Transition Metal Complexes with Heterocyclic Ligands in Catalysis

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by

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Transition Metal Complexes with Heterocyclic Ligands in Catalysis

A THESIS

Submitted in partial fulfillment of the
requirements for the award of the degree
of
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by
UJJWAL VERMA

DISCIPLINE OF CHEMISTRY
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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**Transition Metal Complexes with Heterocyclic Ligands in Catalysis"** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2020 to June 2021 under the supervision of Prof. Suman Mukhopadhyay, Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

ujjwal

Ujjwal Verma

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

01/06/2021

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Dr. Sampak Samanta

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DEVOTED TO….

My loved ones

ABSTRACT

In this present work, focus has been given to the synthesis and detailed study of "**Transition metal complexes with heterocyclic ligands in catalysis".** Importance of catalytic activity of metal azolate complexes in oxidation of organic compound has been explored. Here in, the study is intended to explore complex formation of Cu(II) to form metal azolate framework. There are various types of metal azolate transition metal complexes with framework structures which have been studied. However, reports on mixed ligand metal azolate framework are rare so far. The main objective of the current work is to study the catalytic behavior of Metal Azolate Frameworks (MAFs) for oxidation of various organic compounds. In this present work, the concept of formation of mixed ligand metal azolate complexes with Cu(II) metal using [2 + 3] cycloaddition reaction has been explored. Further, this present work also comprises future plans where it is indicated that the synthesized complexes can be utilized as catalysts for oxidation of organic compounds and the mechanistic pathway can be explored in details. This tetrazole-imidazole complex can be also explored for sensing purpose of different chemical entities.

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LIST OF SCHEMES

NOMENCLATURE

α	Alpha
β	Beta
γ	Gamma
δ	Chemical shift (N.M.R.)
θ	Angle
Å	Angstrom
mg	Milligram
mL	Milli Litre
µL	Micro Litre
υ	Frequency
cm	Centimeter
nm	Nanometer
M	Molar
nM	Milli Molar
mol	Moles
mmol	Milli Mole
%	Percentage
ºC	Degree Centigrade
s	Seconds

ACRONYMS

C	Carbon
O	Oxygen
N	Nitrogen
H	Hydrogen
Cu	Copper
Ar	Argon
Co	Cobalt
MeOH	Methanol
DMSO	Dimethylsulphoxide
DMF	Dimethylformamide
MAF	Metal azolate framework
H_2O	Water
NMR	Nuclear Magnetic Resonance
FT-IR	Fourier Transform-Infrared
ESI-MS	Electrospray Ionization-Mass Spectrometry
UV	Ultraviolet
Single crystal XRD	Single crystal X-ray diffraction

SECTION 1

INTRODUCTION

1.1 General introduction

Alfred Werner launched coordination chemistry in 1893. Since then, it has become a well explored area with many prospective applications in different fields.[1] Catalysis is arguably the most vital application of coordination compounds. Transition metal atoms or ions with vacant d orbitals have geometrical and energetic features appropriate for bonding with different ligands. Transition metals mainly form coordination covalent bonds due to Lewis acid-base interactions. A Lewis base donor and Lewis acid accepter contribute in formation of coordination covalent bond. The Lewis acid in the coordination complexes is the central metal ion, mostly transition metal or inner transition ions. The Lewis base donors are ligands. The structure of metal complexes can be diverse depending upon the nature of the ligands and the characteristics of the metal ion. This kind of flexibility is the basis for the catalytic activity of certain transition metal complexes to a prodigious extent.

1.2 Schiff bases

Schiff bases were introduced by Hugo Schiff in 1864.[2] Wherein he carried out the condensation between an amine & an aldehyde, which resulted in a Schiff base. Schiff bases are considered as privileged ligands.[3] Schiff base ligands can coordinate metals through imine nitrogen & another group, generally connected to the aldehyde. Schiff base ligands can coordinate numerous distinct metals and stabilize them in several oxidation states, allowing them for huge variability of beneficial catalytic transformations. They are one of the utmost extensively used ligands because of their ease of formation and extraordinary flexibility. Consequently, they have exhibited an imperative part in the advance of coordination chemistry. They form stable complexes with transition metals.[4]

1.3 Azoles

Azoles are classified as five-membered heterocyclic compounds. It contains at least one nitrogen and one other non-carbon atom as part of the ring (**Figure 1**) and shows the ability to form metal azolate complexes.

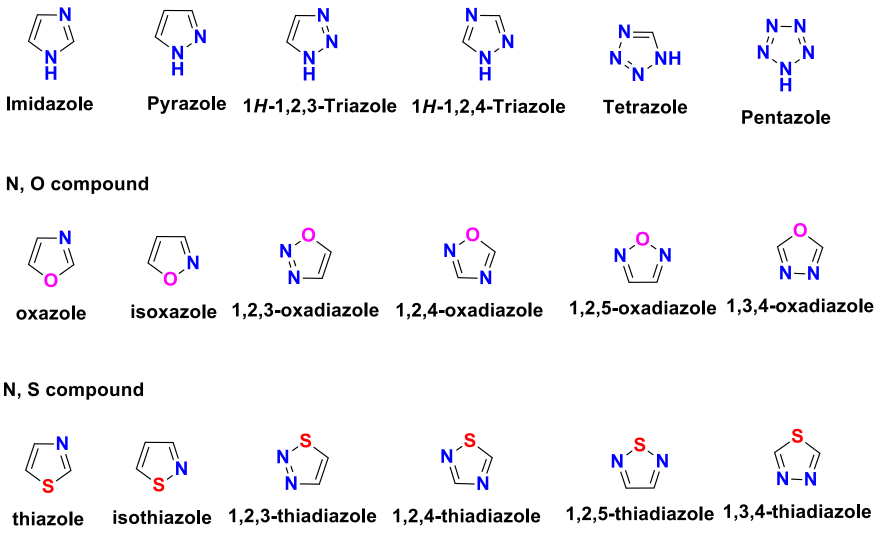


Figure 1. Different types of azolates.

Discrete kind of azolates have several familiar characteristics. Nevertheless, their coordination activities can be distinct according to their positions and number of N-donors. Azoles are generally acknowledged as bases as imidazole (Him), 1,2,4-triazole (Htz), and tetrazole (Httz) can be deprotonated to form the consistent azolate anions **(Figure 2).** As the number of nitrogen atom will increase, azolate ring become more acidic or less basic. For instance, imidazole has a higher basicity as compare to pyridine, due to delocalized 6 electrons on five membered ring, which results higher electron density.[5]

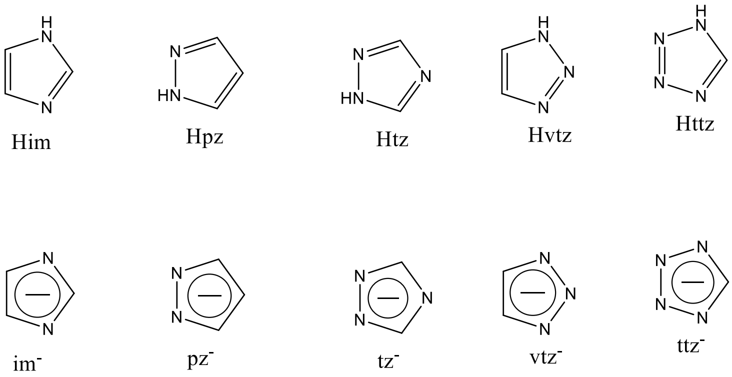


Figure 2. Representation of Structures of Azoles and their Consistent Azolate anions.

