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Enhancement of Activity of Transition Metals Complex's as a Catalyst in Environmentally Friendly Phenol Oxidation

NADIAH S. ALZHARANI[1], MOHAMED R. SHATAT[2,3] and MOHAMED M. AL-SAYED[2*]

[1]Faculty of Sciences, Al-Baha University, Al-Baha, Saudi Arabia.
*[2]Chemistry Department, Faculty of Science, Al-Baha University, Al-Baha, Saudi Arabia.
[3]Chemistry Department, Faculty of Science, Al-Azhar University, Assuit, Egypt.
*Corresponding author E-mail: melsayed@bu.edu.sa & mohamhmoud1973@gmail.com

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ABSTRACT

This study highlights the synthesis, characterization, and catalytic application of a novel copper(II) complex, Cu(II)(FTL), where FTL represents the 2-amino-4-(4-fluorophenyl) pyrazole ligand. Spectroscopic analyses confirmed the successful coordination of the copper(II) ion through the nitrogen atoms of the pyrazole's amino and ring nitrogen groups. The catalytic potential of Cu(II)(FTL) was evaluated for the green oxidation of phenol using hydrogen peroxide (H_2O_2) as the oxidant. Kinetic studies revealed a Michaelis constant (K_m) of 44.7 mM and a turnover number (k_cat) of $2.7\times10^{-7}\ 10s^{-1}$ for the catalyzed reaction, compared to K_m = 37.6 mM and k_cat = $3.5\times10^{-7}\ 10s^{-1}$ for the unanalyzed reaction. The higher K_m value in the presence of the catalyst suggests a lower binding affinity for phenol, consistent with a mechanism where H_2O_2 is the primary substrate activated by the copper center. The relatively low k_cat indicates a slow turnover rate, potentially due to stable intermediate formation or slow product release. Despite these limitations, the study demonstrates the potential of Cu(II)(FTL) as a catalyst for environmentally friendly phenol oxidation, paving the way for further optimization and mechanistic exploration.

Keywords: Copper complex, Benzopyran derivative's, Green oxidation, Phenol, Microwave irradiation.

INTRODUCTION

In fact, water scarcity is becoming a more pressing problem as a result of the increase in industrial production and population growth[1]. In addition to being scarce, water one of the most important resources for people and other living things is becoming more and more contaminated[2]. Water contamination is caused by the widespread use of hazardous organic and inorganic chemical chemicals, such as phenolic compounds, in the petrochemical, chemical, and pharmaceutical industries[3,4]. Both the environment and human health are seriously endangered by these contaminants[5,6].

To guarantee that this valuable resource is available and safe for everyone, these issues must be resolved by more stringent industrial emissions restrictions, sophisticated treatment technologies, and sustainable water management techniques[7].

Phenolic chemicals in wastewater do, in fact, provide serious environmental problems. Even at low doses, phenol is extremely poisonous, making it especially harmful[8]. Its presence in effluent from chemical, pharmaceutical, and petrochemical businesses can seriously contaminate water bodies, harming aquatic life and public health[9]. Phenol is highly toxic and can cause serious environmental harm[10].

Without a doubt, creating environmentally friendly processes to convert phenol in industrial wastewater into carbon dioxide and water is essential for environmental sustainability[11]. Phenol can be broken down into less toxic forms via processes such chemical oxidation, photo catalytic oxidation, and electrolytic oxidation[12]. Using enzymes like horseradish peroxidase to catalyze the phenol's oxidation, which produces carbon dioxide and water[13]. Using inexpensive adsorbents made from agricultural and industrial waste to extract phenol from wastewater. Adsorption is an economical and sustainable technique[14].

