

**SYNTHESIS AND CHARACTERIZATION OF NON-HEME N-DONOR
TETRADENTATE LIGANDS AND THEIR METAL COMPOUNDS**



DISSERTATION

Submitted in partial fulfilment of
The degree of MSc. (Inorganic Chemistry)

By

NARAYAN UMESH GAWADE

To

School Of Chemical Sciences

Goa University

Goa 403206

April 2020

STATEMENT

I hereby declare that the matter presented in this dissertation entitled, “SYNTHESIS AND CHARACTERIZATION OF NON-HEME N-DONOR TETRADENTATE LIGANDS AND THEIR METAL COMPOUNDS” is based on the result of investigations carried out by me in the School Of Chemical Sciences, under the supervision of **Dr. S. N.**

Dhuri and the same has not been submitted elsewhere for the award of a degree or diploma.

Mr. Narayan Umesh Gawade

CH-18-30, MSc-II,

Inorganic Chemistry

Date:

CERTIFICATE

This is to certify that dissertation entitled “SYNTHESIS AND CHARACTERIZATION OF NON-HEME N-DONOR TETRADENTATE LIGANDS AND THEIR METAL COMPOUNDS” is bonafide work carried out by **Mr. NARAYAN UMESH GAWADE** under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in School Of Chemical Sciences, Goa University.

Dr. S.N. Dhuri
Guiding Teacher,
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Goa University
Date:

CERTIFICATE

This is to certify that dissertation entitled “SYNTHESIS AND CHARACTERIZATION OF NON-HEME N-DONOR TETRADENTATE LIGANDS AND THEIR METAL COMPOUNDS” is bonafide work carried out by **Mr. NARAYAN UMESH GAWADE** under the supervision of Dr. S. N. Dhuri in partial fulfilment of the requirement for the award of the degree of Master of Science in School Of Chemical Sciences, Goa University.

Prof. V. S. Nadkarni,
School Of Chemical Sciences,
Goa University, Goa
Date:

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Last but not the least I thank my parents for their great support, help, and encouragement throughout the work. I thank god for his abundant blessings on my dissertation work.

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ABBREVIATIONS

nm: Nanometer

λ : Wavelength

mL: millilitre

ν : Frequency

$^{\circ}\text{C}$: Degree Celsius

cm: Centimeter

BQCNH₂: N,N'-Bis(quinolin-8-yl)cyclohexane-1,2-diamine

BQENH₂: N,N'-Bis(quinolin-8-yl)ethane-1,2-diamine

SCXRD: Single Crystal X-Ray Diffraction

IR: Infrared

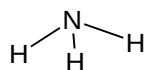
CHAPTER 1

1.1 INTRODUCTION

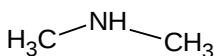
The chemistry of 3-d transition metal compounds containing non-heme N-donor ligands is becoming an area of growing attention among the scientists. Metalloenzymes carry out various enzymatic reactions and a metal active site inevitably plays a vital role. The reason why nature chooses transition elements can be attributed to the fact that these elements exhibit variable coordination number and flexible geometries over conventional sp , sp^2 and sp^3 hybridizations of carbon.^[1] The chemistry of synthetic polydentate ligands with transition metals is extensively researched because of its applications in catalysis and biomimetics wherein synthetic models can guide one towards understanding the working of real systems. In biomimetic chemistry synthetic compounds are made such that, they resemble the metal active sites of the original biomolecules, in this way their structure-function relations can be correlated.^[2] The role of metal ions in biological systems can be understood because of the broad and detailed knowledge that we have of coordination chemistry. Fundamental principles and generalizations about the behavior of complexes are can be applied whether the metal is coordinated by some relatively simple synthetic ligands or by a protein molecule, where the groups are often carboxyl oxygen atoms, thiol sulphur atoms or an amine nitrogen atoms. Since the size and complexity of most the biomolecules is large, it is often advantageous to use smaller and simple models upon which experiments can be performed in a control manner and hypotheses can be tested^[3].

In such systems compounds formed with polydentate ligands offer greater stability than their monodentate analogues owing to their property of chelate formation due to presence of multiple donor atoms in their structure^[4]. The most common coordination number for d-block complexes with polydentate ligand systems is six, five and four. When metal binds to such polydentate

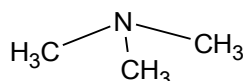
ligands it becomes coordinatively unsaturated and has one or two sites bonded to labile solvent molecules which can serve as the site for catalysis. Bidentate N-donor ligands such as ethylenediamine, 2,2'-bipyridine etc or monodentate N-donor ligands such as imidazole, pyridine etc can replace these labile solvent molecules, thus saturating the metal sites and allowing to study their properties.



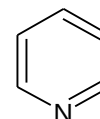
Ammonia



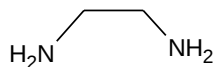
Dimethylamine



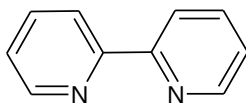
Trimethylamine



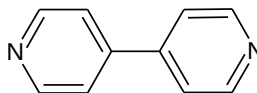
Pyridine



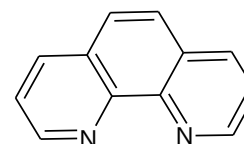
Ethylenediamine



2,2'-bipyridine



4,4'-bipyridine

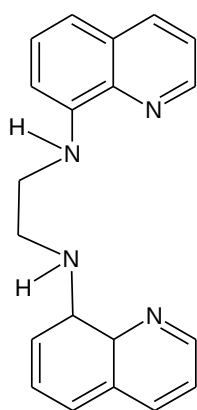


1,10-phenanthroline

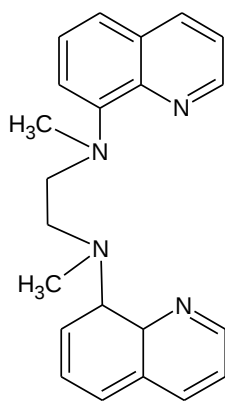
Heme is a coordination complex consisting of an iron ion coordinated to a porphyrin acting as a tetradentate ligand and to one or two axial ligands. Metalloproteins which have hemes as their prosthetic group are known as hemoproteins.^[5] Non-heme ligands are basically any N-donor teradentate ligands which lacks the porphyrine type of system in their structure. Proteins containing nonheme irons are widespread in nature and performs functions such as activating dioxygen for oxidation of various substrates.^[6]

