NATIONAL UNIVERSITY OF LESOTHO

DEPARTMENT OF CHEMISTRY AND CHEMICAL TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF PHTHALOCYANINES

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SYNTHESIS AND CHARACTERIZATION OF PHTHALOCYANINES

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I would like to convey my sincere and heart-felt thanks to my supervisor Dr. Sekota for being more than a supervisor to me and going out of her way to ensure that we reach this far in doing this work.

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Thanks to all my classmates for their support all year long.

Last but not least, great thanks go to all the laboratory technicians. They have indeed played a pivotal role in completing this work.
ABSTRACT

The phthalocyanine compounds $K_2[(CN)_2FePc]$, $K_2[(CN)_2CoPc]$, FePc(Py)$_2$ and CoPc(Py)$_2$ were successfully synthesized and characterized by UV-Visible and IR spectrometry. This was done for application of these compounds as electrode modifiers and as chemical sensors. These coordination compounds were synthesized by the synthesis of the metal-free phthalocyanines followed by the introduction of the axial ligands. The characteristic UV-Visible and IR spectral bands were observed for the four complexes. Therefore it can be concluded that the complexes were successfully synthesized.
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1 Introduction

1.1 Definition and Properties

Phthalocyanines (Pc) are intensely blue-green coloured macrocyclic compounds that are widely used in dyeing[1]. Phthalocyanines form coordination complexes with most elements of the periodic table. These complexes are also intensely colored and also are used as dyes or pigments. Unsubstituted phthalocyanines, abbreviated H$_2$Pc, are 40-$\pi$ electrons aromatic macrocycles containing four isoindole units linked together by aza nitrogen atoms[2].

Unsubstituted phthalocyanine, H$_2$Pc, have low solubility in organic solvents. For instance, benzene at 40 °C dissolves less than a milligram of H$_2$Pc per litre. Metallophthalocyanines also have some slight solubility in higher boiling aromatic solvents such as quinoline, chlorobenzene, and chloronaphthalene. H$_2$Pc or CuPc dissolve easily in sulfuric acid due to the protonation of the nitrogen atoms bridging the pyrrole rings. Phthalocyanines exhibit varying stabilities toward solution in concentrated sulphuric acid. Almost all Pc complexes are freely soluble in this acid; but some, such as PcCu and PcNi are reprecipitated unchanged upon dilution, whereas others, for example, PcNa$_2$ and PcCa, are demetallated. Metal-free phthalocyanine, H$_2$Pc, is itself slowly decomposed in concentrated sulphuric acid. With regard to colour, MPc are all intensely coloured purple, blue, or green compounds with a beautiful red reflex. Thus it can be concluded,
on the basis of colour, that MPcs absorb mostly the red portion of the visible region of the electromagnetic spectrum (600-700 nm). From this, one can furthermore conclude that Pcs relatively split the metal d-orbitals less, thus resulting in less crystal field splitting energy hence radiation corresponding to the blue light is transmitted. Substitution in H₂Pc can shift the absorption towards longer wavelengths, changing the color from pure blue to green to colorless (when the absorption is in the near infrared). With regard to thermal stability, it is worth mentioning that, many phthalocyanine compounds are thermally very stable, do not melt but can be sublimed, CuPc sublimes at >500 °C under inert gases (nitrogen, CO₂). Regarding kinetic stability, the phthalocyanine unit is moderately stable toward oxidation, but may be broken down to phthalimide or phthalic acid by a two-electron oxidation with ceric or dichromate ions. Moreover, oxidation with dichromate has been developed into an elegant method for the quantitative determination of the oxidation state of the central ion. Under certain circumstances, a one-electron oxidation product, having the ring intact, may be detected. This product is paramagnetic and exhibits an electron-spin resonance spectrum typical of a free radical.