Because of their effectiveness and affordability, copper complexes are frequently employed as catalysts in a variety of oxidation processes. Because of their distinct biological activity, copper complexes have in fact attracted a lot of attention in pharmaceutical and medical chemistry[15]. A necessary trace element, copper is involved in many biological processes, such as electron transport and enzyme activity[16]. Copper complexes have antiviral, antibacterial, anticancer, and antioxidant properties[17]. Copper complexes are useful in the development of novel medications because of the substantial overlap between the biological functions of copper and protein biochemistry[18]. They are being investigated as potential therapeutic interventions for a number of illnesses, including inflammatory ailments, cancer, and neurodegenerative diseases[19].

Because copper complexes can go through ligand substitution processes, they are exceptionally adaptable. Their biological activity is greatly enhanced by this characteristic, which enables them to attach to a wide range of biological substances[20]. By exchanging ligands, copper complexes can interact with a variety of substrates. Their ability to adapt is essential to their function in biological systems, as they must bind to different molecules in order to carry out their tasks[21]. Copper complexes can interact with proteins, nucleic acids, and other biomolecules by substituting ligands[22]. This interaction can affect cellular functions, change DNA/RNA architecture, and control enzyme activity[23]. Copper complexes are efficient catalysts in biological reactions, such as oxidation-reduction processes that are essential for metabolism and cellular respiration, because of their capacity to bind and release various ligands. Indeed, tyrosinase is an intriguing enzyme[24]. It is comparable to hemocyanin, a protein that contains dinuclear copper ions and is involved in oxygen transport in certain mollusks and arthropods[25]. The main function of tyrosinase is to catalyze the conversion of phenols to catechols and then catechols to quinones[26].

It is true that peptidyl copper complexes have a lot of potential for simulating catalase, a crucial enzyme in biological systems[27]. Like the natural enzyme catalase, these complexes catalyze the breakdown of hydrogen peroxide (H_2O_2) into water (H_2O) and oxygen (O_2)[28]. This process is essential for shielding cells from hydrogen peroxide's oxidative damage. The stability of peptidyl copper complexes under physiological conditions is guaranteed by their design, which is crucial for their operation in biological settings[29]. Because these compounds are designed to withstand hydrogen peroxide breakdown, their catalytic activity can be sustained over time. Peptidyl copper complexes' stability and efficacy make them promising candidates for use in therapeutic techniques where controlled hydrogen peroxide breakdown is advantageous[30].

Pyrano [2,3-c] Indeed, pyrazole ligands are intriguing substances with a variety of medicinal uses! These substances have demonstrated strong pharmacological and biological action[31]. Anti-inflammatory, anti-cancer, antibacterial, analgesic, anticonvulsant, and vasodilator qualities are among their well-known qualities[32]. They are useful in medicinal chemistry for creating novel therapeutic agents because of their wide range of biological activity[33]. For example, the possibility of some derivatives as inhibitors of the human coronavirus has been investigated[34].

In this study presents an efficient and eco-friendly synthesis of benzopyrane compounds via microwave irradiation, adhering to green chemistry principles. The synthesized compounds were characterized using spectroscopic methods and utilized as ligands to form copper(II) complexes. The catalytic activity of these complexes was investigated in the oxidation of phenol using hydrogen peroxide. Kinetic parameters, including Michaelis constant (K_m) and turnover number (k_cat), were determined. The effects of experimental conditions on catalytic activity were explored, and a plausible mechanism for phenol oxidation is proposed.

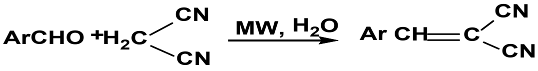
Methodology

Across Organics Co. (Belgium) supplied the aromatic aldehydes, malononitrile, 3-methyl-1-phenyl-2-pyrazolin-5-one, and triethylbenzylammonium chloride (TEBA). Merck Company, located in Germany, provided the copper chloride.