Many tetradentate bis-(quinolyl)-diamine and bis-(quinolylmethyl)-diamine ligands were prepared by Nelson and co-workers. First step of the procedure was the preparation of non-

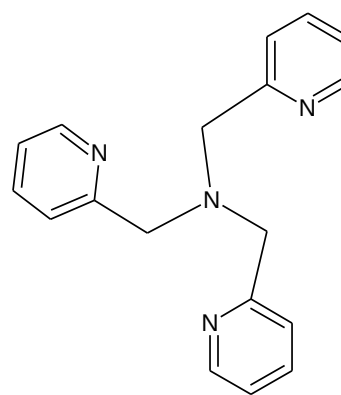
methylated secondary amines using a modified Bucherer reaction followed by deprotonation of the secondary amines using two equivalents of n-butyl lithium giving dianilide salts, which when reacted with methyl iodide gave the desired ligands.^[7] In the initial days BQCNMe₂ was synthesized by addition of n-butyl lithium in hexane to BQENH₂ in THF and stirring at -78 C followed by addition of methyl iodide. But such conditions are difficult to attain and maintain.^[8] Therefore this procedure was then modified wherein, BQCNH₂ was reacted in THF with NaBH₃CN and formaldehyde and stirred overnight at room temperature. Complexation was done using nickel as a central metal ion and it was further reacted with auxillary ligands such as bipyridine with replacement of labile CH₃CN molecules.



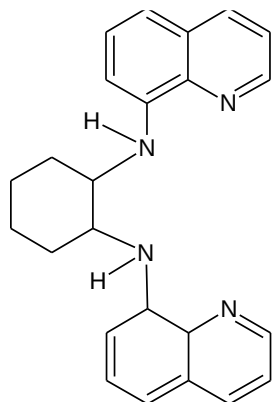
BQENH₂



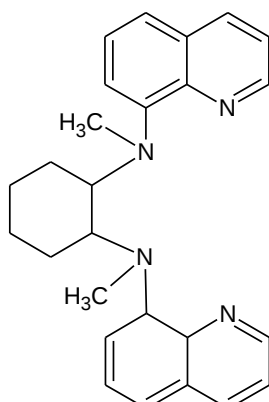
BQCNMe₂



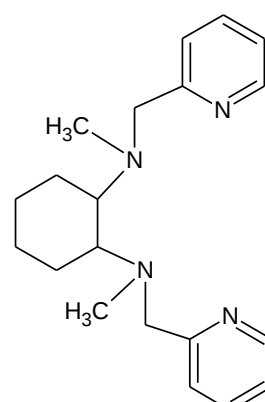
TPA



BQCNH₂



BQENMe₂



MCP

APPLICATIONS

Beside the biomimetic applications of such non-heme ligand coordinated metal compounds, in recent years Heme and non-heme metal-oxo and metal-hydroxo species have drawn the interest of scientific community as these species have been proposed as key intermediates in a variety of biological processes such as photosystem-II, peroxidase, catalases, naphthalene dioxygenase. These species are also capable of oxygenating a large variety of organic and inorganic substrates. Over the last decade, stress is given on the high valent manganese and iron species due to their potent catalytic abilities and their striking resemblance to enzymatic reactivities. As iron and manganese are found in the active sites of many metalloenzymes, their compounds are largely investigated.^[9] Since metalloenzymes catalyze the oxygenation reactions with high regio- and stereoselectivity under mild conditions, biomimetic oxygenation reactions using their model compounds have attracted much attention in the communities of bioinorganic and oxidation chemistry. For example, it has been demonstrated that synthetic iron complexes of heme and non-heme ligands are capable of mimicking the chemistry of cytochrome P450 (CYP 450) and non-heme iron enzymes, respectively, and that the oxygenation reactions by the model compounds proceed via a mechanism involving metal-based oxidants. Similarly, manganese porphyrins have been extensively investigated as chemical models of CYP 450 in various oxygenation reactions. Manganese complexes bearing non-heme ligands, such as salen- and tacn-derived ligands, have shown promise as versatile catalysts in olefin epoxidation and alkane hydroxylation. Very recently, Stack and co-workers⁸ reported a highly efficient epoxidation reaction using peracetic acid as the terminal oxidant, in which terminal olefins are epoxidized to the corresponding epoxides in the presence of the non-heme Mn(II) catalysts (e.g., Mn(BPMEN)(CF₃SO₃)₂ and Mn(BPMCN)(CF₃SO₃)₂). We now report a mononuclear non-

heme manganese complex, $\text{Mn}(\text{BQEN})(\text{CF}_3\text{SO}_3)_2$ that shows a high catalytic activity and stereo- and regioselectivity in the oxidation of olefins, alcohols and alkanes under mild conditions.^[11]