The relationship between phthalocyanine and porphyrin macrocycles is better illustrated by the following diagram. The diagram shows how we can shift from porphyrins to phthalocyanines by first attaching the benzene rings to the pyrrole-like structures followed by substitution of the methines linking the pyrrole-like structures with the nitrogen atoms, and vice-versa.

Fig.2. Relationship of the phthalocyanine with the porphyrin macrocycle
1.2 History

The word phthalocyanine - from the Greek for naphtha (rock oil) and cyanine (blue) was first used by Linstead in 1933 to describe a new class of organic compounds. Phthalocyanine itself was probably discovered by accident in 1907, as a by-product during the synthesis of o-cyanobenzamide, but it was not until almost 20 years later that a patent was filed describing a manufacturing process. The extensive chemical studies by Linstead et al were followed by structural studies by J Monteath Robertson at the Royal Institution and Glasgow - the first crystal structures of relatively large organic molecules. Studies of semiconductivity and gas adsorption effects followed soon after in Nottingham.

1.3 Methods of Preparation

Phthalocyanine metal complexes may be prepared by various methods, the more general methods being illustrated in the following equations:

\[
PcH_2 + MX_2 \xrightarrow{\text{solvent (e.g., quinoline)}} PcM + 2HX
\]

\[
\begin{array}{c}
\text{CN} \\
\text{NC}
\end{array}
\quad + 
\begin{array}{c}
\text{CN} \\
\text{CN}
\end{array}
\xrightarrow{\text{dry or solvent}}
\begin{array}{c}
\text{PcM}
\end{array}
\]

\[
\begin{array}{c}
\text{CONH}_2 \\
\text{CN}
\end{array}
\quad + 
\begin{array}{c}
\text{CN} \\
\text{CN}
\end{array}
\xrightarrow{\text{dry}}
\begin{array}{c}
\text{PcM}
\end{array}
\xrightarrow{\text{300°C}}
\begin{array}{c}
\text{PcM}
\end{array} + 4\text{H}_2\text{O}
\]
The last two reactions may also be carried out with metal salts or metal amides. Metal-free phthalocyanine may be prepared by a number of routes of which examples are given below:

\[
PcH_2 + 2H_3O^\oplus \rightarrow PcH_2 + 2Na^\oplus + 2H_2O
\]

\[
PcH_2 + 4NH_3 \rightarrow PcH_2 + 4NH_3
\]

For basic methods of preparation, many variations are used, particularly in industry, to obtain an economical yield. Phthalic acid, phthalamide, phthalimide, and phthalic anhydride, together with urea, are often used instead of phthalonitrile, and catalysts such as ammonium molybdate or zirconium tetrachloride may be employed. To illustrate the ease with which the phthalocyanine skeleton is formed, the reaction between phthalonitrile and metals (finely divided or acid-etched) is usually very vigorous at 250-300°C, sufficient heat being generated to maintain the reaction temperature. The reaction between phthalonitrile and a finely divided metal, metal hydride, oxide, or chloride is the more generally used, this perhaps may be attributed to the ease with which the phthalocyanines are formed with this method. For more unstable phthalocyanine complexes such as that of silver, the double decomposition reaction is preferred. Nuclear halogenations often occurs when metal halides are reacted directly with phthalonitrile or o-cyanobenzamide, this may be minimized by addition of urea, use of basic solvents, or carrying out the reaction at a lower temperature.

Purification of the products is best effected by sublimation at 400 °C. However, not all phthalocyanines will sublime; recrystallization from chloroform, quinoline, or chloronaphthalene may then be employed. Certain more soluble phthalocyanines may be Soxhlet-extracted with lower boiling solvents such as acetone or alcohol.
Upon coordinating various metals with phthalocyanines, some metals can further be complexed with other ligands so as to move from square planar geometry to octahedral geometry. This is effected by attaching the approaching ligands at the two axial positions as illustrated by the following diagram:

![Diagram showing introduction of axial ligands](image)

Fig. 3. Illustration of introduction of the axial ligands MPc

The axial ligands may be identical or different, thus resulting in a structurally distorted compound.