Synthesis of (2-Amino-4-(4-fluorophenyl)- 5, 6,7,8 tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile) under microwave irradiation. (FTL)[35]

Synthesis of arylidenemalononitrile under microwave irradiation

The synthesis of arylidenemalononitrile under microwave irradiation is a fascinating and efficient method. Combine malononitrile (0.33 g, 5 mmol) and aromatic aldehyde (5 mmol) with 2 ml of water in a tightly closed tube. The tube is subjected to microwave irradiation for a specific amount of time. The reaction progress is monitored using thin-layer chromatography (TLC). Once the reaction is complete, the mixture is filtered and washed with water. The resulting precipitate is the pure arylidenemalononitrile product, characterized by a sharp melting point.This method minimizes the use of solvents and energy, aligning with the principles of green chemistry. It often leads to higher yields and purities of the desired product. (Scheme 1).



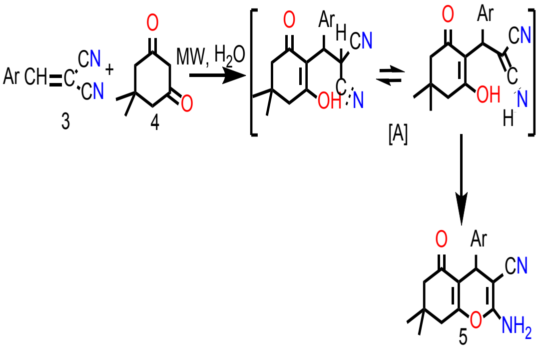
$$\mathrm{ArCHO} + H_2C(CN)_2 \xrightarrow{MW,\ H_2O} \mathrm{Ar\,CH{=}C(CN)_2}$$

1 2 3

Scheme 1

Synthesis of tetrahydrobenzopyran-(4-fluorophenyl) under microwave irradiation

The synthesis of tetrahydrobenzopyran-(4-fluorophenyl) under microwave irradiation is another efficient and fascinating method. Combine equimolar amounts of arylidene malononitrile (5 mmol) and dimedone (0.7 g, 5 mmol) in a firmly closed tube. Expose the tube to microwave irradiation for the necessary time. Monitor the reaction progress using Thin Layer Chromatography (TLC). After the reaction is complete, filter and wash the mixture with water. The precipitate obtained is the pure tetrahydrobenzopyran-(4-fluorophenyl) product (5) (Scheme 2).Often results in higher yields and purity of the product. Uses less energy and solvent, adhering to green chemistry principles.



Scheme 2

Synthesis of Cu(II) complex of (FTL)

The synthesis of the Cu(II) complex of (FTL) involves several steps. Dissolve 0.1 mole of copper(II) chloride in approximately 40 milliliters of absolute ethanol. The ligand used is 2-amino-4-(4-fluorophenyl)-5, 6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (FTL). Add the produced ligand (FTL) to the dissolved copper (II) chloride in ethanol. Heat the mixture under reflux for two hours. During this time, the reaction between the copper(II) chloride and the ligand will form the desired Cu(II) complex. A bluish precipitate will form during the refluxing process. Filter out the precipitate and wash it repeatedly with hot ethanol to purify the product. This method efficiently produces a Cu(II) complex with the ligand 2-amino-4-(4-fluorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile through a straightforward reflux process. The resulting bluish precipitate indicates the formation of the Cu(II) complex, which is then purified by washing.

Physical methods

Carbon, hydrogen, and nitrogen concentrations were measured at Cairo University's Microanalytical Unit in Egypt. The IR spectra of the ligand and its solid complexes in KBr were measured with a Mattson 5000 FTIR spectrometer. Kinetic measurements and electronic spectra were taken using a Varian Cary 4 Bio UV/Vis spectrophotometer. Joel-90Q Fourier Transform (200 MHz) spectrometers were utilized to capture the ligand's 1H NMR spectra in [D6] DMSO. The mass spectra of the ligand and its metal complex were obtained using a direct intake system on a Shimadzu GC-S-QP 1000 EX spectrometer. Thermal analysis (TGA) measurements were performed on 20 mg samples using a Shimadzu thermogravimetric analyzer model TGA-50 H. The heating rate was 10°C min^{-1}, and the nitrogen gas flow rate was 20-cm^{3} min^{-1}. The Gouy balance was used to determine the magnetic susceptibility of the copper(II) complex at room temperature, with Hg [Co(NCS)$_4$] acting as a celebrant.