Another developing and potent application of such synthetic compounds is water oxidation. Artificial photosynthesis is a promising strategy to produce renewable fuels to meet the ever-increasing demand on sustainable energy systems, and to solve increasingly serious climate change caused by the use of conventional fossil fuels such as coal and petroleum. Water oxidation is essential because it is the only ideal way to supply electrons and protons to produce chemical fuels. To overcome the high reaction barrier of oxidizing water, efficient catalysts are in high demand. Molecular catalysts have the advantage of being more suitable for targeted, molecular-level design and guided mechanistic understandings. Transition-metal complexes, for example, ruthenium, Iridium, manganese, and cobalt, have been widely developed as water oxidation catalysts (WOCs). However rich redox chemistry is necessary for the catalysis of water oxidation, which involves the transfer of four electrons and four protons. These are consistent with nature's choice, manganese, for building WOCs. Studies on developing iron-based MWOCs began in 2010, which was about 30 years later than the initial development of ruthenium-based MWOCs. Catalysts based on other earth-abundant metals, such as manganese, cobalt, and nickel, have also been reported for water oxidation, but few of them can perform efficient catalysis of water oxidation with CAN as the oxidant.^[10]

Several coordination compounds containing transition metals like copper, iron, manganese, nickel are known to possess antimicrobial activity owing to their ability to penetrate into microbes and inactivate their enzymes or by generating hydrogen peroxide, thus killing the microorganisms. However, for a compound to show antimicrobial property it should have certain

characteristics such as, high thermodynamic stability to deliver metal to the active site, metal-ligand binding should be hydrolytically stable along with these kinetics and molecular weights of the compound also plays major role.

CHARACTERISATION TECHNIQUES

Infrared spectroscopy (IR)

IR spectroscopy is most widely used characterisation tool. IR region of the electromagnetic spectrum is divided into Near IR, Middle IR and Far IR. Among these most important is Mid IR region which fall in the region $4000\text{--}400\text{cm}^{-1}$. Absorption of Infra- red radiation cause vibrational energy changes in the molecule. The main type are stretching vibration and bending vibrations. The energy required for stretching vibration is greater compared to bending vibration and is therefore bands which arise above 1500cm^{-1} are due to stretching vibrations. If N is the number of atoms in molecule then $3N-5$ modes of vibrations are seen in case if the molecule is linear and $3N-6$ modes of vibration if non-linear molecule. However not all molecules absorb in the IR region. Only molecules which undergo change in dipole moment on absorption of IR regions are said to be IR active.^[13]

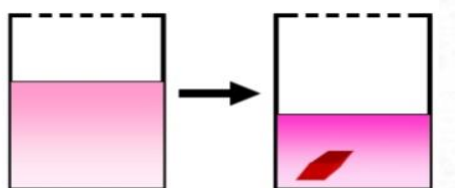
Single Crystal X-Ray Diffraction (SCXRD)

Single crystal X-Ray diffraction technique is immensely important to an inorganic chemist for structural determination. Its basic principle revolves around the Bragg's equation that is, $2d\sin\theta = n\lambda$. Interference between the wave occurs as a result of object in their path, when X-rays are scattered elastically by the electrons in the atoms. Analysis of the diffraction data obtained from single crystal is the most important method to get the structure of solids. But a crystal is only as good as the crystal used for data collection, therefore it is worthwhile to invest time on growing quality crystals. Theoretically crystallization starts when concentration of a compound in a solvent is higher than the solubility product of the compound. Crystallization is preceded by

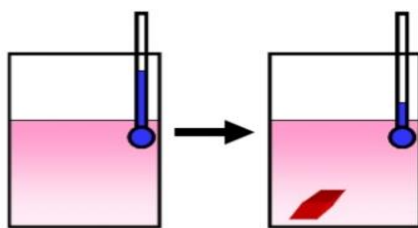
nucleation which either happens spontaneously or can be induced by vibration or particles. Size of the crystals suitable for diffraction is relatively large, generally 0.1-0.3mm in each dimension is a good number. It is important to have less nucleation sites and crystals that grow slower tend to become larger in size.

Crystallization Techniques

Slow Evaporation- It is one of the simplest method to grow crystals. Nearly saturated solution of compound is made in suitable solvent and few millilitres of it is placed in container and covered in a way that will facilitate slow evaporation. It is then kept where it will not be disturbed till crystals occurs.

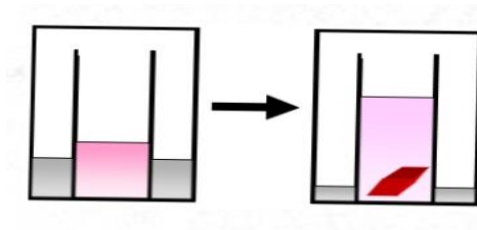


Slow Cooling- Nearly saturated solution of the compound is prepared at or close to the boiling point of the solvent. Container containing this solution is placed in to a water bath at around same temperature and allowed to cool slowly. Variation of this method is to place the container in a cold place leading towards the growth of crystals.



Vapour diffusion- This method requires a binary solvent system. Solvents should be such that they mix well with each other. Compound has to be soluble in the solvent with higher boiling point and insoluble in the other solvent called as the precipitant. Solution of compound is

prepared in small open container and placed in larger container that contains the precipitant and outer vessel is sealed well. Over time volatile precipitant diffuses in to the solvent leading to saturation and crystallization. One can even regulate the diffusion rate by varying the temperature as per the requirement.



