when trifluoroacetic acid was used.

5.1.3 Synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II)

The 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines copper(II) (7) was successfully synthesized by heating copper acetate and 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base in a mixture of chlorobenzene and DMF at 100°C for 18 hours (Figure 4.1.3). After 18 hours, the solvent was removed by rotary evaporation and the blue purple product was purified by column chromatography.

In the process of purifying the copper porphyrazine, three problems were encountered. The first one was that, there were about five other products formed during metallation process and their R_f values were very close to the

R_f value of the major product, the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II). The problem with the R_f 's values which are close to each other is that, the retention time of the different compounds is almost the same and therefore, they always come out of the column at the same time. The repercussion of this is that, the compounds are always mixed and purification becomes difficult.

The second problem was that the major product was tailing on the tlc plate. Due to that, it was difficult to get it pure. To separate and purify individual compounds, column chromatograph of these compounds was done six times before a pure product was obtained. This affected the yield since a lot of the product remained on the column. The third problem was that, the product dissolved partially in several solvents tried, as a result it was not sufficient to take the nmr hence instead microanalysis was done.

5.1.4 Synthesis of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II)

The 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines cobalt(II) (**8**) was also synthesized by heating cobalt acetate and 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base in a mixture of chlorobenzene and DMF at 100°C for 18 hours (Figure 4.1.3). After 18 hours, the solvent was also removed by rotary evaporation and the purple product was purified by column chromatography.

The same problems encountered in the purification of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II) were

encountered in the purification of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II). There were five other products formed together with the major product, 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II). Their R_f values were closer to that of the major product and as a result, they were coming out of the column almost at the same time as the major product.

On the other hand, tailing on the tlc plate, showed that it was difficult to get the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II) pure by one run on column chromatography. To obtain a pure product, the product was subjected to column chromatography five times. Consequently the percentage yield was reduced. The other problem was that the product also dissolved partially in several solvents tried; hence microanalysis was done instead of nmr.

5.1.5 Synthesis of N,N,N',N-tetramethylamino porphyrazine hybrid base

The two dinitriles reacted in this reaction had different substituents as can be seen in Figure 4.1.7. They were 2,3-dipropylmaleonitrile (**16**) which was synthesized from 2,3-dipropylfumaronitrile and iminoisoindoline, 4,7-bis(isopropoxy)-1,3-iminoisoindoline (**15**) which was synthesized from 3,6-bis(isopropoxy)-1,2-benzenenitrile. The reaction resulted into eight different compounds which were not easy to separate on the column due to aggregation tendency by the product mixture.

The route to the formation of the N,N,N',N-tetramethylamino porphyrazines (**18**) hybrid base was fairly easy except that the presence of the nitrogen was critical. However, the most difficult part was when the two dinitriles were prepared, since they gave low yields. Low yield meant that in order to achieve the required amount of product for the next reaction, the reactions had to be repeated more than three times. The presence of magnesium affected purity of the metal porphyrazine hence it was removed immediately after the formation of the macrocycle

5.1.6 Synthesis of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine

The 2,3,9,10,16,17,23,24-octa- substituted phthalocyanine base was prepared from 1,2-diisocyano-4-benzyl alcohol (**18**) which was refluxed in 1-pentanol in the presence of DBU for 16 hours. Soxhlet extraction with methanol and acetone gave a green precipitate which was dried at 60° C and purified by flash chromatography. The yield was 0.294g and %Yield was 98% with the R_f value of 0.58. Synthesis of this phthalocyanine was fairly easy and the percentage yield was very high.

5.2 CHARACTERIZATION OF COMPOUNDS

5.2.1 Nuclear magnetic resonance spectroscopy of the *trans*-dibromoalkene

The ^1H NMR spectra of the *trans*-dibromoalkene (Figure 4.2.1) showed a signal upfield at 0.94 ppm, which was a triplet, and was due to the splitting of the proton next to the double bond. At 1.62 ppm, multiple splitting was observed and was due to splitting of protons at carbon three from the double bond by the protons at carbon two and protons at carbon four respectively.

At 2.49 ppm another triplet was observed which was due to the splitting of the protons at carbon four by protons at carbon three.