**1.4 Electronic Spectra**

All normal oxidation state phthalocyanines are characterized by an intense band near 28,000 cm⁻¹ (Soret band), and another intense band near 14,000-15,000 cm⁻¹. Metal–free phthalocyanine differs in having an intense doublet near 14,000-15,000 cm⁻¹. As mentioned earlier in this text, because of the 14,000-15,000 cm⁻¹ absorption, phthalocyanines generally give deep blue to green solutions.

Below is the diagram that shows the change in electronic spectra moving from a metal-free phthalocyanine to a metallated phthalocyanine (in this case, the metal being zinc):
For the purposes of this particular project, of concern will be iron(II) phthalocyanines and cobalt(II) phthalocyanines.

**1.5 Iron Phthalocyanines**

o-Cyanobenzamide reacts with iron wire at 250 °C to yield ferrous phthalocyanine. Ferrous phthalocyanine is, like most phthalocyanines, virtually insoluble in organic solvents and is certainly insoluble in water, yet it undergoes a reaction of being readily soluble in water and in alcohols, in the presence of cyanide ions. Ferrous phthalocyanine is also soluble in alcohols in the presence of sodium hydroxide, yet no products have been isolated. Many organic bases, such as pyridine, quinoline, imidazole and unsubstituted derivatives thereof, react with ferrous phthalocyanine giving diamagnetic six-coordinate complexes, e.g. dipyridine ferrous phthalocyanine.

**1.6 Cobalt Phthalocyanines**

Cobalt phthalocyanine is most commonly formed when etched massive cobalt metal is heated with phthalonitrile. It is soluble without decomposition in concentrated sulphuric acid and may
be sublimed to dark blue needles with a reddish purple luster. It is not particularly soluble in alcoholic alkali or cyanide solutions, but it is readily soluble in pyridine. Cobalt(II) phthalocyanine cannot be successfully oxidized to cobalt(III) in neutral or basic solvent. Cobalt(II) phthalocyanine is reported to be oxidized to nitratocobalt(III) phthalocyanine by nitric acid in nitrobenzene at 10-20 °C. Regarding reduction, cobalt(II) phthalocyanine is reduced by lithium benzophenone in tetrahydrofuran to lithium phthalocyanine cobaltate(I) and dilithium phthalocyanine cobaltate.

### 1.7 Applications of Phthalocyanines

Approximately 25% of all artificial organic pigments are phthalocyanine derivatives, on that basis, phthalocyanines find a variety of uses in art, printing inks, colouring of plastics, surface coating, paper dyes and textile industry. Copper phthalocyanine (CuPc) dyes are produced by introducing solubilizing groups, such as one or more sulfonic acid functions. Direct blue 86 is the sodium salt of CPC-sulfonic acid whereas direct blue 199 is the quaternary ammonium salt of the CPC-sulfonic acid. Phthalocyanine is also commonly used as a dye in the manufacture of high-speed CD-R media.

Metal phthalocyanines have long been examined as catalysts for redox reactions. Areas of interest are the oxygen reduction reaction and the sweetening of gas streams by removal of hydrogen sulfide. Phthalocyanine compounds have been investigated as donor materials in molecular electronics, e.g. organic field-effect transistors.

The colour change of phthalocyanines has been recognized for some time and has opened up new investigations for its applications in electrochromic displays and these electchomic reversibility allows their use as electro-optic transducers in plate screens.

Phthalocyanines are also promising as electrode materials not only as catalysts but as reactive species in lithium cells. Combined with a lithium anode in an electrochemical cell, low-molecular phthalocyanines have shown discharged capacities ranging from 17 to 26 equivalent electrons per phthalocyanine molecule. The transition-metal N₄-chelates such as CoPc, FePc, NiPc and CuPc; and polymeric pCoPc and pFePc have been employed by either dissolving MPc
in the electrolyte or adsorbing MPc on the cathode in lithium SOCl₂ batteries to increase the battery’s lifetime and discharge rates.