Liquid-Liquid diffusion – This method also requires binary solvent system but boiling points does not matter much here instead specific densities of the two solvents need to be different. Concentrated solution of the compound in solvent is prepared. Solvent with higher specific density is kept in narrow receptacle and carefully layered with other solvent. Over the time two solvents mix and crystals are thrown out of the solution. A variation of this method is to freeze the lower layer before adding the second solvent. This makes it easier to get a clean separation between the two layers.



Convection – Somewhat exotic convection can be a good method to grow high quality crystals. In this method a temperature gradient is created in crystallization vessel by either cooling or heating part of it leading to a slow and steady flow within the liquid phase. The basic idea is that,

more substance dissolves in the hotter part of the container, travels to the colder end where it gets crystallized. Crystals move with the stream to the hotter end where they totally or partially dissolve and the ones dissolving partially grows larger on their next trip.^[14] Several hundred rounds can make a very nice quality crystal. The velocity in vessel is proportional to the heat gradient, which should not be very large as too rapid convection will not give enough time for nucleation.

UV-VISIBLE SPECTROSCOPY

It is also known as absorption spectroscopy which involves ultraviolet and visible radiations. When a sample is exposed to light energy that matches the energy difference between possible electronic transitions within the molecule, a fraction of light energy would be absorbed by it and the electrons would be promoted to higher energy state from ground state. It obeys Beer-Lambert's law which states that, when a beam of a monochromatic light is passed through a solution of an absorbing medium, the amount of light absorbed is directly proportional to the concentration and path length of the absorbing medium. This is the basic principle of UV-Visible spectroscopy and is exploited to perform various qualitative and quantitative analysis, along with the detection of impurities and monitoring the rates of certain reactions.

CYCLIC VOLTAMETRY

Cyclic voltametry is a specific type of potentiodynamic electrochemical measurement. In a cyclic voltametry experiment, the working electrode potential is increased linearly with time. After the set potential is reached, the working electrode's potential is increased in the opposite direction to return to the initial potential. Depending upon the requirement these cycles of ramps

can be repeated. Finally the current at the working electrode is plotted against the applied voltage to give the voltamogram. This technique has become an important and widely used in many areas of chemistry to study redox processes, to determine the stability of reaction products, the presence of intermediates and the reversibility of a reaction. Cyclic voltametry can also be used to determine the electron stoichiometry of a system and the formal reduction potential of an analyte. In addition, because the concentration is proportional to the current, the concentration of the unknown solution can be determined by generating a calibration curve of a current vs. concentration.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 Materials and methods

Chemicals used: 8-hydroxyquinoline, trans-diaminocyclohexane, sodium hydroxide, sodium metabisulphite, ethanol, methanol, formaldehyde, sodium cyanoborohydride, manganese perchlorate hexahydrate, acetonitrile, diethyl ether, chloroform, cyclohexane, acetone. All chemicals used in this work were purchased from chemical sources without further purification. Ligand like BQCN was prepared according to earlier reported procedure. The UV-Visible spectra was recorded in CH₃CN in the range of 200-1000nm using Aligent diode array 8453 UV-Visible spectrophotometer. IR spectra were recorded on IR Prestige-21 (Shimadzu) spectrometer, the compound was made into fine powder and using KBr matrix and spectra was recorded in the region 4000-400 cm⁻¹. Single crystal data was collected on Bruker D8 Quest Eco with graphite monochromated Mo K α radiation ($\lambda=0.71073\text{\AA}$) at 298 K.

2.2 Synthesis of N,N'-Bis(quinolin-8-yl)cyclohexane-1,2-diamine (BQCN-H₂)

A mixture of 8-hydroxyquinoline (35g, 241mmol) with trans-diaminocyclohexane (14.5mL, 120.6 mmol) and sodium metabisulphite (45.82g, 241mmol) in 700mL of water was refluxed at 110 C in an oil bath for about 7 days. Then the solution was cooled to room temperature and sodium hydroxide solution was added to it drop wise till the solution became strongly alkaline (pH>12). The resultant mixture was extracted twice with dichloromethane (50 mL) and as reduced to dryness, using rota vapour. The solid thus obtained was triturated with warm ethanol, which gave the pale yellow colored crystalline solid.

Molecular formula: C₂₄H₂₆N₄

Percentage yield obtained: 32%

2.3 Synthesis of N,N'-Bis(quinolin-8-yl)ethane-1,2-diamine (BQEN-H₂)

A mixture of 8-hydroxyquinoline (35g, 241mmol) with ethylene-1,2-diamine (8.0mL, 120.6 mmol) and sodium metabisulphite (45.82g, 241mmol) in 700mL of water was refluxed at 110 C in an oil bath for about 7 days. Then the solution was cooled to room temperature and sodium hydroxide solution was added to it drop wise till the solution became strongly alkaline (pH>12). The resultant mixture was extracted twice with dichloromethane (50 mL) and as reduced to dryness, using rota vapour. The solid thus obtained was triturated with warm ethanol, which gave the pale yellow colored crystalline solid.

Molecular formula: C₂₀H₂₀N₄

Percentage yield obtained: 43% C₂₈H₃₀Cl₂CuN₆O₈

2.4 Synthesis of [Mn(BQCN-H₂)(H₂O)(CH₃CN)](ClO₄)₂

The solution containing ligand (BQCN-H₂) (1.02g, 2.76mmol) was dissolved in minimum amount of DCM and was slowly added to the round bottom flask containing Mn(ClO₄)₂.6H₂O (1.0g, 2.76mmol) dissolved in acetonitrile at room temperature. The reaction mixture was stirred for about 24 hours. Resultant mixture was added to a beaker containing distilled diethyl ether in a drop wise manner with continuous stirring and light yellow solid was isolated. The solid obtained was washed and dried with diethyl ether.