Kinetic measurements of Phenol oxidation activities

Measurements of the kinetics of phenol oxidation. Copper(II) chloride dissolved in ethanol was added to the organic ligand (FTL) dissolved in 100% ethanol in the UV-Vis cell. Hydrogen peroxide and phenol dissolved in distilled water were then quickly added to the solution. After the addition was complete, the absorbance at 500 nm was measured. The absorbance at 500 nm was seen to increase over time.The experiment was carried out three times to ensure accuracy.[36,37]

RESULTS

Spectroscopic Analysis of 4-Fluorophenyl Benzo Pyran (FTL)

The infrared (IR) spectrum

The infrared (IR) spectrum of 4-fluorophenyl benzo pyran (FTL) in (Fig. S1, supplementary materials) exhibits numerous significant absorption bands, which can be attributed to various functional groups included in the molecule. Bands of 3356 cm^{-1} and 3185 cm^{-1} These are due to the stretching vibrations of the NH_2 group. Band at 1650 cm^{-1}. This represents the stretching vibration of the carbonyl (C=O) group. Band at 2190 cm^{-1}. This is related to the stretching vibration of the cyano (C≡N) group. The νNH2 vibrations exhibit absorption bands at 3447 cm^{-1} and 3332 cm^{-1}. Another noticeable band at 1664 cm^{-1} is due to the νC=O stretching vibration. These IR spectral characteristics provide vital information about the ligand's functional groups, validating structural components and aiding in compound characterization[38].

^{1}H NMR Analysis of 4-Fluorophenyl Benzo Pyran (FTL)

The ^{1}H NMR spectrum of 4-fluorophenyl benzo pyran (FTL) in $CDCl_2$ shows distinct signals for the different protons in the molecule. The spectrum displays singlets at δ = 1.05 and 1.083 ppm that integrate to 3 protons, suggesting the existence of two methyl groups (CH_2). A doublet at δ = 1.67 ppm with a coupling constant JAB = 16 Hz corresponds to one proton (H-8a), while another doublet at δ = 2.23 ppm with the same coupling constant (16 Hz) corresponds to the second proton (H-8b). These signals most likely suggest geminal coupling. The C6-H protons are responsible for a singlet at δ = 2.44 ppm, which can be integrated for two protons. Another singlet at δ = 4.33 ppm, integrating for one proton, corresponds to the C4-H proton. The signal at δ = 5.91 ppm, a singlet integrating for two protons, is ascribed to the NH_2 group, which is D2O exchangeable and confirms the presence of the amino group. Finally, the aromatic area exhibits a multiplet between δ = 6.79-7.23 ppm, integrating for four protons representing aromatic hydrogen atoms (Ar-H). This extensive examination of the ^{1}H NMR spectrum sheds light on the structure and environment of the protons within the FTL molecule, verifying the predicted chemical shifts and coupling patterns for the identified functional groups.

Mass Spectroscopy Analysis of 4-Fluorophenyl Benzo Pyran (FTL)

The mass spectrum of 4-fluorophenyl benzo pyran (FTL) shows a significant peak at m/z=311, corresponding to the molecular ion peak. This peak represents the molecular weight of the FTL molecule, indicating the existence of the 4-fluorophenyl benzo pyran structure. In mass spectrometry, the molecular ion peak is important because it represents the compound's molar mass. The peak at m/z=311validates the calculated molecular weight and confirms the identity of the produced product.