Azolate ligands have the benefit of robust and directional coordination ability. Azole complexes with transition metals show unique catalytic activity for a variety of reactions.[6, 7] As compared to MOFs, Metal azolate frameworks (MAFs) certainly signify an inimitable and fascinating class of coordination polymers. In comparison with another metal ligand structures, several metal azolate frameworks have extremely probable coordination geometries and connectivities. It has high thermal and chemical stability, which is extraordinary. Stability is an acutely imperative problem for practical applications.[8]

1.4 Tetrazole and imidazole

Tetrazoles are classified as a synthetic organic 5-membered heterocyclic compound which contains four nitrogen and one carbon atoms. The name **tetrazole** also denotes to the parental compound with formula CH_2 N_4. Tetrazole was first synthesized by Bladin in 1885.[9] where Bladin and his colleagues recognized the very first way to synthesize tetrazoles, the furthermost extensively exploited process of synthesizing is [2+3] cycloaddition of an azide to a nitrile. Tetrazole shows 9 discrete kinds of coordination mode with metal ion in building of metal azolate framework.[10]

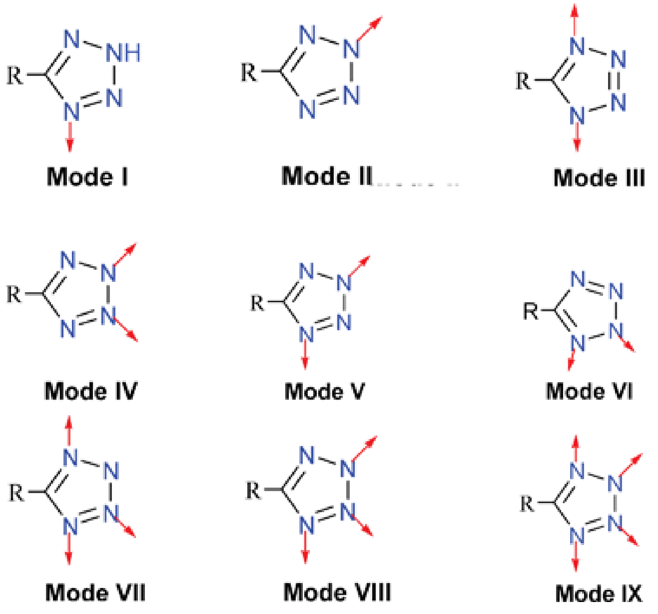


Figure 3. Distinct coordination mode of tetrazole.

The tetrazoles have vast range of applications in various fields.[11] Tetrazoles are an imperative part of heterocyclic ligands with high nitrogen content with substantial biological properties.[12]

Imidazole: Imidazole is a five membered heterocyclic aromatic ring containing two nitrogen and three carbon atoms. The name imidazole also denotes to the parental compound with formula $C_3H_4N_2$.

Imidazole was first synthesized by Heinrich Debus in 1858.[13] A large amount of attention has been given to the synthesis of imidazole and its derivatives, due to their bonding nature with transition metal ions. The ligand has very important and close connection with biological classification of a more intricate nature involving histidine residue. Imidazole forms approximately the maximum stable complexes of all the heterocyclic-N ligands.[14-18]

Metal azolate complexes with transition metal ion are used as building block of many compounds for instance in coordination chemistry for catalysis,[19] industry,[20] agriculture,[21] medicinal chemistry,[22] materials science, organic synthesis,[23] gas generating composition,[24] etc. Due to its unique designable structure MAF can be used in sensing,[25] molecular adsorption, [26] separation.[27]

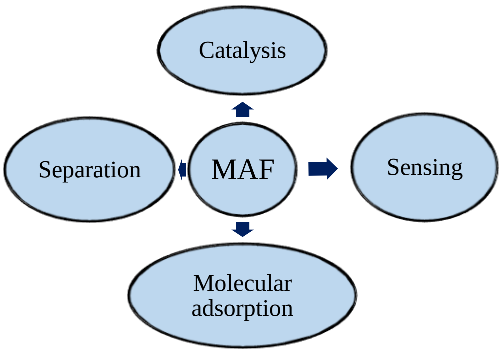


Figure 4. Applications of Metal azolate framework

1.5 Cu(II) Complexes

Copper is a d-block element with an electronic configuration of [Ar]$3d^9 4s^{2.}$ It is most stable in +2 oxidation state and the compound known as cupric compound and mostly stable in aqueous solution. They shows Jahn Teller distortion and often exhibit distorted octahedral geometry.

Copper is a vital metal to all living organisms since it is a significant component of the respiratory enzyme complex. In humans, copper is found primarily in the liver, muscle, and bone. A large amount of attention has been given to the copper-mediated reactions due to its capability to stabilize in different oxidation states, it can contribute in one-electron and two-electron trails in oxidation procedures along with its low toxicity, environmental abundance and flexibility in coordination geometry**.**[28] This permits copper to be an active catalyst in an extensive range of oxidation reactions**.**[29]

The foundation of Cu-mediated chemistry was stablished by Ullmann and Goldberg in 1901.**[30]** In recent few years many copper-mediated tetra-azolate complexes have been studied. Transition metal azolate complexes have been prepared using metal mediated [2 + 3] cycloaddition reactions of azides and nitriles.[31]

A new green colored antibacterial Schiff base cellulose-based fiber (**SCF**) Cu(II) complex was invented, where the **SCF** ligand was introduced with copper ion and resultant complex shows enhanced antibacterial properties and it was greater than Schiff base ligand.[32] Therefore, Cu(II) has the tendency to form a stable complex with Schiff base ligands having good antibacterial applications.

The synthesized complex displayed improved antibacterial activity and upheld decent fibre structure.[32] Herein, Cu(II) complex shows four centre coordinated square planar geometry.

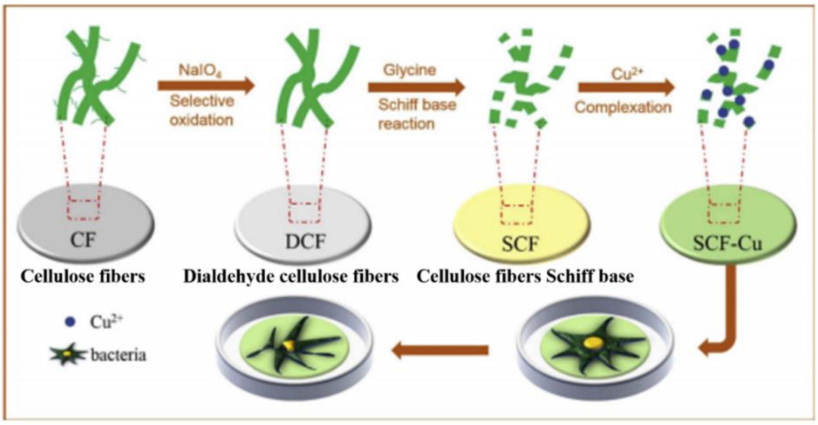


Figure 5. Antibacterial properties of synthesized SCF-Cu complex.