Molecular formula: C₂₆H₂₉Cl₂MnN₅O₉

Percentage yield obtained: 85.95%

2.5 Synthesis of $[\text{Mn}(\text{BQEN-H}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

The solution containing ligand (BQEN-H₂) (1.01g, 2.76mmol) was dissolved in minimum amount of DCM and was slowly added to the round bottom flask containing Mn(ClO₄)₂.6H₂O (1.0 g, 2.76mmol) dissolved in acetonitrile at room temperature. The reaction mixture was stirred for about 24 hours. Resultant mixture was added to a beaker containing distilled diethyl ether in a drop wise manner with continuous stirring and light yellow solid was isolated. The solid obtained was washed and dried with diethyl ether.

Molecular formula: C₂₀H₂₂Cl₂MnN₄O₁₀

Percentage yield obtained: 87.25%

2.6 Synthesis of $[\text{Cu}(\text{BQCN-H}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

The solution containing ligand (BQCN-H₂) (0.99g, 2.69mmol) was dissolved in minimum amount of DCM and was slowly added to the round bottom flask containing Cu(ClO₄)₂.6H₂O (1.0 g, 2.69mmol) dissolved in acetonitrile at room temperature. The reaction mixture was stirred for about 24 hours. Resultant mixture was added to a beaker containing distilled diethyl ether in a drop wise manner with continuous stirring and light yellow solid was isolated. The solid obtained was washed and dried with diethyl ether.

Molecular formula: C₂₈H₃₀Cl₂CuN₆O₈

Percentage yield obtained: 92.34%

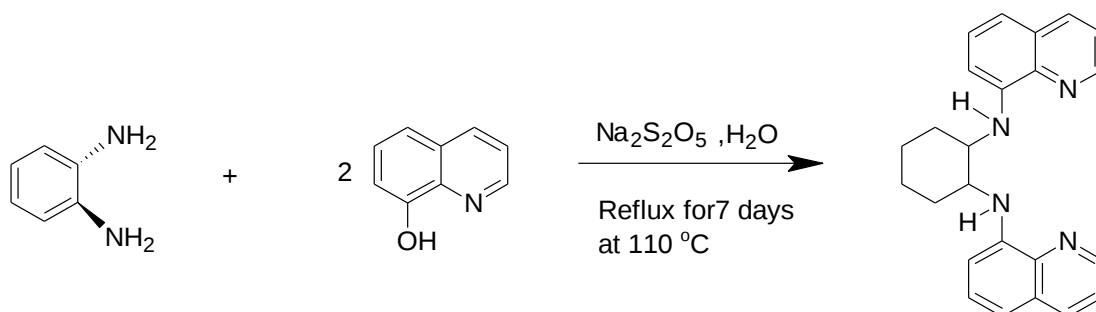
2.7 Synthesis of $[\text{Cu}(\text{BQEN-H}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

The solution containing ligand (BQEN-H₂) (0.845g, 2.69mmol) was dissolved in minimum amount of DCM and was slowly added to the round bottom flask containing Cu(ClO₄)₂.6H₂O (1.0 g, 2.69mmol) dissolved in acetonitrile at room temperature. The reaction mixture was stirred for about 24 hours. Resultant mixture was added to a beaker containing distilled diethyl ether in a drop wise manner with continuous stirring and light yellow solid was isolated. The solid obtained was washed and dried with diethyl ether.