The ^{13}C NMR (Figure 4.2.2) as expected showed four different types of carbons at 13.09 ppm which was due to CH_3 which was shielded from the applied field. Signal at 21.23 ppm was due to the carbons of CH_2 and they are also shielded. The signal at 35.67 ppm was due to carbon bearing the Br. The electronegative Br moves adjacent carbon atom downfield to a larger δ by deshielding. The signal at 115.34 ppm was due to saturated carbon. Carbon at 129.10 ppm confirms the presence of the double bond since the $\text{C}=\text{C}$ is found in this region and the carbons are deshielded. It was important to note it because if too much bromine was added during bromination of the triple bond, it could go beyond expected results to form an alkane.

5.2.2 Nuclear magnetic resonance spectroscopy of the 2,3-dipropylfumaronitrile

The ^1H NMR spectra of 2,3-dipropylfumaronitrile (Figure 4.2.3) showed a triplet splitting at 0.86 ppm due to CH_3 like in the *trans*-dibromoalkene. The signal was shifted about 0.40 ppm downfield compared to the one in *trans*-dibromoalkene due to the presence of CN. Multiple splitting was observed at 1.53 ppm and the other triplet was observed at 2.41 ppm.

The success of the replacement of the Br by CN was confirmed by the ^{13}C NMR (Figure 4.2.4) which showed the presence of five different carbons. The signal at 12.96 ppm was due to the CH_3 carbon which is shielded. The signal at 20.72 ppm was due to carbons of the CH_2 which are also shielded. The signal at 31.75 ppm was due to the carbon of the CH_2 next to the carbon

bearing the double bond. The signal at 116.02 ppm was due to the carbon of the CN. The signal at 128.88 ppm was due to the unsaturated carbon which is deshielded.

5.2.3 Nuclear magnetic resonance spectroscopy of the 2,3-dipropylmaleonitrile

As expected, the ^1H NMR spectral splitting of 2,3-dipropylmaleonitrile resembled that of 2,3-dipropylfumaronitrile since they are isomers. A triplet was observed at 1.62 ppm. Multiple splitting was observed at 2.27 ppm and another triplet was observed at 3.00 ppm (Figure 4.2.5). The ^{13}C nmr (Figure 4.2.6) also showed five types of carbons which were similar to those shown by the 2,3-dipropylfumaronitrile. The carbon at 12.97 ppm was due to the CH_3 and the carbon at 20.73 ppm was due to the carbon of the CH_2 next to the CH_3 . The carbon at 31.76 ppm was due to the carbon of the CH_2 next to the carbon bearing the double bond. The carbon at 116.02 ppm was due to the carbon of the double bond and the carbon at 128.88 ppm was due to the carbon of the CN.

5.2.4 Nuclear magnetic resonance spectroscopy of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base

The ^1H NMR spectrum of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines base showed splitting at high field, -2.11 ppm which was due to the two protons attached to the two nitrogens at the centre of the molecule after the removal of the magnesium ion. The methyl groups of the propyl substituents were also observed at high field of 1.86 ppm and were reflected

as triplet. A quartet was observed at 3.98 ppm and it was due to protons attached to carbons which were linked directly to the pyrrolic rings.

5.2.5 Nuclear magnetic resonance spectroscopy of the 3,6-bis(isopropoxy)-1,2-benzenenitrile

^1H NMR of 3,6-bis(isopropoxy)-1,2-benzenenitrile (Figure 4.2.7) showed a doublet at 1.37 ppm which was due to the methyl protons attached to the carbon linked directly to the oxygen. The signal at 4.55 ppm was due to the two protons of the two carbons attached to the two oxygens. The singlet at 7.13 ppm was due to the two aromatic protons attached to the benzene ring.

The ^{13}C nmr of 3,6-bis(isopropoxy)-1,2-benzenenitrile (Figure 4.2.8) showed six different types of carbons. The signal at 21.91 ppm was due to carbons of the CH_3 , whilst the signal at 73.69 ppm was due to carbon attached to the isopropoxy. The signal at 106.68 ppm and 113.20 ppm were both due to two carbons attaching the CN groups. The signal at 120.54 was due to the two carbons of the benzene ring attaching the hydrogens. The signal at 154.33 ppm was due to carbons attaching the two isopropoxy groups.