Elemental Analysis of 4-Fluorophenyl Benzo Pyran (FTL)

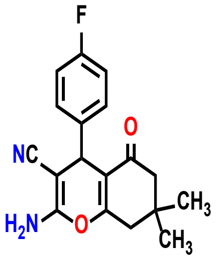
The elemental analysis of 4-fluorophenyl benzo pyran (FTL) reveals important information about its composition and characteristics. The following table summarizes the calculated and found values for carbon (C), hydrogen (H), and nitrogen (N), as well as the melting point (Mp) and molecular weight (MWT).

Table 1: Elemental Analysis of 4-Fluorophenyl Benzo Pyran (FTL)

Element	C	H	N	m.p.(°C)	MWT
Calculated	69.22%	5.49%	8.97%	127.2	312.34
Found	69.02%	5.06%	8.83%	126	311

The calculations are based on the molecule's theoretical makeup. The discovered values were derived by experimental measurements. The modest variations between calculated and measured values are within acceptable experimental error ranges, validating the compound's identity and purity.

The comprehensive characterization of 4-fluorophenyl benzo pyran (FTL) is supported by data from multiple spectroscopic techniques and elemental analysis This multi-technique approach provides a robust validation of the 4-fluorophenyl benzo pyran (FTL) structure and purity, ensuring that the synthesized compound matches the expected characteristics Structure (2).



2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile

Structure (2)

Characterization of Cu(II) (FTL) complex

IR spectral data of Cu (II) (FTL) complex

The infrared (IR) spectrum study of the copper(II) complex reveals important information about its coordination with the ligand (Fig. S1, supplementary materials). Coordination using NH_2 and C-N The copper(II) ion binds to the ligand via the nitrogen atom of the NH_2 group and the C-N link. This is clear when comparing the ligand's IR spectra to that of the Cu(II) complex. The elimination of the cyanide group band in the Cu(II) complex spectra lends weight to the coordination idea. The NH_2 group's wide bands shift slightly to a longer wavelength (3445 cm^{-1}, and 3335 cm^{-1}), showing coordination with the copper(II) ion. The presence of a new band at 580 cm^{-1}, attributable to νM-N, verifies the coordination of the NH_2 nitrogen atom. An extra band at 3390 cm^{-1} is attributable to the OH group and stretching vibration of the water molecule[39]. A new band at 501 cm^{-1}, attributed to νM-O, verifies the proposed structure of the copper(II) complex[40]. These findings support the suggested coordination structure of the copper(II) complex with the ligand.

Electronic spectral data of Cu (II) (FTL) complex

Magnetic moment

At ambient temperature, all Cu complexes have a magnetic moment of around 1.8 Bohr Magnetons (BM), which is compatible with the presence of a single unpaired electron.

Electronic spectrum

In the electronic spectrum (Fig. S2, supplementary materials) of the Cu (FTL) complex in ethanol, a strong absorption band at 480 nm is visible. The square-planar geometry around the Cu core has a substantial impact on the d-d transition ($^2B_{1g}\rightarrow{}^2A_{1g}$) that causes this band to exist[41]. The absorption bands at 260 nm and 380 nm are associated with charge transfer (CT) transitions, when electrons are transferred from Cu's filled orbitals to the ligand's anti-bonding π^* orbitals[42].

The ESR spectra of complexes

The ESR spectra of Cu complexes were recorded on an X-band spectrometer at a frequency of 9.1 GHz under a magnetic field strength of 3400 G, with a scan rate of 2000[43]. The spectra were measured at room temperature and exhibit a single anisotropic broad signal (Figure 1).

Observations

The anisotropic spectrum shows $g_{\|}>g_{\perp}$, with the following values' $\|$ = 2.2238 $g_{\perp}$ = 2.14102. The condition $g_{\|}>g_{\perp}>2.0023$, calculated for Cu(II) complexes, suggests that the unpaired electron is localized in the $dx^2{-}y^2$ orbital. These values indicate a square planar geometry for the copper complex[44].

The $g_{\|}$ value for Cu (FTL) is less than 2.3, suggesting that the bonds between. The organic ligand and the copper ion exhibit a covalent character rather than an ionic character.

