Synthesis And Characterization Of Metallocorroles And It’s Application

A Dissertation Report Submitted
In Partial Fulfilment of the Requirements
For the Degree of

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in
Chemistry

by

KUSHWAHA ANKIT
(24/MSCCHE/22)

ANKUSH PATEL
(24/MSCCHE/40)

Under the Supervision of
Dr. ANIL KUMAR

Department of Applied Chemistry

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahabad Daulatpur, Main Bawana Road, Delhi-110042, India
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DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahabad Daulatpur, Main Bawana Road, Delhi-110042, India

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DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-42

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This is to certified that Kushwaha Ankit (24/MSCCHE/22) & Ankush Patel (24/MSCCHE/40) has carried out their rsearch work presented in this thesis entitled **"Synthesis And Characterization of Metallocorroles And It's Application"** for the award of Master of Science from Department of Applied Chemistry, Delhi Technological University, Delhi, under my supervision. The dissertation embodies results of original work, and studies are carried out by the students himself and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

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(Supervisor)

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-42

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List Of Abbreviations

DDQ - 2,3 Dichloro-5,6 -dicyano-1,4-benzoquinone

DMF - Dimethylformamide

HCL - Hydrochloric Acid

UV -Vis - Ultra violet visible

NMR – Nuclear Magnetic Resonance

DCM – Dichloromethane

Py – Pyridine

THF – Tetrahydrofuran

TLC – Thin Layer Chromatography

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Abstract

Corroles are a group of tetrapyrrolic macrocycles that have drawn a lot of interest from researchers be cause of their special structural, electronic, and coordination properties. They are closely connected to porphyrins, but with one key difference — they are missing one meso-carbon atom. This makes their macrocyclic cavity smaller and gives them a trianionic ligand character. Because of these features, corroles can hold metals in uncommon oxidation states, which makes them useful in many scientific and technological areas.

This dissertation covers the synthesis of corroles, their structural features, metallation reactions, methods of functionalization, and growing applications. A major focus is placed on developing efficient synthetic routes, which have made it much easier to prepare meso-substituted corroles. The work also discusses key reaction intermediates, the mechanisms behind macrocycle formation, and the factors that affect how well the synthesis works.

The study also looks at how corroles coordinate with different metal ions, such as transition metals, lanthanides, and heavy metals. When a metal is inserted into the corrole ring, it changes the electronic and photophysical behaviour of the compound, leading to complexes with better catalytic and functional properties.

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We would like to sincerely thank everyone who helped and guided us throughout this dissertation titled **“Synthesis and Characterization of Metallocorroles And It’s Application”.**

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Kushwaha Ankit

Ankush Patel

Chapter 1 – Introduction

1.1 Background and Historical Context

Corroles belong to a fascinating group of tetrapyrrolic macrocycles that have caught the attention of synthetic and inorganic chemists for more than two decades. These molecules are closely related to porphyrins but differ in one important way: they have one fewer meso-carbon atom, which makes their coordination core more compact and trianionic in nature. Research on corroles really gained momentum after simple one-pot synthesis methods were discovered, which opened up a lot of new possibilities for studying these unique macrocyclic compounds. Before these methods were developed, making corroles was a difficult and often unpredictable process that required many steps and gave poor yields.

The most defining feature of corroles is their smaller tetrapyrrolic framework, which changes how they behave chemically compared to porphyrins. While porphyrins act as dianionic ligands with a relatively large coordination cavity, corroles function as trianionic ligands with a tighter binding space for metal ions. This structural difference has a big impact on their coordination chemistry, photophysical properties, and possible applications. The electron-rich nature of the corrole ring makes it especially good at stabilizing metal centers in both high and low oxidation states — a property that has made corroles increasingly useful in catalysis.

1.2 Significance and Applications

The importance of corrole synthesis goes well beyond academic interest. These molecules have shown remarkable versatility across many fields. In photodynamic therapy, corrole-based photosensitizers have demonstrated strong effectiveness against cancer cells and harmful microorganisms. Their ability to generate reactive oxygen species when exposed to light makes them promising candidates for medical treatments. Corroles have also been studied as electrocatalysts for important reactions such as hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and carbon dioxide reduction.