5.2.6 Nuclear magnetic resonance spectroscopy of 4,7-bis(isopropoxy)-1,3-iminoisoindoline

^1H NMR of 4,7-bis(isopropoxy)-1,3-iminoisoindoline showed a doublet at 1.39 ppm which was due to the protons of the methyl groups attached to the carbons which are directly linked to the oxygens of the molecule. The signal at 4.63 ppm was due to the protons attached to the carbons next to the oxygens. On the other hand, the singlet at 6.93 ppm is due to the two protons

attached directly to the benzene ring. The singlet at 8.18 is due to the proton attached to nitrogen which forms part of the five-membered ring of the molecule.

The ^{13}C NMR showed different types of carbons at 21.79 ppm which was due to the carbons of the CH_3 , whilst the signal at 22.20 ppm was due to CH groups attached to oxygen. The signal at 71.55 ppm was due to the carbons common between the benzene and the five membered rings. The signal at 117.51 ppm was due to the aromatic carbons of the benzene ring, whilst the signal at 123.41 ppm was due to the carbons attached to the isopropoxy. The signal at 148.10 ppm was due to the carbons attached to NH groups.

5.2.7 Nuclear magnetic resonance spectroscopy of the N,N,N'-N-tetramethylamino porphyrazine hybrid base

The ^1H NMR showed a singlet at 1.23 ppm which was due to the two hydrogens at the centre of the molecule after the removal of magnesium. The signal at 1.52 ppm was a doublet of doublets and was due to the protons of the methyl groups attached to the carbons linked to the oxygens of the molecule and which are *trans* to each other. The other doublet at 1.70 ppm was due to the protons of the methyl groups attached to the carbon attached directly to the oxygen and which are *cis*- to the other two methyl groups attached to the cyclohexanes of the molecule. A singlet at 5.27 ppm was due to the protons attached to nitrogen of the substituents $[\text{N}(\text{Me})_2]$. The signal at 5.15 ppm showed multiple splitting which were due to the protons of the carbons attached directly to the oxygens.

The ^{13}C NMR showed different types of carbons. The signal at 22.71 ppm was due to the carbons of the CH_3 . The signal at 44.99 ppm was due to the carbons attached to the nitrogen of the amino group. The signals at 70.76 ppm - 75.53 ppm were due to the carbons linked directly to the oxygens of the isopropoxy group. The signals at 114.50 ppm to 124.26 ppm were due to the carbons of the benzene ring which are adjacent to the carbons bearing the isopropoxy group. The signal at 150.477 was due the carbon in the benzene ring bearing the isopropoxy group.

5.2.8 Nuclear magnetic resonance spectrum of the 2,3,9,10,16,17,23,24-octa- substituted phthalocyanine

The ^1H NMR signal at -2.016 ppm is due to the two protons at the centre of the molecule. The signals at 7.6-6.8 ppm are due to the benzyl protons. On the other hand the ^{13}C NMR showed eleven types of unsaturated carbons at 114.91, 115.34, 117.58, 120.59, 121.35, 126.27, 130.64, 135.33, 157.05 and 161.74 ppm. The signals at 114.91- 120.59 ppm were due to the carbons of the benzene rings attaching the hydrogens. The signals at 121.27 -1.61.74 ppm were due to carbons attaching the oxygen groups in the molecule.

5.2.9 Ultraviolet-visible spectroscopy of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II)

The ultraviolet-visible spectroscopy is divided into visible (400-750 nm) and near ultraviolet (200-400 nm). The radiation of these wavelengths cause promotion of loosely held electrons such as nonbonding electrons or electrons involved in a π bond to higher energy level. It usually shows the presence of conjugated unsaturated systems. The electron transitions taking

place in the porphyrazines are mostly due to the π electrons of the macrocycles as opposed to the transitions due to the metal ion present in the macrocycles.

Like typical porphyrazine, the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II) molecule shows intense B (soret) band at $\lambda_{\text{max}} = 345 \text{ nm}$ (3.3×10^7) and a Q-band that has its principal band at $\lambda_{\text{max}} = 600 \text{ nm}$. The shoulder at 550 nm (5.3×10^7) is due to $n \rightarrow \pi^*$ transition of the nonbonding electrons on the meso-nitrogen atoms of the macrocycle (Figure 4.3.1).