Ligand filed strength.

According to Hathway and Billing, the g-values can be used to calculate the G-value using the equation[45]. $G=(g_{\parallel}-2.002)/g_{\perp}-2.002$. This factor evaluates the exchange interaction between copper centers in a polycrystalline solid. The G-value for the Cu complex was found to be less than 4.0, indicating considerable exchange interaction within solid complex.

A G-value less than 4.0 suggests that the ligand forming the Cu complex acts as strong field ligand[46]. The predominance of the $dx^2–y^2$ orbital in the ground state and the covalent nature of the ligand- copper bond are consistent with the observed spectroscopic parameters[47].

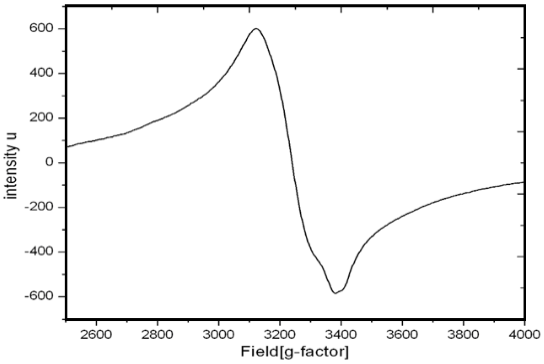


Fig. 1. ESR spectra of Cu complex

Thermal analysis of Cu (II) (FTL) complex

The thermogravimetric analysis (TGA) in (Fig. S3, supplementary materials) of the Cu(II) complex provides valuable insights into the thermal stability and decomposition pattern of the complex. First Stage (25-100°C) Weight loss calculated = 4.37%, found = 3.2% description: Elimination of one water molecule within the coordination sphere.

Second Stage Weight Loss calculated = 36.9%, Found = 38.09% description: Elimination of two NH_2 molecules, two CO_2 molecules, and two water molecules.

Third and Fourth Stages description these stages indicate the formation of metal oxides, carbides, metallic residue, or combinations thereof as the final products of thermal decomposition.

Stability Observation: The weight remains constant at 800°C, suggesting that the copper complex is relatively stable up to this temperature. This analysis helps in understanding the thermal behavior and stability of the Cu(II) complex, which is crucial for its potential applications[48].

Mass spectroscopy of Cu (II) (FTL) complex

The mass spectrum of the copper complex Cu(II) with the molecular formula $C_{18}H_{21}CuFN_2O_4$ shows a molecular ion peak at m/z=412.

This peak represents the intact copper complex, indicating its molecular weight. The presence of this peak confirms the formation of the copper complex and provides valuable information about its composition Figure 2.

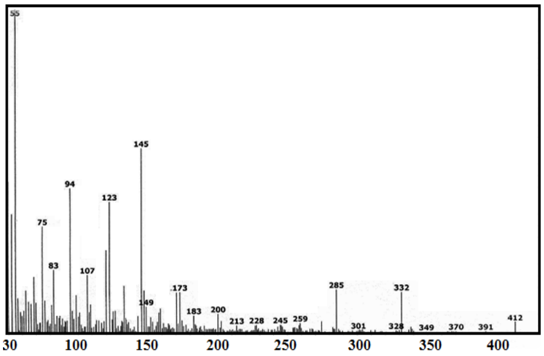


Fig. 2. Mass spectrum of Cu complex

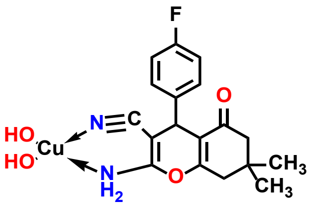
Elemental analysis

This Table 2 shows the calculated and found percentages of carbon (C), hydrogen (H), and nitrogen (N) in the copper complex. The melting point (m.p.) and molecular weight (M.WT) are also provided, with the found melting point being 280°C and the calculated molecular weight being 410.06 g/mol.