Yaning Guo, et al synthesized a new mononuclear Cu (II) complex by using a bidentate Schiff base ligand **HL**. The photophysical property of Cu (II)-binuclear Schiff base complex has been explored. According to the UV-Vis spectra, the ligand **HL** exhibited one absorption peak at 262 nm which was shifted to 265 nm and the one at 340 nm which was shifted to 381 nm, in the complex. This data shows the stiffness, which was increased after the interaction of ligand with copper ion. Due to π → π* transition the Cu (II) complex shows a peak at 381 nm and at 265 nm due to n → π* transitions.[33]

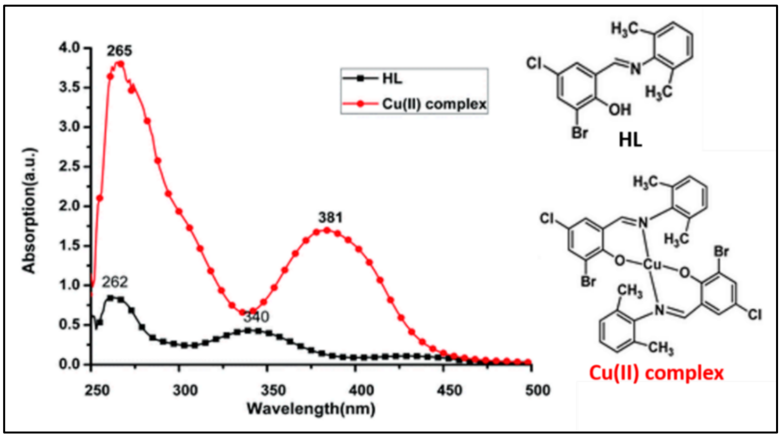
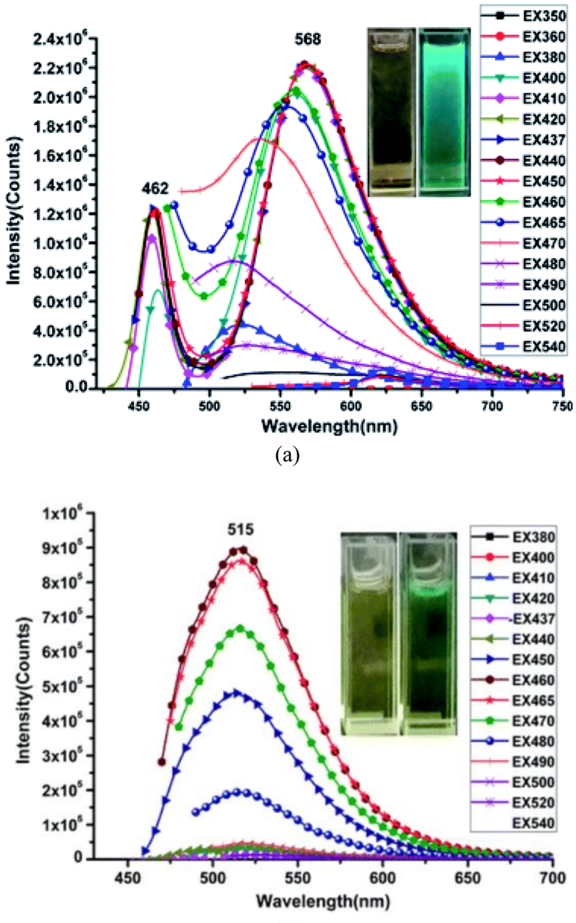


Figure 6. UV-Vis spectrum of HL and Cu(II) complex.

The fluorescence study of HL and the Cu(II) complex were done (Fig. 7). The excitation wavelength (λ_{ex}) utilized for HL was about 450 nm and for Cu(II) complex, it is about 460 nm. The highest emission band for HL was found at 568 nm, whereas for the Cu(II) complex at about

515 nm. The quenching of fluorescence occurred in Cu(II) complex because of the perturbation effect of metal atom.[33]



(a)

(b)

Figure 7. Fluorescence spectrum of (a) The **HL** and (b) The Cu (II) -binuclear Schiff base complex.

The HOMO and LUMO energy gap of the Cu(II) complex is lower as compare to the ligand, demonstrating that the consistent electron transition from the HOMO→LUMO for the complex is easier than ligand. This helps us to recognize the nature of transition and absorption spectra of the ligand and the complex.

1.6 Organization of the Thesis

The aim of this project is to design and synthesized tetrazole-imidazole ligand which can be used for the synthesis of tetrazole-imidazole Cu(II) meditated metal complex which may be useful for catalytic and sensing applications.

Section 1. This chapter includes general introduction of azoles and their application of complexation.

Section 2: This chapter includes past work done in the similar field and inspiration behind the work done during the project.

Section 3: This chapter contains materials, instrumentation and experimental procedure for the synthesis of ligands and complexes

Section 4: This chapter contains the results obtained after the synthesis of ligands and complexes.

Section 5: This chapter includes the conclusion of the work done and possible future scope and applications.

SECTION 2

2.1 Electrochemical Sensor

Metal-organic frameworks (MOFs) have an imperative subclass known as Metal Azolate frameworks (MAFs). MOFs have vast area of application in molecular reorganization and electrochemical sensor but their poor chemical stability in water or polar solvent restrict their role as a highly stable sensor.[33-37] Therefore, MAFs have been synthesized to overcome from this restriction and obtain a high stable sensor for electrochemical system.[38] The presence of inert or hydrophobic linkers such as imidazole, tetrazoles in MAF protect the central metal ion from the attack of solvent molecules.[39]

N.S. Lopa, et al. have synthesized Co-based **MAF-4-Co^{II}** used for the detection of glucose oxidation. The Co^{II} to Co^{III} reduction in MAF-4 permits the oxidation reaction. It is highly stable in liquid phase. The GCE modified **MAF-4-Co^{II}/GCE** is a stable sensor shows good electrocatalytic activity. The generated current was almost unchanged for 3600 s, shows higher stability of the sensor. It was confirmed by the XPS studies (**Figure 9).** XPS data shows that before and after the electrocatalytic reaction, there is almost unchanged peaks values of Co^{II} for electrochemical sensor proved its high stability.

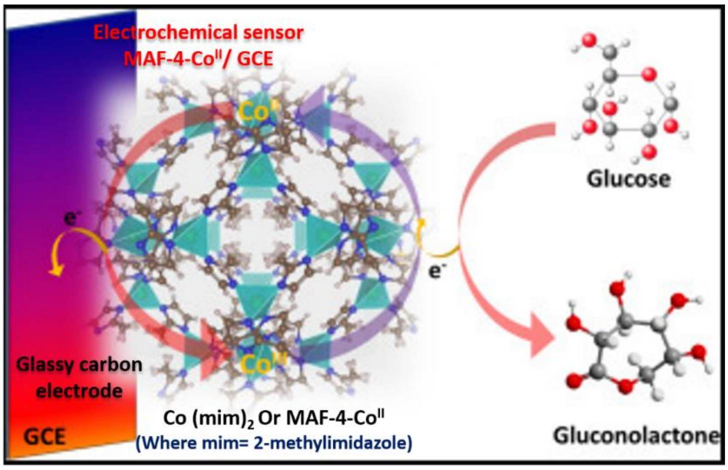


Figure 8. Detection and oxidation of Glucose at **MAF-4-Co^{II}/GCE sensor**.