5.2.10 Ultraviolet-visible spectroscopy of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base

The removal of the central magnesium metal ion resulted in the formation of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base. The spectrum of the free base is qualitatively similar to that of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II) except that the Q-band is split into Q_x [$\lambda_{\text{max}} = 558 \text{ nm}$ (4.9×10^7)] and Q_y [$\lambda_{\text{max}} = 626 \text{ nm}$ (5.5×10^7)]. The splitting of the Q-band shows that the 2,3,7,8,12,13,17,18-octa (propyl) porphyrazine base has shifted from a D_{4h} symmetry of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II) to a D_{2h} symmetry.

The difference that exists between the electronic transitions of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines base and 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines magnesium(II) is explained by Gouterman's³⁶ four orbital model for porphyrinic macrocycles (Figure 5.2.1).

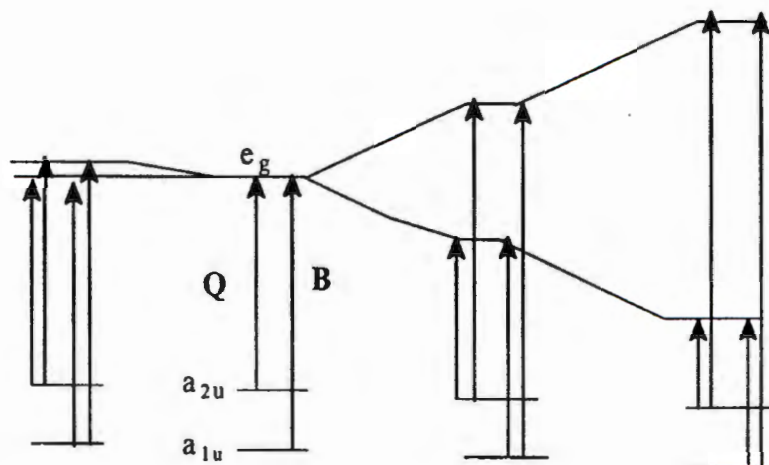


Figure 5.2.1 Orbital energy diagram showing electron transition in macrocycles

Since 2,3,7,8,12,13,17,18-octakis (propyl) porphyraines magnesium(II) is a D_{4h} symmetric macrocycle, the LUMO is doubly degenerate (e_g) and the Q and B bands are due to transitions from the two highest occupied MO's (a_{1u} and a_{2u}) into the LUMO. The reduction in symmetry of the macrocycle removes the degeneracy of the e_g orbital and hence LUMO gives rise to a split Q-band.

5.2.11 Ultraviolet-visible spectroscopy of the N,N,N',N'-tetramethylamino porphyraine hybrid base

The N,N,N',N'-tetramethyl-amino porphyraine hybrid showed an intense B (soret) band at $\lambda_{\max} = 325 \text{ nm}$ (3.9×10^7) and a Q-band that is split into Q_x [$\lambda_{\max} = 556 \text{ nm}$ (6.7×10^7)] and Q_y [$\lambda_{\max} = 742 \text{ nm}$ (9.0×10^7)]. These transitions are due to $\pi \rightarrow \pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the

porphyrazine ring. The shoulder at $\lambda_{\max} = 650 \text{ nm}$ (7.3×10^7) is due to $n \rightarrow \pi^*$ transition from the meso nitrogens to the macrocycle.

5.2.12 Ultraviolet-visible spectroscopy of the 2,3,9,10,16,17,23,24-octa- substituted phthalocyanine

The ultraviolet-visible spectrum of 2,3,9,10,16,17,23,24-octa-substituted phthalocyanine exhibited characteristic B-band at $\lambda_{\max} = 337 \text{ nm}$ (5.3×10^8), which arise from the deeper π levels to the LUMO transition. In the visible portion of the spectrum two intense absorptions of comparable intensity were observed. These are due to the splitting of Q-band into Q_x [$\lambda_{\max} = 666 \text{ nm}$ (1.0×10^9)] and Q_y [$\lambda_{\max} = 703 \text{ nm}$ (1.1×10^9)]. This splitting also reflects the movement of the phthalocyanine from D_{4h} to D_{2h} by removal of the central magnesium. The transitions at the Q-band are also responsible for the green colour of the complex. These transitions are assigned to $\pi \rightarrow \pi^*$ transitions. The signals at $\lambda_{\max} = 606 \text{ nm}$ (9.6×10^8) and $\lambda_{\max} = 639 \text{ nm}$ (1.0×10^8) were assigned to the sublevels within the Q_x and Q_y states.