Metallophthalocyanines promote the electro-oxidation of formic acid, sulphur dioxide, oxalic acid, hydrazine, mercapto-ethanol, cysteine hydroxylamine, glycine, alanine, tyrosine, the evolution of oxygen, the reduction of hydrogen peroxide and the electroreduction of carbon dioxide, alkyl chlorides, molecular nitrogen, nitric oxide, nitrate ions, thionyl chloride, and sulphuryl chloride. Most of these reactions are important for use in organic synthesis, removal of waste from water, and detection of low concentrations of compounds. For instance, hydrazine is detected and quantified by use of CoPc containing chemically modified electrodes as sensors in the electrochemical detection in liquid chromatography (LCEC) determination of hydrazine. Oxalic acid, ascorbic acid and α-keto acids can be determined in blood, plasma or urine by reversed-phase HPLC using CoPc modified electrode. CoPc has been employed as an electrocatalyst for the oxidation of coenzyme-A and it has been found that CoPc reduces the overpotential required the oxidation of coenzyme-A. Carbon paste electrodes (CPE) containing CoPc have been used for the amperometric detection of compounds that are virtually non-electroactive or oxidizable at extreme potentials. The use of metallophthalocyanine-coated electrodes provides fast, accurate, on-line monitoring of sulphide concentrations in aqueous effluent.

2. Experimental

2.1 Methods of Synthesis

2.1.1 Phthalamide

Phthalamide was prepared by adding phthalimide (40.0124g) to ammonia (120ml) and stirring the solution for approximately 24 hours. The mixture was filtered and crystals were obtained and dried at 115 °C. Melting point 224-228 °C.
2.1.2 o-Cyanobenzamide

o-Cyanobenzamide was prepared by refluxing the mixture of phthalamide (16.0546 g) and acetic anhydride (60 ml) for 3 hours. Upon cooling, yellowish-white crystals were formed. The crystals were washed with ice-cold ethanol and dried at 114 °C. Melting point 168-176 °C.

2.1.3 (Phthalocyaninato)ferrous(II)

This was prepared by heating the mixture of FeCl$_2$ (0.6256 g), o-cyanobenzamide (4.0105 g) and naphthalene (1.6138 g) at 290 °C for 20 minutes. Upon cooling, the mixture was washed with 95% ethanol and filtered. The dried residues were Soxhlet-extracted with glacial acetic acid until the washings were colourless. The remaining greenish black solid was dried in the oven at 114 °C to remove excess acetic acid.

2.1.4 (Phthalocyaninato)cobalt(II)

This was prepared by heating the mixture of CoCl$_2$ (0.9366 g), o-cyanobenzamide (6.0118 g) and naphthalene (2.4044 g) at 290 °C for 20 minutes. Upon cooling, the mixture was washed with 95% ethanol and filtered. The dried residues were Soxhlet-extracted with glacial acetic acid until the washings were colourless. The remaining greenish black solid was dried in the oven at 114 °C to remove excess acetic acid.

2.1.5 Potassium (biscyanato)(phthalocyaninato)ferrous(II) (K$_2$[(CN)$_2$FePc])

K$_2$[(CN)$_2$FePc] was prepared by treating crude FePc (0.1499 g) with excess potassium cyanide (0.1413 g) in refluxing dimethylformamide (DMF, 120 ml) for 3 hours. After evaporation of the solvent, the resulting solid was washed with chloroform and recrystallized once in acetonitrile.