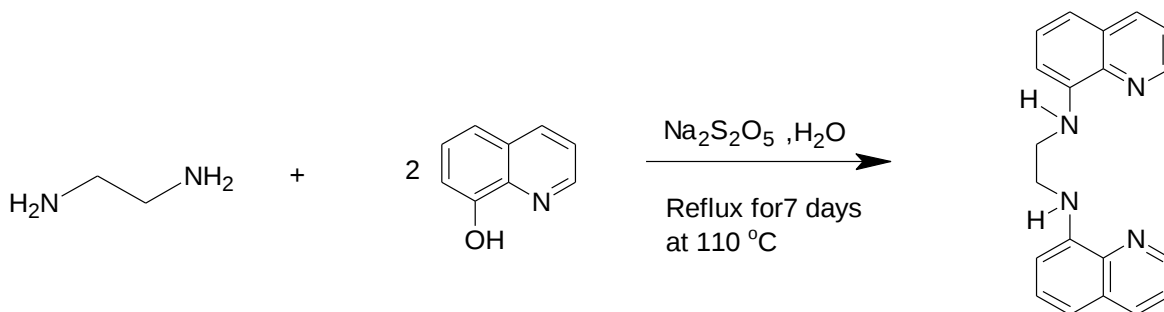
Molecular formula: C₂₄H₂₄Cl₂CuN₆O₈

Percentage yield obtained: 90.41%

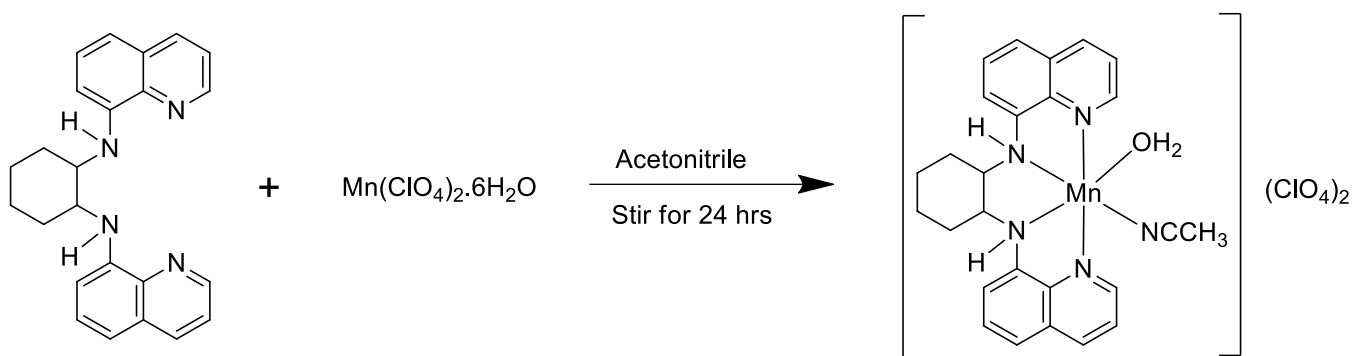
2.8 Scheme for Synthesis of N,N'-Bis(quinolin-8-yl)cyclohexane-1,2-diamine (BQCN-H₂)



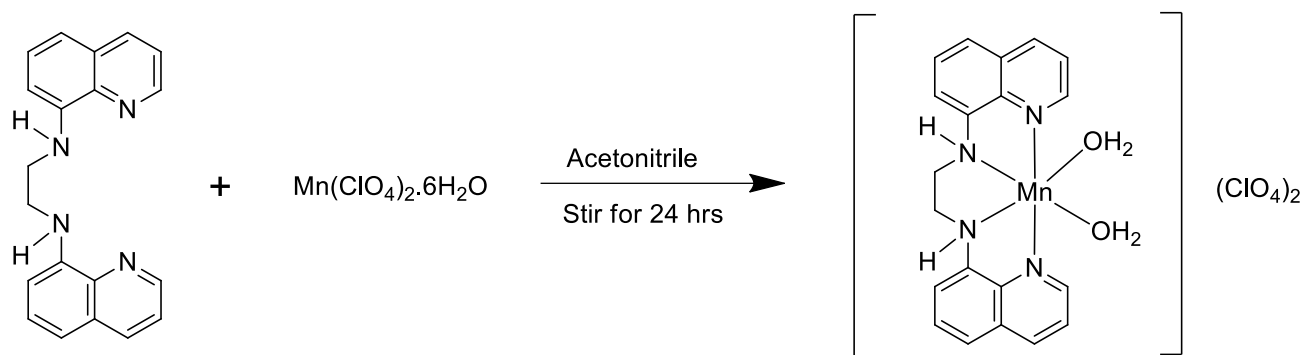
2.9 Scheme for Synthesis of N,N'-Bis(quinolin-8-yl)ethane-1,2-diamine (BQEN-H₂)



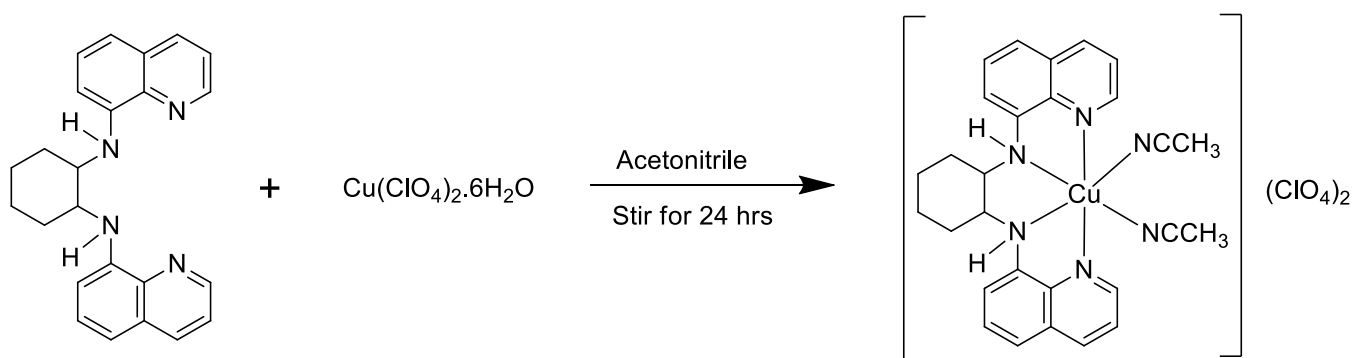
3.0 Synthesis of $[\text{Mn}(\text{BQCN-H}_2)(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$



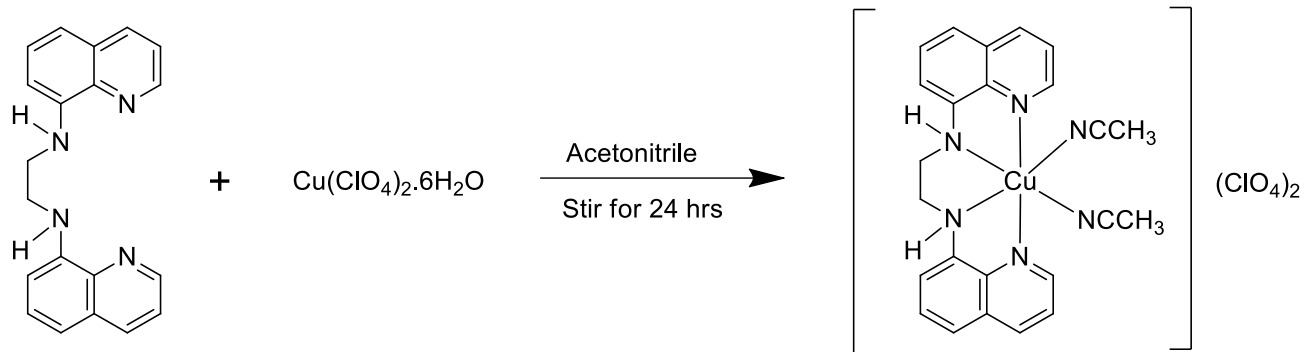
3.1 Synthesis of $[\text{Mn}(\text{BQEN-H}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$