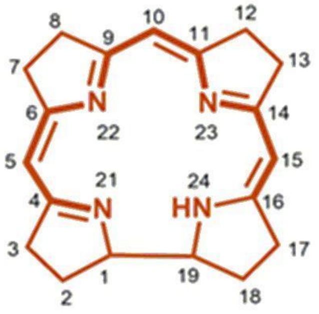
1.3 Molecular Structure and Nomenclature

Corroles are tetrapyrrolic macrocycles made up of four pyrrole units joined together by three methine bridges (CH) and one direct carbon-carbon bond. This arrangement makes them different from porphyrins, which have four methine bridges linking the pyrrole rings. The absence of this 'missing' meso-carbon creates a contracted and asymmetric cavity that strongly influences the properties of the ligand. The corrole skeleton is labeled with numbered positions — positions 1 to 4 represent the first pyrrole ring, 5 to 8 the second, and so on, with the region of the direct C-C bond being the most unique structural feature.

The naming system for corroles follows IUPAC conventions, though in everyday use, simpler descriptive names are common. For example, meso-triarylcorroles are corroles that have three aryl groups attached at the three meso-positions (the methine carbon bridges).

porphyrin

corrole



corrin

1.4 Electronic Structure and Aromaticity

The electronic structure of corroles has been studied in detail through both theoretical and experimental work. Free-base corroles maintain an 18π-electron aromatic system, though how these electrons are distributed and delocalized across the ring complex. It depends on the protonation state of the nitrogen atoms. The corrole ligand can exist in equilibrium with its deprotonated anionic form, which sets it apart from porphyrins. Recent work has confirmed the structure of the free-base corrole anion, showing that the negative charge is spread over the macrocycle, with hydrogen atoms preferentially sitting on pairs of opposite pyrrole nitrogen.

1.5 Comparison with Porphyrins and Phthalocyanines

To understand corroles properly, it helps to place them within the broader family of tetrapyrrolic macrocycles. Porphyrins, with their symmetrical four-bridge structure and over a century of well-established chemistry, serve as the natural reference point. However, corroles are different enough that many general rules from porphyrin chemistry do not apply directly.

Phthalocyanines and naphthalocyanines make up another important class of tetrapyrrolic macrocycles. Their extended aromatic character sets them apart from both corroles and porphyrins. Together, these three families form the core of macrocyclic ligand chemistry, each offering unique advantages for different applications. Studying corroles deepens our understanding of all tetrapyrrolic systems by showing how small structural changes can lead to significantly different chemistry.

1.6 Types of Corrole

Nomenclature of substituted corroles have same analogy like meso substituted porphyrin.

A3 corrole :

A3 Aryl corroles can be synthesized using aromatic aldehydes and pyrrole. Because of the oxidation potential of the electron-donating aliphatic substituents is too low to allow the stable product. The reactivity of carbonyl group depends on the attached substituents, which increase the positive charge on carbon atom of carbonyl group. In this way, Gross group synthesised first A3 corrole by the reaction of pentafluorobenzaldehyde and pyrrole under neat conditions and added 2.3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for aromatization . The 5,10.15-tris(pentafluorophenyl) corrole was obtained with 13% yield. Using the same procedure synthesis of the meso-alkyl-substituted corrole with 1% yield by the reaction haptafluorobutylaldehyde hydrate and pyrrole was carried out Gryko's group presented the facile route of synthesis of corroles. In 2000, Lee and co-worker reported the bilanes in the literature . In addition, Paolesse et al introduced the universal conditions with a pyrrole aldehyde ratio of 10:1 for corrole synthesis with good yields.