2.1.6 Potassium (biscyanato)(phthalocyaninato)cobalt(II) (K$_2$[(CN)$_2$CoPc])

K$_2$[(CN)$_2$CoPc] was prepared by treating crude CoPc (0.1496 g) with excess potassium cyanide (0.1398 g) in refluxing dimethylformamide (DMF, 120 ml) for 3 hours. After evaporation of the solvent, the resulting solid was washed with chloroform and recrystallized once in acetonitrile.
2.1.7 Bis(pyridine)(phthalocyaninato)ferrous(II) (Fe(Pc)(Py)$_2$)

FePc(Py)$_2$ was prepared by refluxing crude FePc (0.2051g) in pyridine (40ml) for 8 hours. The resulting solution was left for evaporation of the solvent. After evaporation of the solvent, the resulting solid was dissolved in chloroform, after which the resulting solution was filtered so as to acquire the solution with no suspended solids. After evaporation of the solvent, a purple solid was obtained.

2.1.8 Bis(pyridine)(phthalocyaninato)cobalt(II) (Co(Pc)(Py)$_2$)

FePc(Py)$_2$ was prepared by refluxing crude FePc (0.2043g) in pyridine (40ml) for 8 hours. The resulting solution was left for evaporation of the solvent. After evaporation of the solvent, the resulting solid was dissolved in chloroform, after which the resulting solution was filtered so as to acquire the solution with no suspended solids. After evaporation of the solvent, a greenish-black solid was obtained.

2.2 Characterization

The synthesized compounds were characterized with UV-Visible spectrometry and IR spectroscopy using 1201 Shimadzu UV-Visible spectrophotometer and Magna 760 FTIR spectrophotometer.

3.0 Results and Calculations

The stoichiometric relationship for the synthesis of (Phthalocyaninato)ferrous(II) and (Phthalocyaninato)cobalt(II) complexes is demonstrated by the following reaction equation;

\[
\text{CONH}_2 + M \xrightarrow{30\text{Pc}} \text{PcM} + 4\text{H}_2\text{O}
\]

where M is the metal (Co$^{2+}$ or Fe$^{2+}$) that constitute the chloride salt of either of the two metals. The percentage yields for different synthesized phthalocyanine complexes were calculated and recorded in the tables below.
Table 1: The analytical data for the synthesis of (Phthalocyaninato)ferrous(II) and (Phthalocyaninato)cobalt(II)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass yield (g)</th>
<th>Percentage yield (%)</th>
<th>Limiting reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Phthalocyaninato)ferrous(II)</td>
<td>0.3795</td>
<td>60.7</td>
<td>FeCl₂</td>
</tr>
<tr>
<td>(Phthalocyaninato)cobalt(II)</td>
<td>0.6655</td>
<td>71.1</td>
<td>CoCl₂</td>
</tr>
</tbody>
</table>

The stoichiometric relationship for the synthesis of both K₂[(CN)₂FePc] and K₂[(CN)₂CoPc] is demonstrated by the following reaction equations:

\[
2\text{KCN} + \text{FePc} \rightarrow \text{K}_2[(\text{CN})_2\text{FePc}]
\]

\[
2\text{KCN} + \text{CoPc} \rightarrow \text{K}_2[(\text{CN})_2\text{CoPc}]
\]

Table 2: Analytical data for synthesis of K₂[(CN)₂FePc] and K₂[(CN)₂CoPc

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass yield (g)</th>
<th>Percentage Yield (%)</th>
<th>Limiting reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂[(CN)₂FePc]</td>
<td>0.0430</td>
<td>28.7</td>
<td>FePc</td>
</tr>
<tr>
<td>K₂[(CN)₂CoPc]</td>
<td>0.0463</td>
<td>30.9</td>
<td>CoPc</td>
</tr>
</tbody>
</table>

The stoichiometric relationships between FePc and CoPc with pyridine (Py) for the synthesis of FePc(Py)₂ and CoPc(Py)₂ respectively are illustrated by the following reaction equations:

\[
\text{FePc} + 2\text{Py} \rightarrow \text{FePc(Py)}_2
\]

\[
\text{CoPc} + 2\text{Py} \rightarrow \text{CoPc(Py)}_2
\]