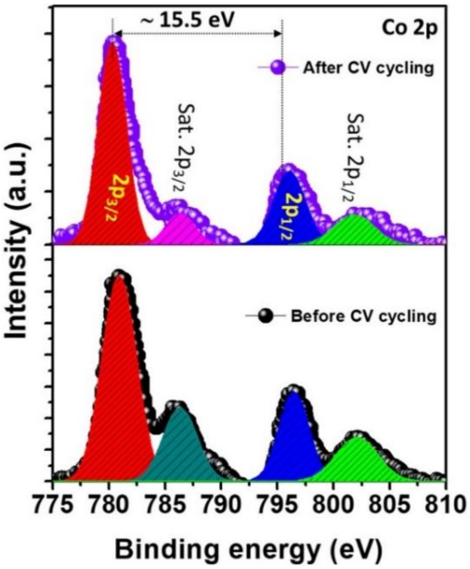


Figure 9. HR- XPS spectra of Cobalt of MAF-4-Co^{II} before and after glucose electrocatalysis

2.2 Catalysis

Catalysis is one of the most vital application. Porous coordination polymers (PCPs) have highly designable, ordered structures. They have attracted extensive attention. Metal azolate frameworks are an exclusive type of CPs containing of N-heterocyclic ligands.[38] Catalysis is one of the most efficient method for the synthesis of organic compounds. In the conventional method, it is multiple step slow process. But with the use of metal azolate frameworks as a catalyst, it can be converted into swift method which shows remarkable activity.

X. W. Zhang et al. have synthesized porous material from three PCP isomers with indistinguishable chemical compositions but diverse supramolecular structures. Further, detailed studies about their porosity have been done by various analytical methods.[40]

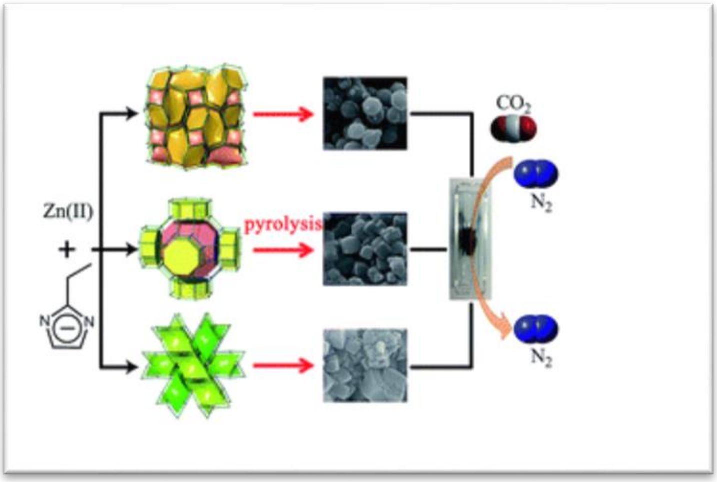
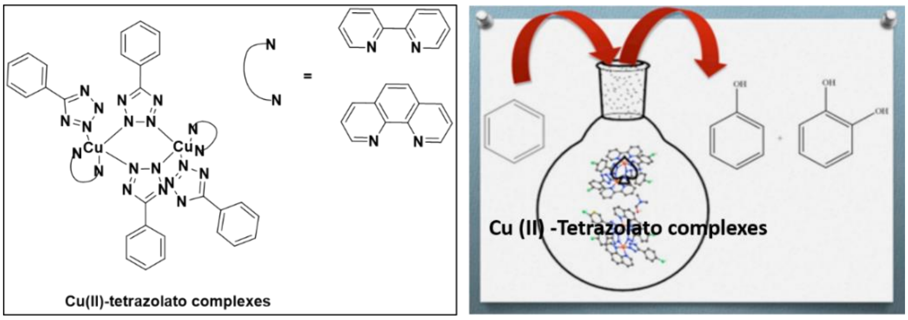


Figure 10. N-doped porous carbons from three PCP isomers with indistinguishable chemical compositions.

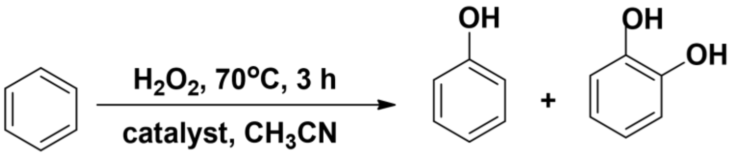
J. Kumari, et al. have synthesized copper(II) tetrazolato complexes using [2+3] cycloaddition reaction between copper mediated azide and nitriles. Further they have used formed complex for efficient oxidation of benzene to phenol.[41]



Scheme 1. Representation of Cu (II)-tetrazolato complexes

This turns out to be an efficient method for oxidation of benzene to phenol than the conventional method. Because in the conventional method, it is a three-stage procedure with low phenol yields. But due to the help of metal azolate complex as a catalyst, it is simply a one-step process.

The catalytic efficacy of Cu(II)-tetrazolato complexes on the immediate oxidation of benzene to phenol in presence of H_2O_2 showed capable catalytic activity with high selectivity where H_2O_2 as an oxidant.



Scheme 2. Schematic representation of Oxidation of benzene by Cu(II) complexes using as a catalyst.

The resulted mixture has revealed extraordinary selectivity. The production of phenol has noticed up to 91%. The obtained yields are rather high. This catalytic system represents several benefits in terms of sustainability: these are swift, simplistic workup procedure.[41]

M. Saha et al. have synthesized copper(II) tetrazolato complexes using [2+3] cycloaddition reaction between copper mediated azide and nitriles, which was found to catalyze oxidation of cyclohexane to cyclohexanol.**[8]**

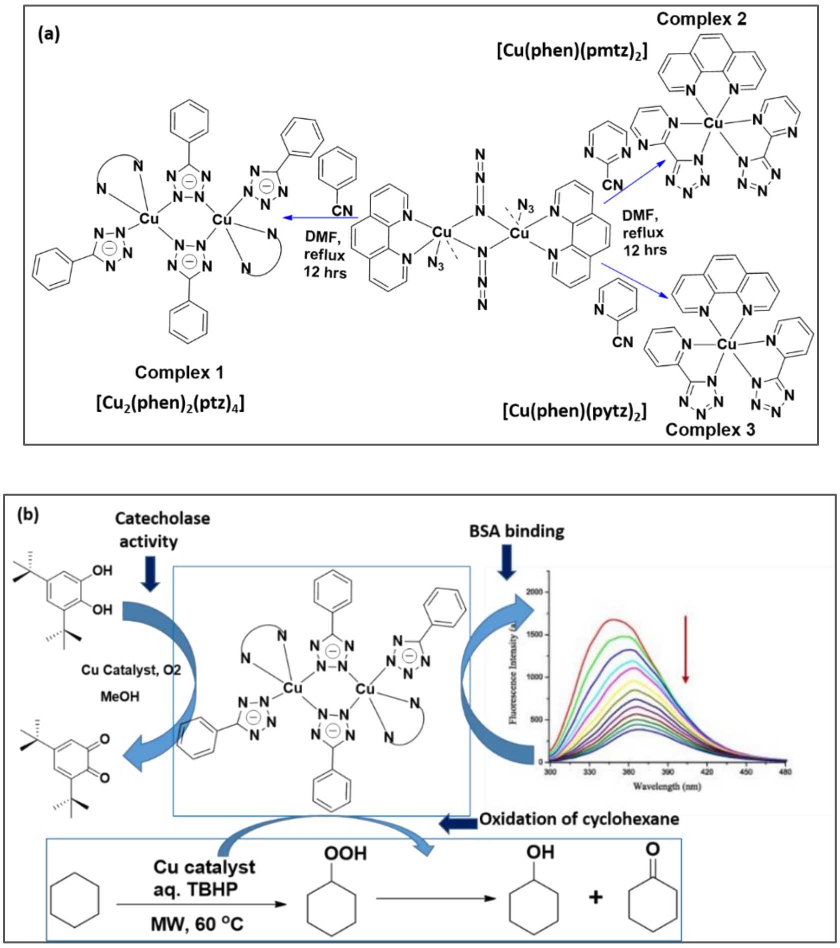


Figure 11. (a) Synthesis of Cu(II) complexes and (b) Schematic representation of catecholase activity and fluorescence quenching of BSA by complex.