Cis-A2B corrole

Tanaka and Osuka and co-worker reported facile protocol for cis-A2B corrole by acid catalyzed [2+2] condensation using carbinol and dipyrrane with DDQ In addition, they explored this method to synthesise the meso-free corrole. In 2002, Chandrashekar et al proposed the first methodology of cis-A2B corrole via [3+1] condensation of tripyrrane with pyrrole-2-carboxaldehyde .

trans-A2B corrole

The idea of synthesis of trans-A2B corrole came from the Landesy's work on tram A2B-porphyrins from dipyrranes and aldehydes. In 2000, Gryko el al proposed the first method to synthesise the trans A2B corrole without acidic catalyst Later many research groups reported the methodology of trans-A2B comule using the aromatic aldehydes and dipyrrane Collman and Deereau synthesised trans A2B corrole by the condensation of dipyromethane dicarbinols with 2.2'-bipyrrole In addition, Gryko and co-workers reported the synthesis of warm-AB-Comoles from ethyl cxalyl chloride and dipyrrane Later, Gryko and Gerer et al synthesized of trans-A2B corrole from dipyrrane Dios and Pyrrole.

Chapter 2 – Literature Review

Corroles are a well-recognized class of tetrapyrrolic macrocycles that have received growing attention due to their distinctive structural and electronic characteristics. They are related to porphyrins but have a smaller macrocyclic ring and a trianionic ligand core, which allows them to stabilize metals in high oxidation states. Since efficient synthesis methods were introduced in the late 1990s, research on corroles has grown rapidly.

One of the biggest breakthroughs in corrole chemistry was the development of the one-pot synthesis method by Gryko and co-workers. This method provided a straightforward and efficient route for making meso-substituted corroles. It works by combining dipyromethanes with aldehydes under acid catalysis, followed by oxidative cyclization. This made corrole synthesis much more accessible and consistent.

Several researchers have studied the metalation of corroles with transition metals such as cobalt, iron, manganese, copper, and gallium. The resulting metallocorroles show remarkable catalytic, magnetic, and photophysical properties. Studies have demonstrated that corrole complexes work well as catalysts for important reactions including hydrogen evolution, oxygen reduction, and carbon dioxide reduction.

In recent years, significant work has been done on the functionalization of corroles to change their electronic and optical properties. Various synthetic approaches have been developed to attach substituents at the meso and beta positions, leading to corrole derivatives with improved stability and broader application potential.

The photophysical properties of corroles have also been widely explored. Because they absorb strongly in the visible region and can efficiently generate reactive oxygen species, corroles have shown promise in photodynamic therapy (PDT) for cancer treatment and fighting microbial infections. Gallium and phosphorus corrole complexes, in particular, have shown excellent biological activity.

Additionally, corroles have emerged as attractive materials in energy conversion and storage. Their unique redox behavior and ability to exist in multiple oxidation states make them suitable for electrocatalysis, solar energy conversion, and chemical sensing.

Chapter 3 – Experimental Procedure

The synthesis process was carried out in the laboratory following the steps described below.

1. A round-bottom flask was set up on a magnetic stirrer using a stand. 590 ml of distilled water was added to the flask, and a magnetic bead was placed inside. The stirrer was turned on at room temperature with a speed of 350 RPM.

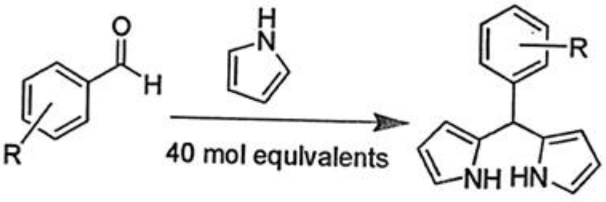
2. Using a pipette, 9 ml of HCl was added to the round-bottom flask, followed by 1.2 ml of pyrrole and 0.724 g of p-nitrobenzaldehyde.

3. Once the solution turned light green in colour, it was left to stir for 2 hours. After this, the mixture was filtered using a funnel and filter paper.

4. A light yellow compound was collected as a solid (precipitate) on the filter paper. This compound was identified as Dipyromethane (DPM).