5.2.13 Infrared spectroscopy of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II)

Infrared spectrum is used to determine bond types and functional groups in a molecule. It is usually divided into two sections. The area from about 1400 cm^{-1} - 3500 cm^{-1} is the functional group area. The other area 1300 cm^{-1} and below is called the fingerprint region. Since different bonds and functional groups absorb at different frequencies, an infrared spectrum is used in qualitative analysis.

In the Infrared analysis of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines magnesium(II) (Table 4.4.1), the C-H aromatic stretching vibrations were observed at 2928 and 2851 cm^{-1} . The strong bands at 1464 and 1379 cm^{-1} could be regarded as alkyl C-H bending asymmetric vibrations and bending symmetric vibrations originating from the alkyl substituents of the macrocycle. The signal at 1643 cm^{-1} is due to N-Mg vibration (Figure 4.4.1).

5.2.14 Infrared spectroscopy 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines base

The Infrared spectrum of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines base is similar to that of octakis (propyl) porphyrazine magnesium(II) except that instead of the N-Mg stretching vibration, a weak N-H stretching vibration at about 3021 cm^{-1} was observed due to the loss of the magnesium ion (Figure 4.4.2). The alkyl C-H stretching vibration is also at 2928 cm^{-1} and 2851 cm^{-1} (Table 4.4.1)

5.2.15 Infrared spectroscopy of the N,N,N',N'-tetramethyl-amino porphyrazine hybrid base

The infrared spectrum of the N,N,N',N'-tetramethyl-amino porphyrazines hybrid base showed absorption at 733 cm^{-1} which was due to C-H wagging (Figure 4.4.3). The isoindole and C-H bending were observed at 1040 and 1265 cm^{-1} . The pyrrole breathing was observed at 1137-1198 cm^{-1} . The aromatic C=C peak was observed at 1593 cm^{-1} . The aromatic C-H peak was observed at 3329 cm^{-1} . The characteristic N-H stretching was observed at 3508 cm^{-1} and the C-O band was observed at 1111 cm^{-1} (Table 4.4.1)

5.2.16 Infrared spectroscopy of the 2,3,9,10,16,17,23,24-octa-substituted phthalocyanine

The infrared spectrum of 2,3,9,10,16,17,23,24-octa-substituted phthalocyanine indicated absorption corresponding to the C-H wagging at 743 cm^{-1} , and the isoindole breathing and C-H bending were observed at $1091\text{--}1250\text{ cm}^{-1}$. The pyrrole breathing was observed at $1163\text{--}1229\text{ cm}^{-1}$ and the pyrrole stretching was observed at 1321 cm^{-1} . The isoindole stretching was observed at $1378\text{--}1465\text{ cm}^{-1}$ whilst the aromatic C=C was observed at 1582 cm^{-1} and the aromatic C-H peak was observed at 3000 cm^{-1} and the N-H vibration was observed at 3620 cm^{-1} . The *ortho*-substituted benzene stretching was observed at $1685\text{--}1700\text{ cm}^{-1}$ (Table 4.4.1).

5.3 ELEMENTAL ANALYSIS OF THE SYNTHESIZED COMPOUNDS

Elemental analysis of all the synthesized compounds corresponded well with the calculated results as given in Tables 4.5.1 – 4.5.10. This confirmed the purity and identity of the compounds.

5.4 KINETIC STUDIES

5.4.1 Insertion of copper(II) ion into 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base

The reaction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines base in dichloromethane with copper(II) ion in acetic acid was followed by ultraviolet-visible spectrophotometer between 300 nm and 800 nm. The

reaction was observed under different temperatures, namely, 293, 298, 303, and 313 K at 5 minutes interval, (Figure 4.6.1).

As the reaction progressed, the spectrum showed that the Q-band centred at 627 nm (5.5×10^7) decreased in intensity and a new band at 585 nm (1.8×10^8) was formed. This new band was formed with isosbestic points at 605 nm (5.8×10^7) and 566 nm (4.9×10^7) and they were maintained throughout the reaction.