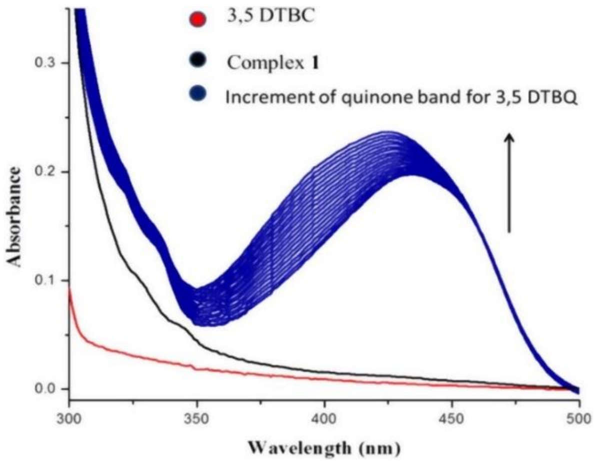


Figure 12. Spectral outline of catecholase-like activity over time for complex-**1 [$Cu_2(phen)_2(ptz)_4$]** after addition of 3,5-DTBC.

Aurel Tabacaru, et al. have synthesized five metal azolate/carboxylate (MAC) compounds and out of them, Cu-dmpzc shows catalytic oxidation of CyH and 1-phenylethanol.[42]

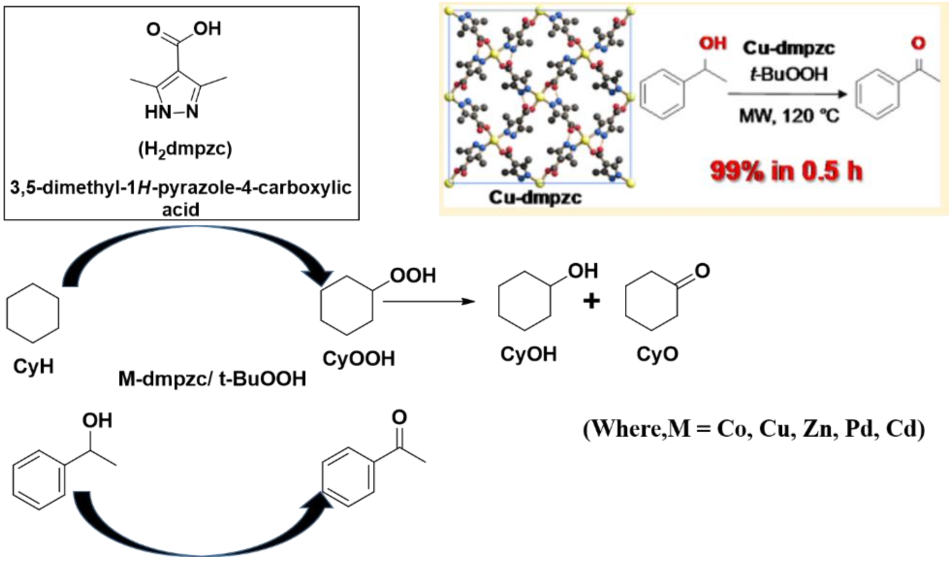


Figure 13. Oxidative and C-C coupling reaction catalysed by Metal azolate/ carboxylate framework.

On the basis of existing outcomes, these compounds appears to be precise and recyclable catalysts. There have not been many types of research on the mixed ligand concept, so here they have taken pyrazole, and carboxylic acid and further used this mixed ligand complex framework as a catalyst for oxidation of organic compound which showed very remarkable catalytic applications.

2.3 Magnetic properties

Tetrazole and imidazole complexes are extensively examined for their exhilarating magnetic properties. Song-Liang Cai, et al. reported reactions of Co (II) with **HIPT** and synthesized three compounds **1**, **2** and **3 (Figure 14)** whose magnetic vulnerability displayed widespread antiferromagnetic interactions. The structural variety is persuaded by inorganic anions and temperatures.[43]

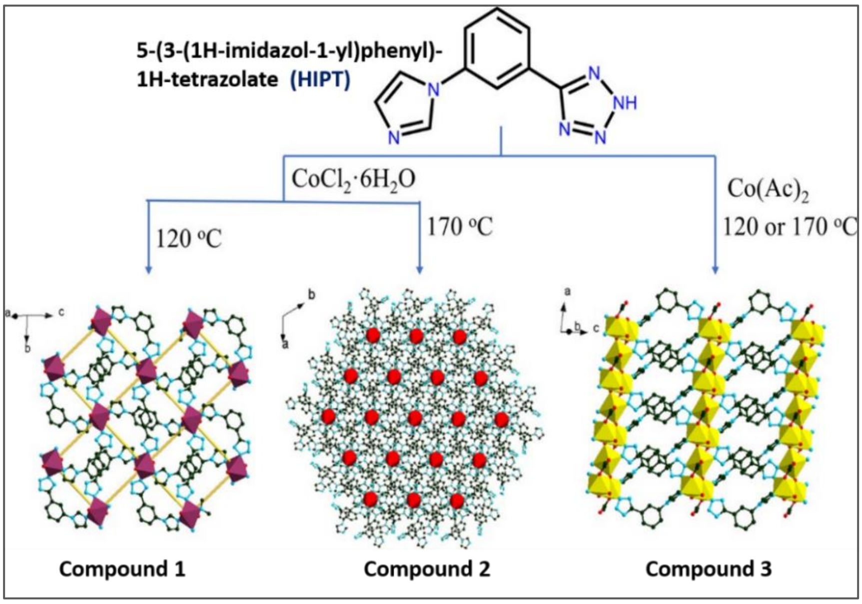


Figure 14. Structure of tetrazole and imidazole complex 1$\mathbf{\{[Co(IPT)_2(H_2O)_2]\cdot 2H_2O\}_{\mathit{n}}}$, 2 $\mathbf{[Co(IPT)_2]_{\mathit{n}}}$ and 3 $\mathbf{\{[Co_3(IPT)_2(CH_3COO)_2(OH)_2(H_2O)_2]\cdot 2H_2O\}_{\mathit{n}}}$.

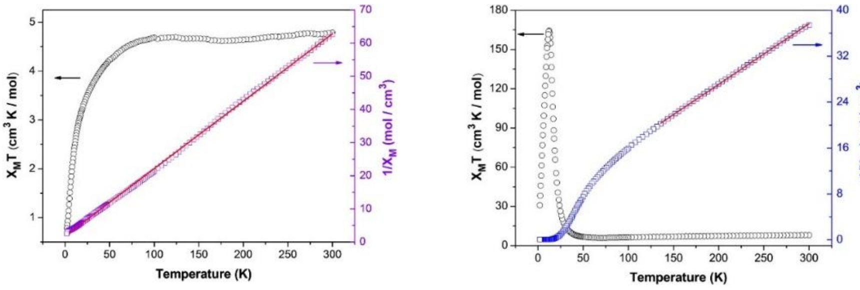


Figure 15. The $\chi_M T$ Vs temperature and χ_M^{-1} Vs temperature Plots for compound 2 and 3.

Here, the mixed ligand shows their combine effect for formation of compound framework. The tetrazolic part of ligand play their role for development of secondary building units (SBUs), however the imidazolic part show contribution for linkage in frameworks. The given reaction temperature and presence of anion from metal salt shows their greater effect on constructions of framework. The resultant outcome may assist to build novel CPs related to bifunctional ligands. This is a great work to explain the effective role of bifunctional ligand on the metal framework. There is only few report which contain the concept of bi-functionality in the form of different behavior of combined part of ligand.