5. The compound was then purified by recrystallization using

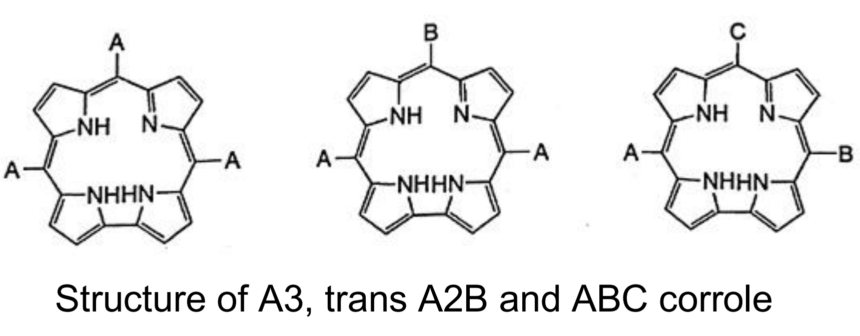
dichloromethane.



Synthesis of dipyrrolemethane

3.1 Free-Base Corrole Synthesis

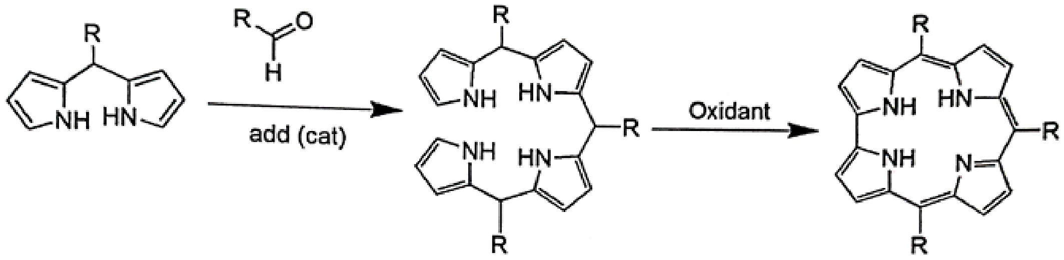
The methods for making free-base corroles have improved significantly over the years. The earliest corroles were made in the 1960s through long, multi-step procedures involving the condensation of tetrapyrrole precursors with oxidizing agents. These methods gave only small amounts of product and were not easy to adapt for different meso-substituents. The field did not see much progress until the late 1990s, when more modern approaches were developed.



Structure of A3, trans A2B and ABC corrole

A major step forward was the discovery that corrole rings could be formed using a simple '2+1' condensation approach. In this method, two equivalents of a dipyrromethane are reacted with one equivalent of an aromatic aldehyde in the presence of an acid catalyst. This approach works well because the dipyrromethane has a more reactive site for condensation. By carefully controlling the stoichiometry, a useful intermediate is formed, which then undergoes further condensation and oxidative cyclization to give the corrole product.

This procedure was greatly improved by the Gryko synthesis, which optimized the choice of acid catalyst, solvent, and reaction conditions. In this method, trifluoroacetic acid (TFA) or trichloroacetic acid (TCA) is used as the catalyst, and the reaction takes place in organic solvents like dichloromethane or chloroform. The oxidative cyclization to complete the corrole ring is driven by oxygen in the air, which makes this method very convenient compared to older procedures that required chemical oxidants. This one-pot method turned corrole synthesis from a complicated, specialist procedure into a straightforward reaction that most organic chemistry labs could carry out.

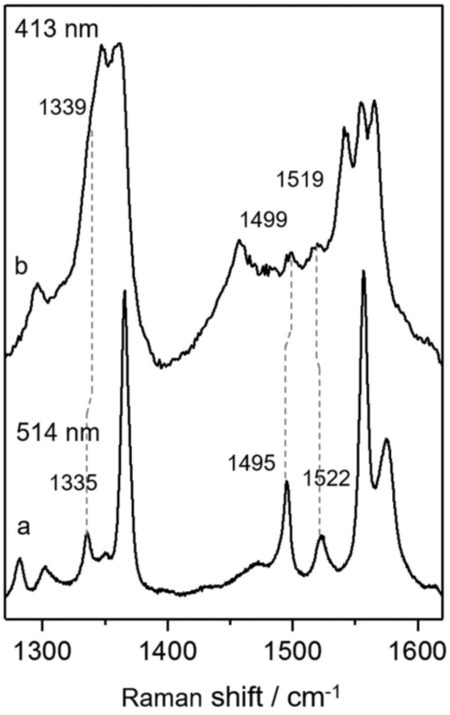


Synthesis of Corrole from via Dipyrromethane (DPM)