Table 3: Analytical data for the synthesis of FePc(Py)₂ and CoPc(Py)₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass yield (g)</th>
<th>Percentage yield (%)</th>
<th>Limiting reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePc(Py)₂</td>
<td>0.1584</td>
<td>77.5</td>
<td>FePc</td>
</tr>
<tr>
<td>CoPc(Py)₂</td>
<td>0.1636</td>
<td>79.8</td>
<td>CoPc</td>
</tr>
</tbody>
</table>
Table 4: Colour observations for the synthesized phthalocyanine complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Observed colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePc</td>
<td>Greenish-black</td>
</tr>
<tr>
<td>CoPc</td>
<td>Purplish-black</td>
</tr>
<tr>
<td>K₂[(CN)₂FePc]</td>
<td>Blue-black</td>
</tr>
<tr>
<td>K₂[(CN)₂CoPc]</td>
<td>Green</td>
</tr>
<tr>
<td>FePc(Py)₂</td>
<td>Greenish-black</td>
</tr>
<tr>
<td>CoPc(Py)₂</td>
<td>Purple</td>
</tr>
</tbody>
</table>

The synthesized phthalocyanine complexes were characterized by UV-Visible spectroscopy and their spectral data is given in the tables below.

Table 1: UV-Visible data for K₂[(CN)₂FePc] dissolved in N,N-dimethylformamide (DMF)

<table>
<thead>
<tr>
<th>Maximum wavelength(nm)</th>
<th>Absorbance</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>663.00</td>
<td>1.635</td>
<td>Q band (HOMO-LUMO)</td>
</tr>
<tr>
<td>601.00</td>
<td>0.417</td>
<td>LMCT</td>
</tr>
<tr>
<td>428.00</td>
<td>0.398</td>
<td>MLCT</td>
</tr>
<tr>
<td>355.00</td>
<td>0.958</td>
<td>Soret band</td>
</tr>
<tr>
<td>306.00</td>
<td>1.084</td>
<td>B band</td>
</tr>
</tbody>
</table>

Table 6: UV-Visible data for K₂[(CN)₂CoPc] dissolved in N,N-dimethylformamide (DMF)

<table>
<thead>
<tr>
<th>Maximum wavelength(nm)</th>
<th>Absorbance</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>671.00</td>
<td>2.128</td>
<td>Q band (HOMO-LUMO)</td>
</tr>
<tr>
<td>606.00</td>
<td>0.491</td>
<td>LMCT</td>
</tr>
<tr>
<td>428.00</td>
<td>0.293</td>
<td>MLCT</td>
</tr>
<tr>
<td>343.00</td>
<td>0.630</td>
<td>Soret band</td>
</tr>
</tbody>
</table>
Table 7: UV-Visible data for FePc(Py)$_2$ dissolved in N,N-dimethylformamide (DMF)

<table>
<thead>
<tr>
<th>Maximum wavelength (nm)</th>
<th>Absorbance</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>661.00</td>
<td>1.033</td>
<td>Q band (HOMO-LUMO)</td>
</tr>
<tr>
<td>315.00</td>
<td>1.411</td>
<td>B band</td>
</tr>
</tbody>
</table>

Table 8: UV-Visible data for CoPc(Py)$_2$ dissolved in N,N-dimethylformamide (DMF)

<table>
<thead>
<tr>
<th>Maximum wavelength (nm)</th>
<th>Absorbance</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>659.00</td>
<td>0.775</td>
<td>Q band (HOMO-LUMO)</td>
</tr>
<tr>
<td>597.00</td>
<td>0.184</td>
<td>LMCT</td>
</tr>
<tr>
<td>327.00</td>
<td>0.478</td>
<td>B band</td>
</tr>
</tbody>
</table>

The graphical presentation of the above given UV-Visible data is given below as UV-Visible spectra;
The IR spectra of the synthesized phthalocyanine complexes is presented graphically below.
4.0 Discussion