2.4 Gas adsorption properties

The well-known roll of azoles are recognized for the inhibition of corrosion for copper metal. [44, 45] For showing good corrosion inhibitor effect, the adsorption of organic compound on the surface of metal is the first step of stop the corrosion.

Dunja and Anton reported the adsorption properties of tetrazole (Tz), triazole (Trz) and imidazole (Imz) on the oxidized surface of Cu_2O (111) and Cu_2O (111)-w/o-Cu^{CUS}. Adsorption bonding interaction of Tz, Trz and Imz to the copper oxide and CUS and CSA surface was explained by DFT studies which show the description about atomic level interaction between azole and copper different sites.[46] The magnitude of adsorption shown in (**figure 16)**.

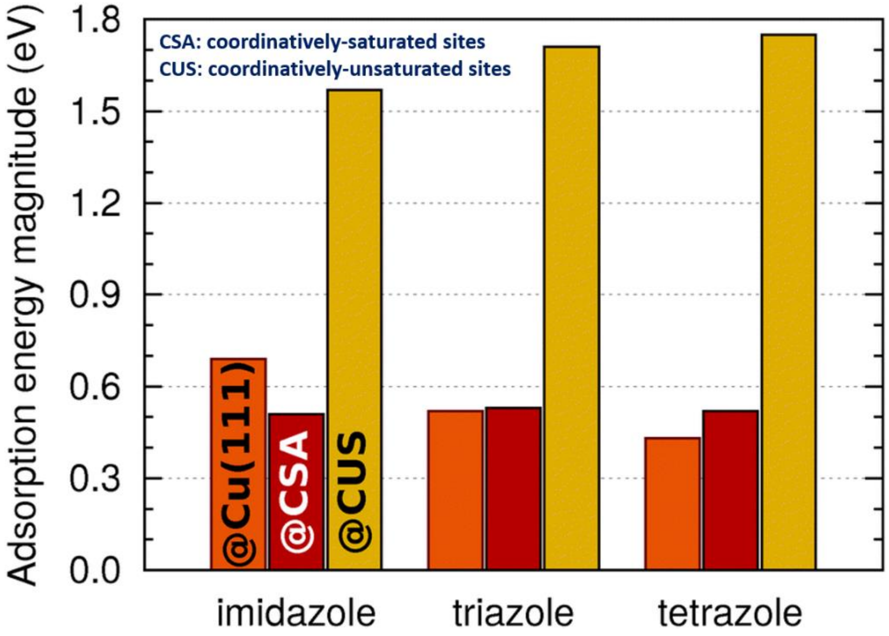


Figure 16. Magnitudes of adsorption energies of Imz, Trz, and Tz on Cu_2O different site.

This figure visibly divulges that, at CUS sites the bonding is significantly robust than to Cu (111) and to CSA sites. The resultant outcome from figure 16 appears that magnitudes of adsorption energies following the trend **Imz ≈ Trz > Tz** respectively. But the following trend has been altered at a high exposure. Because of the imidazole exhibiting repulsive nature. On the contrary, tetrazole displays attractive lateral dipole–dipole interactions.

SECTION 3

Experimental Section

3.1 Reagents and Chemicals

All the reagents used were of analytical grade and were used further without any purification. All the experiments were carried out in open atmosphere. 1*H*-tetrazol-5-amine monohydrate, 1*H*-imidazole-2-carbaldehyde, copper perchlorate hexahydrate, sodium azide, methanol are used as received.

3.2 Methods and Instrumentation

The structural characterization of the complex will be recognized by several physicochemical techniques alike IR spectroscopy, NMR spectroscopy, UV spectroscopy, single crystal X-ray diffraction, mass spectrometry.

1. **IR spectroscopy**

   IR spectroscopy is a technique of measurement of the interaction of infrared radiation with matter by emission, reflection, absorption**.** It is a specific technique that can be used to help identify the functional groups. It can be used in solid, gas, liquid form.

2. **NMR Spectroscopy**

   It is use to check types of atom, Comparative amounts and precise electronic atmospheres of atom, Purity and composition of a sample, structural info about a molecule.

3. **Mass Spectroscopy**

Mass spectrometry is an analytical method suitable for calculating the mass-to - charge ratio (m / z) of molecules in the sample and frequently be used to determine the accurate molecular weight of the sample components. It helps us to prove the identity of isotopes.

4. **X- Ray Diffraction Spectra**

The X-ray diffraction (XRD) is the most widely used non-destructive technique for general crystalline material characterization, to identify crystalline phase and orientation and to determine the structural property of a crystalline material. The single crystal X-ray diffraction will disclose the geometry of the complex.

5. **UV Spectroscopy**

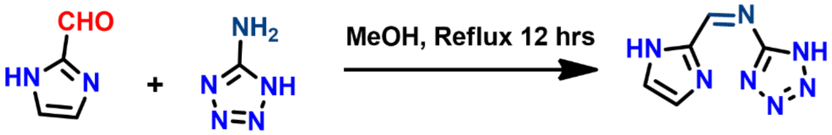
It is an absorption spectroscopy and it is used for quantitative determination of different analyte such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. It is one of the best methods to determine the impurities in the organic molecule.

SECTION 4

Results and Discussion

4.1 Synthesis of Schiff base azide ligand (TzL)

The synthesis of Schiff base was done by taking tetrazole and imidazole in methanol and refluxing it for 12 hrs. 2 mM, 0.206 g of 1H-tetrazol-5-amine monohydrate was taken in 20 mL of methanol and 2 mM, 0.192 g of 1H-imidazole-2-carbaldehyde was added into it. The reaction mixture was refluxed for 12 hours with stirring at 65 °C. At the end of the reaction, the obtained yellow-colored solution was evaporated at room temperature. Further, a white-yellow solid was obtained which was used for further analysis and reactions. Yield: 96%. ^{1}H NMR of **TzL** (400.13 MHz, 298 K, DMSO d_6): δ 8.94 (1H, imine), δ 7.02 (2H, imidazolic proton), d). ^{13}C NMR of **TzL:** δ 157.40 (imine carbon), δ 156.16 (tetrazolic carbon), δ 141.03 (imidazolic carbon), δ 129.71 (imidazolic carbon). ESI-MS $[M+H]^{+}$ *m/z:* 164.0691, $[M-H]^{+}$ (in negative mode) *m/z:* 162.0729. FT-IR: 3412, 1633, 1561, 1410, 1104 cm^{-1} **(Scheme 3).**



Scheme 3. Synthesis of ligand TzL

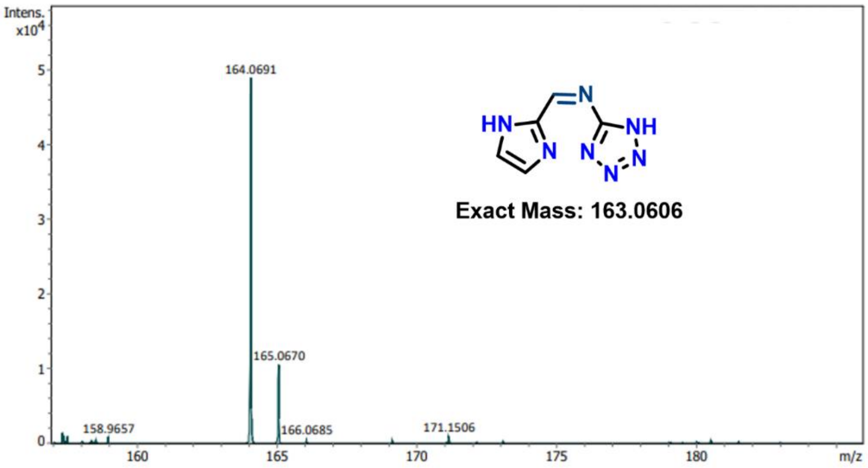


Figure 17: ESI-MS of ligand TzL in positive mode.