3.2 Synthetic Variations and Improvements

Over the past two decades, many variations of the basic Gryko synthesis have been developed to tackle specific challenges or to make corroles with new substitution patterns. Some of these changes focus on making corroles with unsymmetrical meso-substituents (known as A2B- or A3-corroles, where A and B represent different aryl groups). Making these asymmetrical corroles selectively usually requires careful control of the ratios of starting materials and careful purification.

Other modifications address the difficulty of incorporating bulky meso-substituents, which can be hard to add due to steric hindrance. Different acid catalysts have been tested, with some research groups finding better results using specific Brønsted or Lewis acids under certain conditions. The effect of electron-withdrawing or electron-donating groups at the meso-aryl positions has also been systematically studied. It has been shown that these substituents affect the corrole-forming reaction by influencing the reactivity of intermediates and the stability of the final products.



3.3 Metalation of Corrole

One of the first examples of corrole synthesis using substituted pyrrole involved the building of the corrole structure around a cobalt metal ion. In this case the metal acted as a template and was an integral part of the building of the macrocycle. Corrole macrocycles synthesised as outlined in the previous section, without a templating metal ion, are excellent chelators of many metal ions of different sizes and oxidation states. Bilanes can act as excellent chelators, and can be cyclised to form a corrole macrocycle during coordination with a metal carrier under basic conditions . In some cases, the oxocorrole is formed, with an ethereal bridge replacing one of the methine bridges. This method requires that the metal ion is able to catalyse the ring closure. Cobalt is particularly effective in the catalysis of ring formation from pyrrole derivatives and ring closure of bilanes, and thus there are many methods available for metallation of corroles with cobalt. Alternatively, metallation can occur after the macrocycle has been formed During the metallation, the macrocycle is treated with a metal carrier, generally at reflux in a solvent such as methanol or pyridine. Various metal carriers can be used such as metal acetates for cobalt, vanadium, titanium, niobium, manganese, palladium, zinc, nickel and copper metal chlorides for chromium, molybdenum, rhenium, iron, cobalt, rhodium, indium, tin and phosphorus and metallocarbonyls for chromium, molybdenum manganese, iron and rhodium.

After a free-base corrole has been made, the next major step for most applications is inserting a metal ion into the ring. The metalation of corroles follows some general principles, though corroles often behave quite differently from porphyrins. The corrole ring is smaller and more electron-rich than the porphyrin ring, so it can hold metal ions in unusual oxidation states. This ability has become one of the most important and distinguishing features of corrole chemistry.

The basic approach to metalating corroles involves mixing the free-base corrole with an appropriate metal source under conditions that encourage metal insertion into the corrole ring. For many first-row transition metals —

iron, cobalt, nickel, copper, zinc, and manganese — simply heating the corrole with a metal salt (usually the chloride or acetate) in an organic solvent such as dichloromethane or dimethylformamide is enough to achieve metalation. The reaction can often be sped up by adding a base or using reflux conditions.

3.4 First-Row Transition Metal Complexes

The coordination chemistry of corroles with first-row transition metals is the most well-studied area of metallocorrole chemistry. Cobalt corroles have proven to be particularly important and have been extensively characterized. Cobalt(III) corroles show a wide range of coordination behavior — they can bind additional ligands at axial positions, forming complexes with pyridine, carbon monoxide, phosphines, and other ligands. The nature of these axial ligands has a significant influence on the structure and reactivity of the cobalt corroles.

Iron corroles present both interesting challenges and opportunities. The iron center in Fe(III) corroles can exist in different spin states depending on the ligand field around it. The corrole ligand itself often acts as an electron acceptor, taking electron density from the iron center to form corrole radical species. This behaviour has been confirmed through multiple spectroscopic and crystallographic studies and represents one of the most fascinating aspects of transition metal corrole chemistry. Understanding the electronic structures of iron corroles has required advanced techniques such as X-ray absorption spectroscopy.