4.1 Synthesis

Synthesis of crude metallophthalocyanine is characterized by relatively low percentage yields. This is illustrated by percentage yields of 60.7% and 71.1% for synthesis of the complexes FePc and CoPc respectively. This can be explained by a number of reasons which include the following amongst others. Regarding the reaction between o-cyanobenzamide and the corresponding metal chloride for either of the two MPc, the reaction is between two solid reagents and this lead to relatively low degree of interaction between the two reagents. Furthermore, the reaction is carried out in naphthalene. Although the use of naphthalene increases interaction between the two reagents by providing the medium for the reaction to take place, it does not maximize it since both MPc’s and the reagents exhibit relatively lower solubilities in the given solvent and many other solvents including higher boiling solvents such as quinoline and chlorobenzene. Also synthesis of MPc’s is characterized by low percentage yields because, nuclear halogenations often occurs when metal halides are reacted directly with phthalonitrile or o-cyanobenzamide, even though the use of solvents such as urea minimizes it.

Regarding the observed colour of the two synthesized MPc’s, the greenish-black and the purplish-black colours for FePc and CoPc complexes indeed conform to the expected colours of MPc’s. Theoretically, MPc’s are expected to exhibit colours ranging from blue to green since they absorb mostly the red portion of the visible region of the electromagnetic spectrum (600-700nm).

The synthesis of both \( K_2[(CN)_2FePc] \) and \( K_2[(CN)_2CoPc] \) yielded relatively low percentage yields than expected and these are 28.7% and 30.9% respectively. This low percentage yields can be explained by the fact that there is a dynamic equilibrium in which either the cyanide ions (CN) occupy the two axial positions or N,N-dimethylformamide molecules do occupy the axial positions. This is because the reaction is carried out in DMF which is also an electron pair donor by its nature of being a ligand. The distinguishing factor is that cyanide is more thermodynamically favoured to occupy the axial points in forming the octahedral geometry than DMF. But this does not dispute that a given portion of MPcL\(_2\) will have L as DMF rather than cyanide thereby reducing the amount of \( K_2[(CN)_2MPc] \).
The synthesis of both FePc(Py)$_2$ and CoPc(Py)$_2$ give relatively higher and expected percentage yields of 77.5% and 79.8% respectively. This can be attributed to longer refluxing times (8 hours) when carrying out the reaction. This implies that the reaction mixture was given adequate energy and time for the substantial amount of the reagents to react and produce a satisfactory amount of the desired product.

4.2 Characterization by UV-Visible spectrometry

All MPc’s show a characteristic intense band in the visible region at around 655-675 nm. With the exception of FePc(Py)$_2$, all the synthesized MPcs showed relatively weaker bands at a slightly higher energy of around 600nm. A characteristic intense band found in the Soret region (340-380nm) is exhibited by some MPcs and a more intense band at around 300-320nm.

The conjugated ring system of phthalocyanine comprises of 40 atoms. The metallated phthalocyanines belong strictly to D$_{4h}$ (square planar) symmetry, whereas unmetallated phthalocyanine, by virtue of the two replaceable hydrogen atoms, belong to D$_{2h}$ (planar with inversion centre) symmetry. According to Gouterman’s four orbital theory, the highest occupied molecular orbital (HOMO) of the phthalocyanine ring is the $a_{1ux}$, the next low lying filled orbital is the $a_{2ux}$. The lowest unoccupied molecular orbital (LUMO) of the ring is the $e_{g*}$ and the next highest unoccupied orbital is the $b_{1ux*}$.

The characteristic band observed in the region 600-700nm of the visible region, also known as the Q band, is due to the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Therefore, the Q band is due to the transition from $a_{1ux}$ to $e_{g*}$. This is also confirmed by the fact that, high intensity and relatively low energy of these bands imply that they arise from $\pi-\pi^*$ transitions.

The transition from the $a_{2ux}$ to LUMO yields a band known as the Soret band. This band is of higher energy because $a_{2ux}$ is at lower energy level than $a_{1ux}$, thus affording a relatively higher energy gap hence lower wavelength (340-380nm).