3.2 Scheme for Synthesis of $[\text{Cu}(\text{BQCN-H}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$



3.3 Scheme for Synthesis of [Cu(BQEN-H₂)(H₂O)₂](ClO₄)₂



CHAPTER 3

3.1 INFARED SPECRTAL STUDIES

Ligand BQCN-H₂ and its complexes

The Infrared spectrum of the free ligand BQCNH₂ shows a strong peak at 3299cm⁻¹, 1550cm⁻¹ and 1121cm⁻¹ which corresponds to the stretching frequencies of secondary N-H, bending frequencies of N-H and C-N stretching frequencies respectively. The aromatic -C=N functionality is suggested by the presence of a band at 1487cm⁻¹. Strong bands at 2934cm⁻¹ and overtone pattern between 1600-2000cm⁻¹ are seen, which are characteristic peaks of aromatic C-H stretching and bending respectively. The primary amine shows two bands in he region between 3300-3500cm⁻¹ which is absent in the spectrum confirming that the reactant trans-diaminocyclohexane is totally consumed in the reaction. Absence of bands in the region between 3400-3600cm⁻¹ indicates that no hydroxyl group is present in the product.

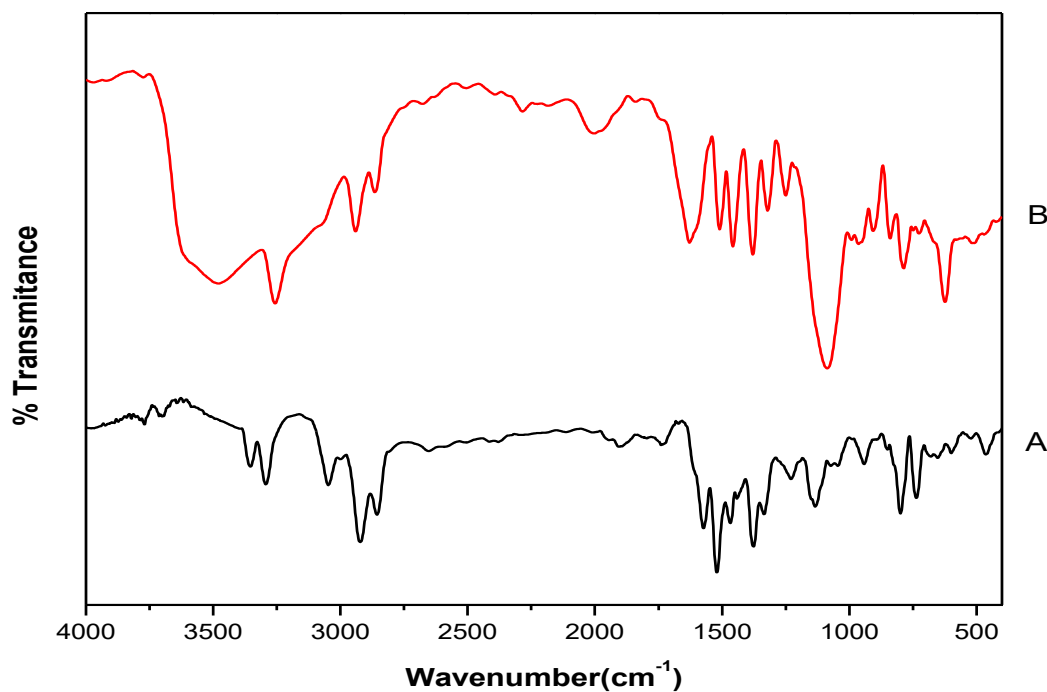


Figure 1: Overlaid spectra of A- (BQCNH₂) and B- [Mn(BQCN-H₂)(H₂O)(CH₃CN)](ClO₄)₂

The IR spectrum of the metal complex differs from that of ligand. The changes in the bands are given in following table.

Compound	$\nu_{\text{O-H}}$ (cm^{-1})	$\nu_{\text{N-H}}$ (cm^{-1})	$\nu_{\text{C=N}}$ (cm^{-1})
(BQCNH ₂)	-	3299	1551
[Mn(BQCNH ₂)(H ₂ O)(CH ₃ CN)](ClO ₄) ₂	3478	3252	1625