3.5 Lanthanide and Actinide Corroles

The lanthanides (4f elements) and actinides (5f elements) offer a chance to explore corrole chemistry with larger metal ions whose coordination behavior often differs greatly from that of first-row transition metals. Lanthanide corroles are typically made through a metal-alkyl approach, where the free-base corrole is first deprotonated using an alkyllithium reagent to form a lithio-corrole, which is then treated with a lanthanide chloride or similar salt. This method avoids the high temperatures that might be problematic for thermally sensitive lanthanide complexes.

Actinide corroles represent a newer and still growing area of corrole chemistry. Only a few examples have been thoroughly characterized so far. The high coordination numbers and unique electronic properties of actinide metals make them interesting from a fundamental coordination chemistry perspective, and further work in this area is expected in the coming years.

3.6 5d Transition Metal Corroles

Some of the most distinctive metallocorrole chemistry involves the heavier group 8-11 transition metals, known as 5d elements including rhenium,osmium, iridium, platinum, gold, and mercury. These complexes often display remarkable properties that make them attractive for advanced applications. Inserting 5d metals into corroles can be mechanistically challenging, and special synthetic approaches have had to be developed for these particular metals.

Chapter 4 – Results and Discussion

The synthesis of corroles was successfully carried out using the acid-catalyzed condensation of dipyrromethane with aromatic aldehydes, followed by oxidative cyclization. The corroles were obtained in moderate to good yields and showed the expected spectroscopic characteristics.

UV-Visible spectroscopy revealed strong Soret bands and clear Q bands, confirming that the corrole macrocycle had formed. The structures were further confirmed using NMR, IR, and mass spectrometry. Metalation reactions with selected metal ions were also successfully performed, giving stable metallocorrole complexes.

The synthesized corroles showed excellent electronic and coordination properties because of their trianionic ligand nature. Based on existing literature, these types of compounds have strong potential in catalysis, photodynamic therapy, and energy-related applications.

Overall, the results confirm that corroles can be made efficiently using modern synthetic methods, and their unique structural features make them promising candidates for various advanced scientific and technological applications.

4.1 Meso-Position Functionalization

One of the most useful ways to adjust the properties of corroles for specific purposes is to modify the macrocycle after it has been made. The meso-positions the three aryl-carbon bridges offer several points where further modification can be introduced. One of the most common approaches is using transition-metal-catalyzed cross-coupling reactions on the aryl groups themselves. If the meso-aryl groups carry halogen or triflate substituents, these can act as starting points for Suzuki-Miyaura, Sonogashira, or other palladium-catalyzed coupling reactions.

4.2 Beta-Position Functionalization

The beta-positions of corroles — the carbon atoms on the pyrrole rings — represent another key site for adding functional groups. Unlike porphyrins, where beta-functionalization usually requires organometallic methods, corroles can be modified through electrophilic aromatic substitution. Reactions such as nitration, bromination, and formylation of corroles all proceed through this type of mechanism, though the selectivity and reaction pathways may differ somewhat from similar porphyrin reactions.

4.3 Electrochemistry and Spectroscopy of Corroles

The electrochemical behavior of corroles provides important clues about their electronic structure and how different substituents affect their properties. Most corroles show characteristic electrochemical behavior they can undergo reversible oxidations and reductions within accessible potential ranges. The redox potentials depend strongly on the nature of the metal center, the type of meso-substituents (especially whether they are electron-donating or electron-withdrawing), and the beta-substituents.