Maintenance of the isosbestic point throughout the reaction meant that a simple reaction was being followed, that is, one reagent (A) was converted into another reagent (B). Isosbestic point is obtained where two reagents have the same molar absorptivities. Maintenance of the isosbestic point was important in the diagnosis of the reaction taking place because it eliminated other possible reactions that could be occurring. The other possible reactions include, reduction of copper(II) ion, reaction with the double bonds in the macrocycles, impurities in the solution or simple dissolution where more compound is dissolving as time goes by or decomposition of the product. The plots of $1/[A]$ versus time were linear, which suggested that the reactions followed second order kinetics (Figure 4.6.8 -4.6.11).

5.4.2 Insertion of cobalt(II) ion into 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base

The reaction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine base in dichloromethane with cobalt(II) ion in acetic acid was also followed by ultraviolet-visible spectrophotometer between 300 nm and 800 nm. The

reaction was observed under different temperatures, namely, 313, 328, 333 and 338 K at 5 minutes interval (Figure 4.6.2).

The reaction was not much different from the reaction with copper (II) ion except that the temperatures required for the reactions were a little elevated as compared to those required for the reaction with copper (II) ion. The Q-band at around 650 nm (6.29×10^5) disappeared and a new one appeared at 580 nm (5.89×10^5). Isosbestic points were maintained at 560 nm (4.1×10^5) and 620 nm (5.28×10^5) respectively. The plots of $1/[A]$ versus time were linear, which suggested that the reactions followed second order kinetics (Figure 4.6.14 -4.6.18).

5.4.3 Insertion of copper(II) ion into 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium(II)

The insertion of copper(II) metal ion into 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazines magnesium(II) without first removing the magnesium(II) metal ion was also observed. In this reaction as shown by Figure 4.6.3, three isosbestic points were maintained at 624 nm (5.25×10^7), 580 nm (3.32×10^6) and 540 nm (3.02×10^6). The plots of $1/[A]$ versus time were linear, which suggested that the reactions followed second order kinetics (Figure 4.6.20 - 4.6.23).

5.4.4 Insertion of cobalt(II) ion into N,N,N',N'-tetramethyl-amino porphyrazine hybrid base

The spectral changes of the reaction of the N,N,N',N'-tetramethyl-amino porphyrazines hybrid base in dichloromethane with the cobalt(II) metal ion

in acetic acid were monitored by ultraviolet-visible spectrophotometer at 5 minutes interval at different temperatures (Figure 4.6.4).

As the band at 960 nm (5.2×10^6) disappeared, a new band was formed around 800 nm (4.63×10^6). Three isosbestic points at 780 nm (4.12×10^6), 820 nm (2.23×10^6) and 840 nm (2.13×10^6) were maintained throughout the reaction. The plots of $1/[A]$ versus time were linear, which suggested that the reactions followed second order kinetics (Figure 4.6.25 - 4.6.28).

5.4.5 Insertion of copper(II) ion into N,N,N',N'-tetramethyl-amino porphyrazine hybrid base

Insertion of copper metal ion happened at slightly higher temperatures than that of the insertion of cobalt metal ion to the macrocycle. During the reaction, isosbestic point was also maintained at 720 nm (6.23×10^7) throughout the reaction.

At higher temperatures the reaction of the copper metal (ion) with the macrocycle was starting to deviate from the isosbestic point, which suggested that another reaction might have been taking place. The possible reactions to that affect would be that the ring open up and link the metal at the periphery. The plots of $1/[A]$ versus time were linear, which suggested that the reactions followed second order kinetics (Figure 4.6.31 - 4.6.33).

5.4.6 Insertion of cobalt(II) metal ion into 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base

The reaction of insertion of cobalt metal ion into the centre of the 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base was also monitored by ultraviolet-visible spectrophotometer at five minutes intervals and different temperatures (Figure 4.6.6).

In this reaction isosbestic points were maintained at two positions, which were at 590 nm (2.7×10^8) and 715 nm (4.1×10^8) respectively. As the band at 666 nm (3.9×10^8) disappeared, the band at 639 nm (3.2×10^8) increased in size, and a new band was formed at 500 nm (2.2×10^8). The plots of $1/[A]$ versus time were linear, which suggested that the reactions were second order reaction (Figure 4.6.36 - 4.6.39).