2. Ligand BQEN-H₂ and its complexes

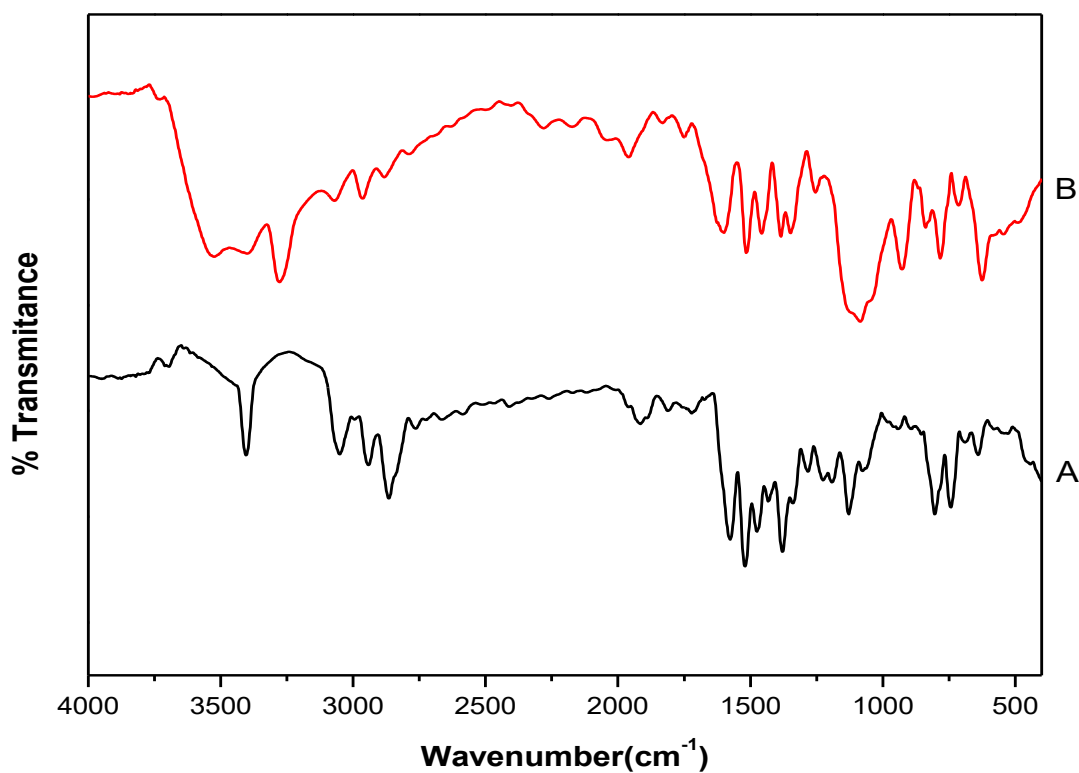


Figure 2: Overlaid spectra of A- (BQENH₂) and B- [Mn(BQCNH₂)(H₂O)₂](ClO₄)₂

Compound	$\nu_{\text{O-H}}$ (cm^{-1})	$\nu_{\text{N-H}}$ (cm^{-1})	$\nu_{\text{C=N}}$ (cm^{-1})
(BQENH ₂)	-	3402	1522
[Mn(BQCNH ₂)(H ₂ O) ₂](ClO ₄) ₂	3524	3281	1498

The Infrared spectra of above compounds exhibit an intense peak in the region 3200-3500 cm^{-1} corresponding to the N-H stretching vibration of the ligand BQENH₂. Based on the comparison of the N-H vibration of the free ligand and with the signals of the compound, it is observed that the N-H bands are shifted to lower wavenumbers, which can be attributed to the bonding of ligand to the metal. The vibrations corresponding to the perchlorate anions are seen at 1090 and 622 cm^{-1} .

REFERENCES

1. Sarvesh S. Harmalkar, Dattaprasad D. Narulkar, Raymond J. Butcher, Mahesh S. Deshmukh, Anant Kumar Srivastava, Mariappan Mariappan, Prem Lama, Sunder N. Dhuri; *Inorganica Chimica Acta*. **2019**, DOI: 10.1016/j.ica.2018.10.069
2. D.D. Narulkar, C.C. Naik, S.N. Dhuri; *Inorganica Chimica Acta*. **2015**, 427, 248-258
3. Basic Inorganic Chemistry, 3rd edition, F. Albert Cotton, Geoffrey Wilkinson, Paul Gaus; 730
4. E. Ramchandran, D.S. Raja, J.L. Mike, T.R. Wagner, M. Zeller, K. Natarajan; *RSC Adv.* **2012**, 2, 8515
5. <https://en.wikipedia.org/wiki/heme>
6. Yukiko Mishina, Chuan He; *Elsevier*. **2004**, DOI: 10.1016/j.cbpa.4004.02.002
7. J. England, G.J.P. Britovsek, N. Rabadl, A.J.P. White; *Inorg. Chem.* **2007**, 46, 3752-3767
8. Tanase, S. Bouwman, E. Adv; *Inorg. Chem.* **2006**, 85, 29-75

9. Bhawana Pandey, Azaj Ansari, Nidhi Vyas, Gopalan Rajaraman; *J. Chem. Sci.* **2014**, 02, 343-352
10. Tianqi Liu, Biaobiao Zhang, LichengSun; *ACES*. **2019**, DOI :10.1002/asia.201801253
11. Kasi Nehru, Soo Jeong Kim, In Young Kim, Mi Sook Seo, Youngmee Kim, Sung-Jin Kim, Jinheung Kim and Wonwoo Nam; *Chem. Commun.* **2007** DOI: 10.1039/b708976g
12. Metal Complexes As Antimicrobial Agents; Marcela Rizzotto, National University of Rosario
13. Infrared and Raman spectra of Inorganic and Coordination compounds Part B, by Kazuo Nakamoto, A John Wiley & son, Inc., Publication, New Jersey. **2009**, 1-408.
14. <http://web.mit.edu/x-ray/crystallize.html>
15. Sarvesh S.Harmalkar, Raymond J.Butcherb, Vivekanand V.Gobre, Sanket K.Gaonkar, Luann R. D'Souza, Muniyandi Sankaralingamd, Irene Furtado, Sunder N.Dhuri; *Inorganica Chimica Acta*. **2019**, DOI: 10.1016/j.ica.2019.119020

CONCLUSION

- N₄ tetradentate ligands and their complexes with Manganese and Copper were prepared and characterised.
- IR analysis of ligands indicated that the expected ligands were formed with no remaining reactant.
- Shifts in the IR bands of the compounds indicated that the ligand was coordinated to the metal.