4.4 Optical Properties and Spectroscopy

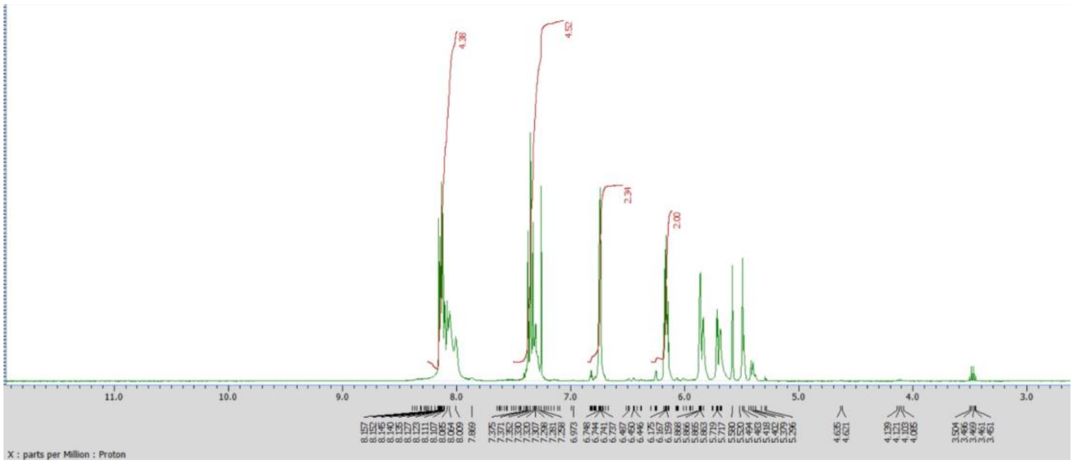
Corroles have distinctive absorption spectra. They show strong Soret bands, typically in the range of 380 to 450 nm depending on the specific corrole, and weaker Q bands at longer wavelengths. The molar extinction coefficients are usually in the range of 10^4 to 10^5 M^-1 cm^-1, which means that corroles are strongly colored and easy to detect in solution. The exact wavelengths of the absorption peaks are sensitive to the corrole's electronic structure and are affected by the presence of substituents and metal ions.

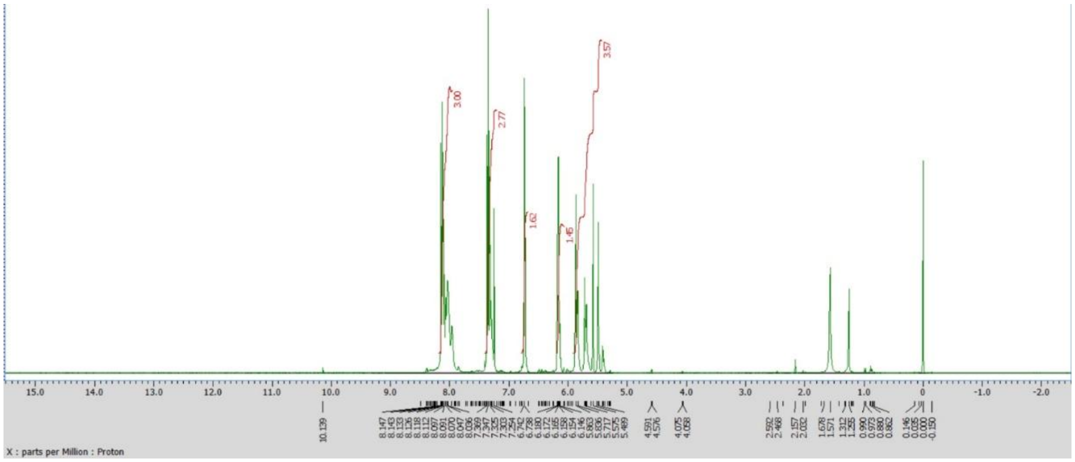
Corroles can also show fluorescence, though the quantum yields are often not very high. However, when heavier metals are incorporated, corroles can exhibit phosphorescence with much longer lifetimes because of the enhanced spin-orbit coupling that these metals provide.

4.5 NMR Spectroscopy and Structural Characterization

1H NMR spectroscopy is routinely used to characterize corroles and confirm their structures. The pyrrolic protons typically appear at relatively downfield positions (around 10-12 ppm) because of the aromatic ring current of the corrole macrocycle. The signals from the meso-aryl protons and the beta-pyrrolic protons can be used to check the purity of samples and to determine the symmetry of the corrole.