5.4.7 Insertion of copper(II) metal ion into 2,3,9,10,16,17,23,24-octa substituted phthalocyanine base

With regard to the insertion of copper (II) metal ion into the macrocycle, the isosbestic point was maintained at 690 (5.2×10^8) nm and as the reaction progress it started to deviate from the isosbestic point which suggested that other reaction were taking place (Figure 4.6.7).

This reaction reached completion in a short space of time hence observation was done at one minute interval. The plots of $1/[A]$ versus time were linear, which suggested that the reactions followed second order kinetics (Figure 4.6.42 - 4.6.44).

5.4.8 Proposed reaction mechanism for insertion of copper(II) metal ion into 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine

The insertion of Cu(II) metal ion into the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine ligand can occur in two ways (Figure 4.8.1). The first mechanism would be the removal of the central magnesium(II) metal ion from the macrocycle, followed by a fast pick up of the Cu(II) metal ion by the resulting free base (**route 1**). The second mechanism would be direct exchange of positions between the Cu(II) metal ion and the Mg(II) metal ion without forming the free base first (**route2**).

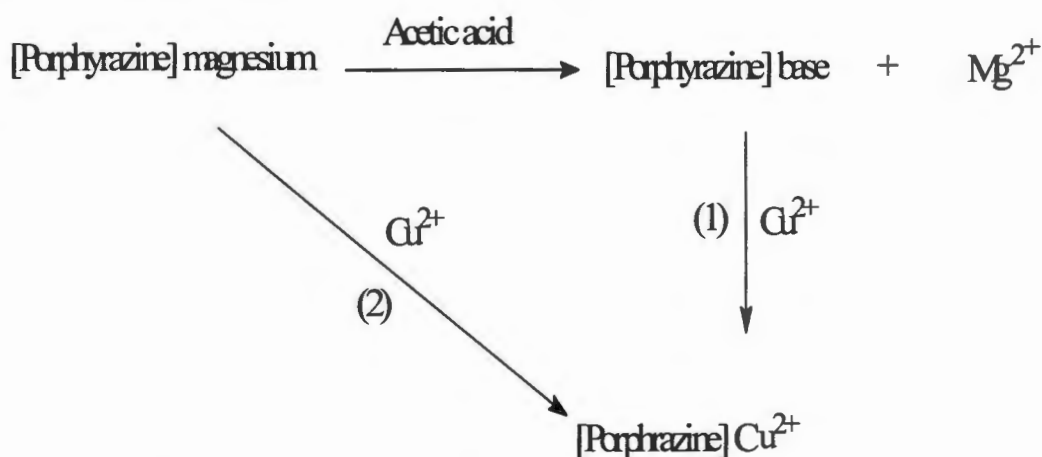


Figure 4.8.1 Figure showing the two possible mechanisms for the insertion of copper(II) metal ion to 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine macrocycle

According to the activation energy requirements, route (1) is the possible mechanism since the activation energy requirement for the formation of the 2,3,7,8,12,13,17,18-octakis (propyl) porphyrzine copper(II) is lower than route (2) (Table 4.7.4).

The proposed mechanism explains what actually happens in the process in which porphyrazines encounter metal ions in their applications and use. This means that magnesium has to be removed first before it can be replaced by the metal ion.

5.5 KINETICS OF REDUCTION OF COPPER(II) COMPLEXES

5.5.1 Reduction of 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II)

Preliminary repetitive scanning of the ultraviolet-visible spectral region during reduction of Cu(II)-pz^1 to Cu(I)-pz^1 by Cu(II)-pz^1 gave well defined isosbestic points at 570 nm (2.7×10^8) and 630 nm (3.0×10^8) for more than two half lives (Figure 4.7.1).