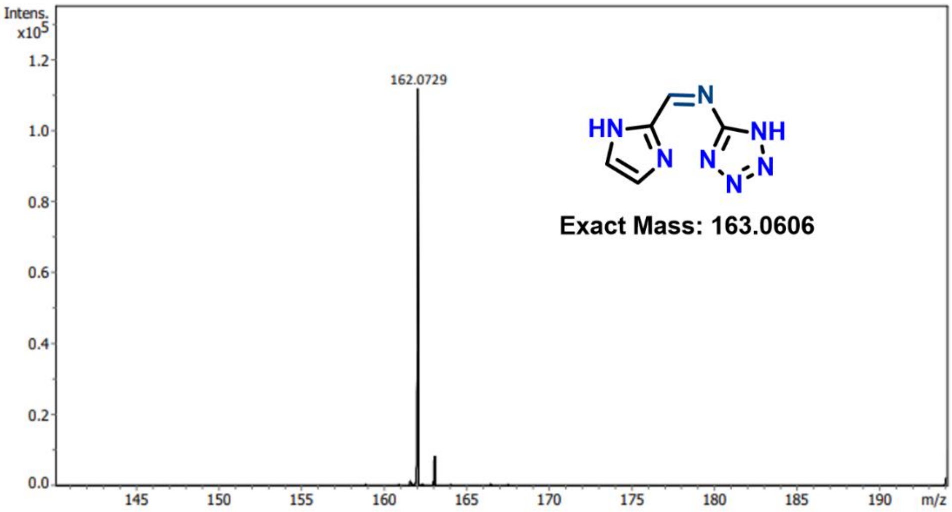


Figure 18: ESI-MS of ligand TzL in negative mode

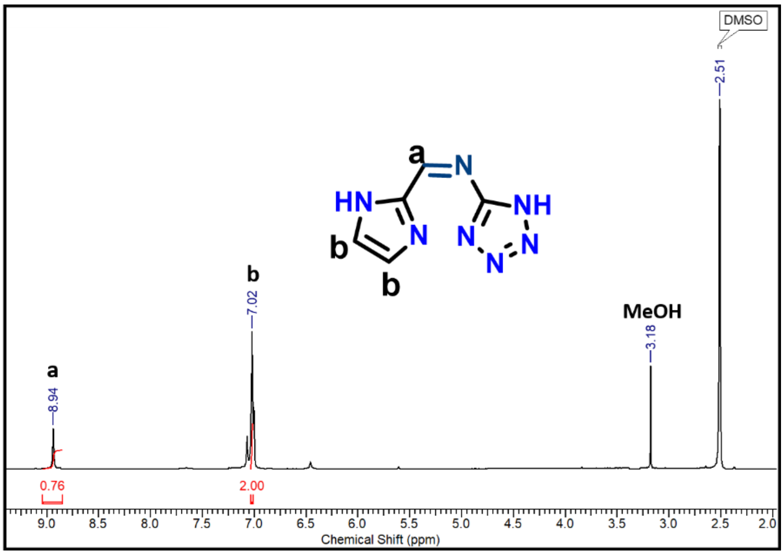


Figure 19: ^{1}H NMR of ligand TzL.

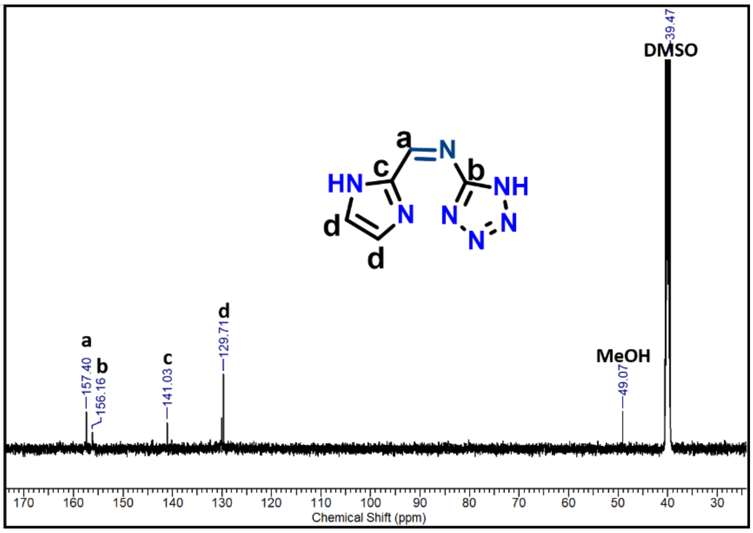


Figure 20: ^{13}C NMR of ligand TzL.

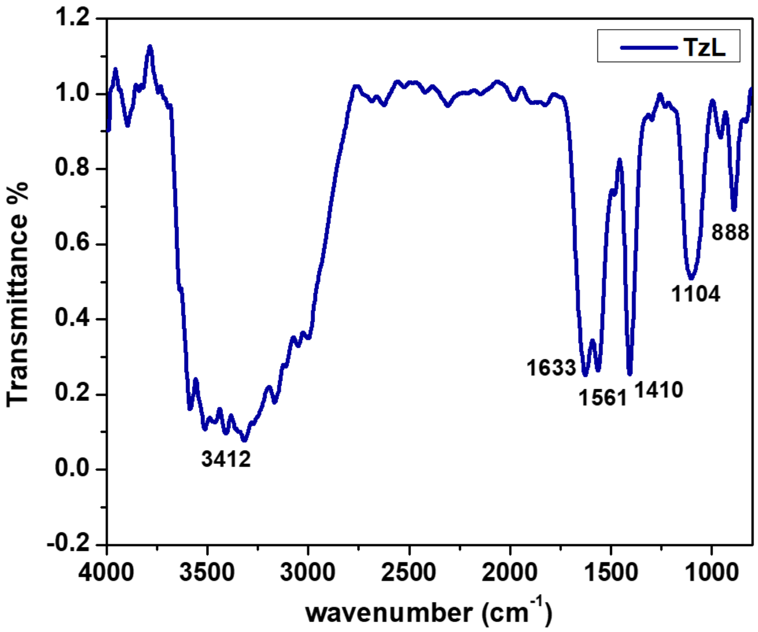
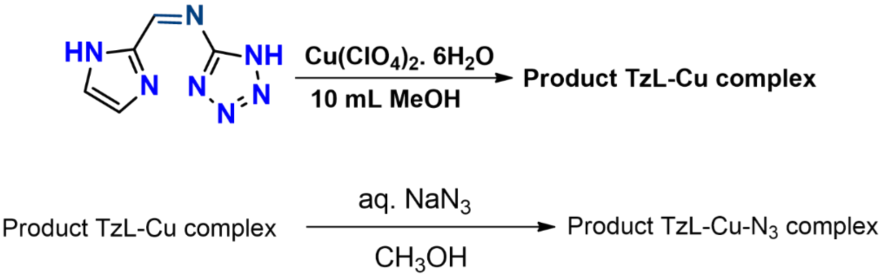


Figure 21: FT-IR of ligand TzL.