For metalated corroles, the 1H NMR spectra are often simpler than those of free-base corroles, because the metal locks the tautomerism that complicates the free-base spectra. In some cases, metalation gives rise to paramagnetic species, which can be studied using paramagnetic NMR techniques or other methods such as electron paramagnetic resonance (EPR) spectroscopy.





4.6 Applications of Corroles in Catalysis

1.Hydrogen Evolution Reaction (HER)

The hydrogen evolution reaction is important for producing clean hydrogen fuel. Metal corroles, especially cobalt corroles, act as efficient electrocatalysts by helping reduce protons to hydrogen gas.

Reaction: $2H^+ + 2e^- \rightarrow H_2$

Advantages:

- High catalytic activity
- Good stability
- Lower cost compared to platinum-based catalysts

2. Oxygen Reduction Reaction (ORR)

The oxygen reduction reaction is a key process in fuel cells and metal-air batteries. Iron and manganese corrole complexes have shown strong catalytic performance in reducing oxygen to water or hydroxide ions.

Reaction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Applications:

- Fuel cells
- Metal-air batteries
- Energy conversion systems

3. Oxygen Evolution Reaction (OER)

Corrole complexes containing cobalt and manganese can catalyze water oxidation to produce oxygen gas.

Reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

This reaction is needed for:

- Water splitting
- Artificial photosynthesis
- Renewable energy technologies

4. Carbon Dioxide Reduction

Corrole-based catalysts can convert carbon dioxide into useful chemicals and fuels such as carbon monoxide, methanol, and ethanol.

Benefits:

- Lowers greenhouse gas levels
- Produces useful fuels
- Supports sustainable energy production

5. Oxidation Reactions

Metallocorroles work well as oxidation catalysts because they can stabilize high-valent metal-oxo species.

Applications:

- Oxidation of alcohols to aldehydes and ketones

- Hydrocarbon oxidation
- Industrial organic synthesis

6. Reduction Reactions

Corrole complexes can catalyze various reduction reactions involving small molecules such as nitrite and nitrate ions.

Applications:

- Environmental cleanup
- Wastewater treatment
- Green chemical processes

6. Small Molecule Activation

Corroles are capable of activating stable molecules, including:

- Oxygen (O2)
- Carbon dioxide (CO2)
- Nitric oxide (NO)
- Hydrogen peroxide (H2O2)

This property makes them useful in both biomimetic and industrial catalysis.

Chapter 5 – Conclusion

Corroles are a uniquely important group of tetrapyrrolic macrocycles whose chemistry is distinct enough from related porphyrins to justify continued, dedicated research. The steady development of corrole synthesis methods over the past two decades has moved these molecules from being laboratory novelties to practical materials used in fields ranging from catalysis to medicine. The trianionic nature of the corrole ligand, combined with its capacity to stabilize unusual metal oxidation states and its special photophysical properties, ensures that it will remain a relevant and attractive subject for further study.

5.1 Current Limitations and Research Gaps

Despite the impressive progress made in corrole chemistry, a number of important challenges still remain. Making unsymmetrical corroles with precisely controlled substitution patterns is still difficult and often requires lengthy chromatographic separations. The metalation chemistry, although widely explored, still presents surprises and challenges — particularly for certain metal ions such as zinc and nickel, or when metals with very specific desired properties are needed.

There is also a lack of long-term stability data for some corrole complexes, especially under physiological conditions or in biological environments. This is a concern for biomedical applications. Additionally, questions about the toxicity and bioavailability of corrole-based therapeutic compounds still need to be answered before they can be considered for clinical use.

5.2 Emerging Directions and Opportunities

Several exciting new directions are opening up for corrole chemistry. For example, incorporating corrole ligands into polymeric materials, nanoparticles, and inorganic frameworks could lead to hybrid materials with entirely new properties. Exploring corrole chemistry with rare earth elements and actinides offers the chance to access coordination chemistry that is fundamentally different from what is possible with first-row transition metals.

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