The reaction of Cu(II)-pz^1 with Co(II)-pz^1 is a complementary reaction in which the Cu(II) is reduced to Cu(I) and the Co(II) is oxidized to Co(III) as shown in equation [5.1]



The reduction reaction of Cu(II)-pz^1 by Co(II)-pz^1 followed a second order kinetics (Figures 4.7.4 - 4.7.6). The reduction was relatively slow compared to similar reactions.¹⁴⁹ The proposed mechanism of the reduction of Cu(II)-pz^1 by Co(II)-pz^1 is an outer-sphere reaction mechanism. This is because the pz^1 to which the Cu(II) metal ion is coordinated does not have a bridging group which is common to the coordination sphere of both Cu(II)-pz^1 and Co(II)-pz^1 . The reaction therefore followed an electron tunnelling mechanism. Although such reactions are fast, the size of the macrocycle

clearly affected the rate. For the reaction to take place the reactants have to rearrange before electron transfer could take place to satisfy the Franck Condon requirements. This stipulates that the oxidant and the reductant must reorganised themselves before the act of electron transfer in a way that ensures that the energies of the oxidant and reductant in their transition state are identical. Porphyrazines being relatively large take time to rearrange. This inevitably slows the reaction.

5.5.2 Reduction of N,N,N',N'-tetramethylamino porphyrazine hybrid copper(II) and 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II)

The UV-vis spectrum of the formation of Cu(I)-pz² and Cu(I)-pc were also monitored. The reaction of the formation of Cu(I)-pz² (Figure 4.7.2) maintained the isosbestic points at 580 nm (3.21×10^7) and 620 nm (4.23×10^7) and that of the formation of the Cu(I)-pc (Figure 4.7.3) maintained the isosbestic points at almost similar positions, 577 nm (5.32×10^8) and 620 nm (6.01×10^8). They both follow the second order kinetics and the reaction mechanism is also the outer-sphere reaction mechanism.

Compared to the reduction of Cu(II)-pz¹, the reaction was slow and the reason is the size difference. The Cu(II)-pz² ligand which is larger will take time to rearrange itself in the transition state than the Cu(II)-pz¹. The reduction of Cu(II)-pc was faster than that of Cu(II)-pz¹ and Cu(II)-pz¹. This is believed to be due the presence of the benzene rings.

5.5.3 Activation Parameters

The relatively high activation entropies are reflective of the sizes of the macrocycles and the rearrangements that they undergo in the transition state. The insertion of copper in the Mg(II)-Pz has higher entropy than all the insertions into the free base. This is expected since less movement are required with the free base compared with the complexed ligand. The activation entropy trends for Pz¹-base, Pz²-base and Pc-base cannot be generalized with such few results (Table 4.8.1 – 4.8.3)

The activation energies and activation enthalpies are reflective of ease of formation of the metal porphyrazines. Although the results are few, the general trend is that the cobalt(II)-porphyrazines are difficult to form than the corresponding copper(II) porphyrazines. The proposed outer sphere mechanism is supported by the large entropy changes in the transition state compared with values obtained for inner sphere mechanism.¹⁴⁹

CHAPTER SIX

CONCLUSIONS

6.1 CONCLUSIONS

In conclusion, the following new compounds were successfully synthesized: 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine magnesium, 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine copper(II), 2,3,7,8,12,13,17,18-octakis (propyl) porphyrazine cobalt(II), 2,3,9,10,16,17,23,24-octakis substituted phthalocyanine cobalt(II), 2,3,9,10,16,17,23,24-octa substituted phthalocyanine copper(II), N, N, N', N'-tetramethylamino porphyrazine copper(II) and N, N, N', N'-tetramethylamino porphyrazine cobalt(II). They were fully characterized by NMR, IR, UV-vis spectrophotometer and elemental analysis.

In demetallating the porphyrazines it was better to use acetic acid than trifluoroacetic acid since yield was improved to about two folds of what is obtained when trifluoroacetic acid was used.

From the information obtained from kinetic studies of metallation of the porphyrazines and phthalocyanine, it was deduced that the reactions were second order and the phthalocyanine metallation was faster than that of the porphyrazines. This might be due the presence of the extra benzene rings at the periphery as compared to porphyrazines.

Kinetic studies of metallation of the porphyrazines and phthalocyanine assisted in proposition of the mechanism of metallation. Due to the

difference in the activation energies of the direct insertion of metal ions to porphyrazines and phthalocyanine and formation of porphrazine or phthalocyanine base first, it was concluded that the reaction took place by first creating porphyrazine or phthalocyanine base before metal ion can be inserted and this happen by outer-sphere mechanism.

The reduction followed outer sphere mechanism. Although outer sphere reactions are very fast, the sizes of the macrocycles seem to have slowed them down.

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