4.2 Synthesis of metal complex

A 5 mL methanolic solution of copper perchlorate hexahydrate (185 mg, 0.5 mmol) was carefully added dropwise to previously stirred 5 mL methanolic solution of Schiff base tetrazole ligand TzL (81 mg, 0.5 mmol). The resultant solution was refluxed with stirring for 20 min and a green colored solution was formed (**TzL-Cu)**. Further, at room temperature, 5 mL aqueous sodium azide (65 mg, 1 mmol) solution was added to the reaction mixture and green color precipitate was obtained (**TzL-Cu-N$_3$**). **(Scheme 4).**

The FT-IR data of **TzL-Cu** shows the changes of IR band at 1561 and 1410 cm^{-1} and with very less shifting and low intensity band appear at 1569 and 1404 cm^{-1} . This data indicate that the C=N and N=N group of tetrazolic and imidazolic part interact with Cu(II) and formed Cu-N interaction (Fig. 22).However, the FT=IR data of **TzL-Cu-N$_3$** shows a new IR band at 2063 cm^{-1} confirmed the presence of azide in in Cu(II) complex (Fig. 23).



Scheme 4. Synthesis of Complex of TzL with Cu.

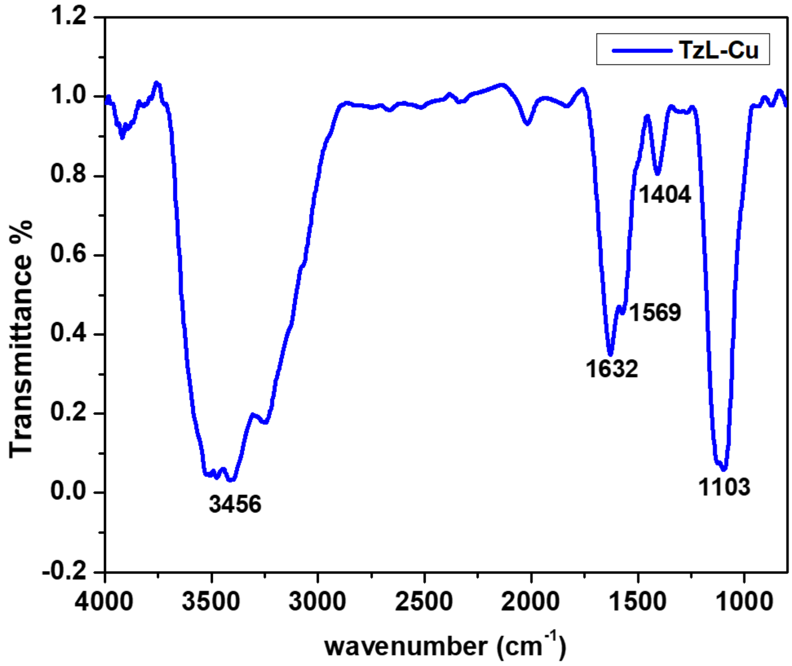


Figure 22: FT-IR of Complex TzL-Cu**.**

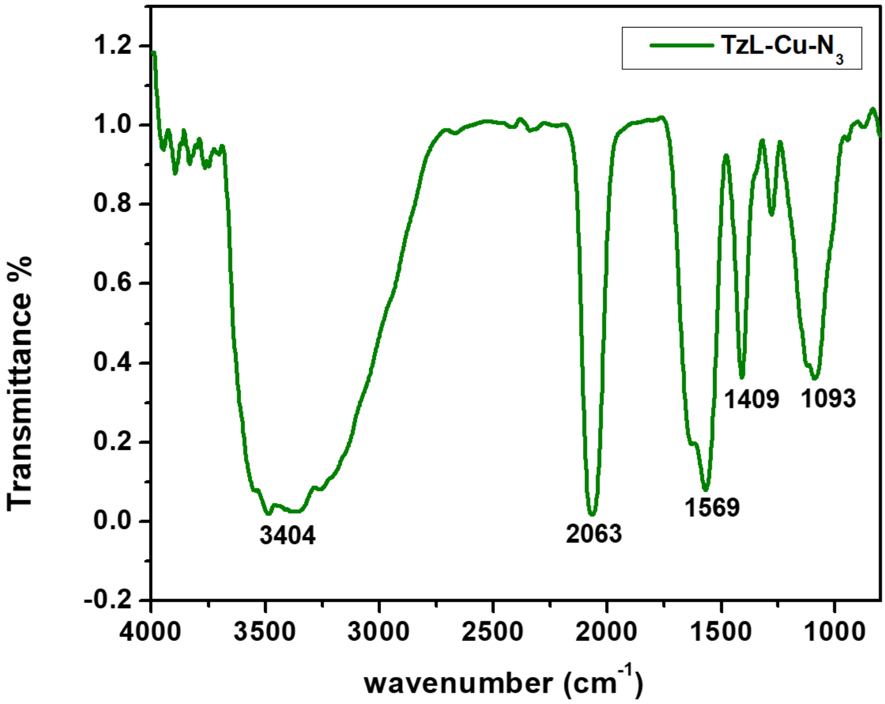


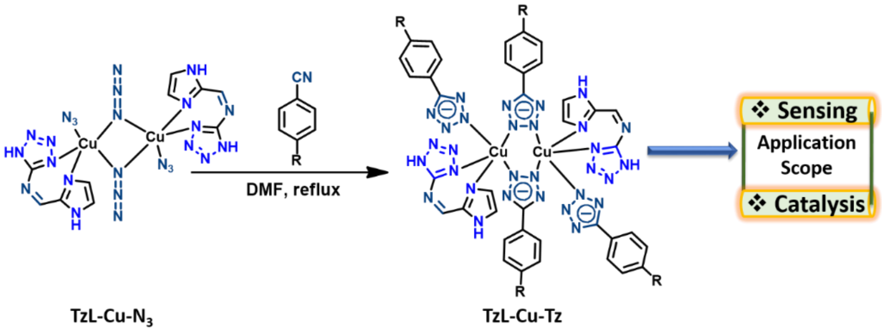
Figure 23: FT-IR of Complex TzL-Cu-N$_3$.

SECTION 5

Conclusion and Future scope

In the present work, the synthesis of imidazole-tetrazole ligand TzL has been done, and the complexation of the ligand with copper perchlorate and sodium azide was examined. The synthesis of TzL was confirmed by ESI-MS, ^{1}H, and ^{13}C NMR spectroscopy. The molecular structures of synthesized complexes viz. TzL-Cu and TzL-Cu-N_3 have not been confirmed yet. The present work has been focused on the synthesis and catalytic application of imidazole-tetrazole ligand containing transition metal complex and to find out the combined effect of imidazole-tetrazole moieties on the catalytic activity of the metal complex. A large amount of attention has been given to copper- mediated reactions because they show variable oxidation states, along with its low toxicity, environmental abundance, and flexibility in coordination geometry. These two azoles have different nature, imidazole has higher basicity than pyridine. On the contrary, tetrazole has acidity analogous to carboxylic acid. Imidazole can coordinate easily as compared to tetrazole. So, it has been studied that if Cu(II) can form a complex with tetrazole-imidazole ligand, which is different in nature but has not been confirmed yet. There have not been many research works reported in mixed ligand metal azolate framework so far.

The synthesized TzL ligand can be used in the synthesis of transition metal and azide-containing complexes which can be used further for the catalytic reaction like catecholase oxidation activity and also in sensing apart from the catalyst.



Scheme 5. Future expectation from the research project

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