Given that the central metal d-orbitals lye within the HOMO-LUMO gap, charge transfer (CT) transitions are likely to occur. Charge transfer transitions from the d-orbitals of the central metal to the unoccupied molecular orbitals, that is to $e_{g*}$ and $b_{1ux*}$, is specifically called the metal to
ligand charge transfer (MLCT). Those charge transfer transitions from occupied molecular orbitals, that is $a_{2u}$ and $a_{1u}$, to the empty d-orbitals, are specifically called ligand to metal charge transfer transitions (LMCT). Charge transfer transitions in MPc’s are normally characterized by weak absorption bands which lie between the Soret band and the Q band, in the range 400-600 nm. Charge transfer absorption bands are not typical of all MPc’s, but only those MPc’s whose central metal ion d-orbitals lie between the HOMO-LUMO gap.

The electronic spectra of the metallophthalocyanine complexes are known to vary considerably depending on the nature of the ligands coordinated on the axial positions of the metallophthalocyanine complex. The properties of the spectra of metallophthalocyanine complexes are also affected by the nature of the solvent. The weakly coordinating solvents such as dimethylacetamide (DMA), dimethylsulfoxide (DMSO), and dimethylformamide (DMF) provide a consistent environment from which to compare different metals and different axial ligands. For most metallophthalocyanine species, the Q band is found within the 600-700 nm region in weakly coordinating solvents. Spectra recorded in sulfuric acid solutions exhibit a red shifted Q band which appears between 700-800 nm.

The above given information is best illustrated by the following simplified energy level diagram for metallophthalocyanines.

![Fig.5. A simplified energy level diagram for metallophthalocyanines](image)
Both the Q and the Soret bands have shoulders and these are attributed to the charge transfer transitions between the metal and the ligand.

4.3. Characterization by IR spectrometry

In view of the large size and complexity of the phthalocyanine ligand, it is perhaps not surprising that the IR spectra of MPcs appear complex as they do. With the exception of that of $K_2[(CN)_2FePc]$, the spectra of the synthesized phthalocyanines exhibit complexity. The only difference in preparing the samples for running the IR is that the disk for the compound $K_2[(CN)_2FePc]$ was placed in the oven at 100 °C before running.

This difference in complexity can then be attributed to the fact that the infrared spectrum depends markedly upon the particular polymorph involved, hence the technique can be used to distinguish between the different polymorphic forms. Theoretically, the disks maintained at a temperature of about 100 °C result in thin layers of the α polymorph. The β polymorphs are obtained by taking the disks and subjecting them to temperatures of about 280-300 °C. The β modification is richer in spectral absorption than the α modification, perhaps owing to the more compact packing of the molecules in the former case resulting in stronger intermolecular interactions. In this way, lines which were forbidden in the α form, may become allowed in the β form.

Taking into consideration the spectrum of $K_2[(CN)_2FePc]$ for analysis. The absorption band near 725 cm$^{-1}$ is assigned as a C-H out-of-plane deformation, the 1610 cm$^{-1}$ and 1475 cm$^{-1}$ bands to C-C benzene-ring skeletal vibrations and the 3030 cm$^{-1}$ to the C-H stretching vibration. The Fe-C-N bond is shown by the band at 2030 cm$^{-1}$.

5.0 Conclusion

The phthalocyanine compounds $K_2[(CN)_2FePc]$, $K_2[(CN)_2CoPc]$, FePc(Py)$_2$ and CoPc(Py)$_2$ were successfully synthesized and characterized by UV-Visible and IR spectrometry.
6.0 Recommendations

Those phthalocyanine complexes that were to be synthesized under nitrogen atmosphere were not successfully synthesized. This was indicated by the existence of some complexes as solid suspensions rather than solutions as expected and some solutions giving pale colours rather than deep colours as per literature. The recommendation would be that the nitrogen supply be ascertained as nitrogen before carrying out the experiment.
7.0 References