Table 2: Elemental analysis of the complex

Element	C	H	N	m.p.	M.WT
Calculated	52.67%	4.67%	6.82%	---	410.06
Found	52.01%	4.32%	6.41%	280	412

Based on the comprehensive analysis from various techniques, including IR spectral data, magnetic moment measurements, electronic spectrum, ESR spectra, thermal analysis, mass spectrometry, and elemental analysis, it is evident that the structure of the copper complex aligns with the proposed Structure (2). These combined results strongly support the proposed structure of the copper complex.



Structure (2)

Catalytic activity study of phenol

Metal complexes like Cu(II) FTL act as enzyme mimics or biomimetic catalysts[49]. These complexes are designed to replicate the active sites of natural enzymes, which are highly efficient and selective catalysts in biological systems[50]. By mimicking these natural enzymes, metal complexes can achieve similar levels of efficiency and selectivity in catalytic processes[51]. This approach is inspired by the sophisticated functionality of enzymes, which often involves highly organized cavities and specific interactions with substrates.

The catalytic oxidation of phenol is indeed a crucial reaction in environmental chemistry, especially for treating wastewater. Phenol and its derivatives are common pollutants, and their effective removal from wastewater can significantly reduce environmental hazards. In your described process, the initial rate of phenol oxidation is monitored by measuring the increase in absorbance at 500 nm over time. The choice of the metal complex as a catalyst can greatly influence this rate, making it an essential variable to optimize for efficient phenol oxidation. The oxidized product's concentration was computed using the extinction coefficient, $\varepsilon = 32\ L\ M^{-1}\ cm^{-1}$.[52]

The Role of Metal Complexes in Advancing Phenol Oxidation Catalysis

Certainly, the study of metal complexes and their effects on the catalytic oxidation of phenol is an important and intriguing area of green chemistry[53]. These metal complexes have a significant impact on the reaction kinetics, selectivity, and overall efficiency of the oxidation process, making them invaluable when constructing environmentally friendly catalytic systems.

Table 3: Oxidation rate of phenol using metal salts and metals complexes with H_2O_2

Metal salt and Metal complex	Observed rate VomMS^{-1}	Standard error
$CuCl_2$	1.298×10^{-6}	1.312×10^{-7}
Cu (II)FTL	3.949×10^{-5}	1.455×10^{-6}
$MnCl_2$	1.161×10^{-6}	5.774×10^{-8}
Mn(II)FTL	2.846×10^{-5}	1.033×10^{-7}
NiCL	8.909×10^{-6}	6.956×10^{-8}
Ni(II)FTL	2.340×10^{-5}	4.147×10^{-6}
$FeCl_2$	7.483×10^{-6}	1.341×10^{-7}
Fe(II)FTL	1.981×10^{-5}	1.201×10^{-7}

The data presents in Table 3, the concentration of various metal ions (Fe(II), Ni(II), Mn(II), Cu(II)) in their free form (MCl_2) and as complexes with a ligand (FTL) over time. The data suggests that the presence of the metal ions has a significant impact on the oxidation of phenol[54]. The concentration of each metal ion increases over time, indicating that they are not consumed but potentially involved in a catalytic process. Comparing the concentrations of free metal ions (MCl_2) with their respective complexes (M(II)(FTL)) reveals that the presence of the FTL ligand generally leads to a higher concentration of the metal ion over time. This suggests that the ligand may stabilize the metal ion, enhance its reactivity, or prevent its precipitation or other deactivation pathways. Fe(II) Shows a consistent increase in concentration over time, both in the free and complexed forms. Ni(II) Exhibits a moderate increase in concentration over time, with the complexed form showing slightly higher concentrations. Mn(II) Shows a significant increase in concentration over time, particularly in the complexed form. Cu(II) Exhibits a substantial increase in concentration over time, with the complexed form showing the highest concentrations among the tested metals. These observations suggest that the metal ions, particularly in their complexed form with FTL, act as catalysts in the oxidation of phenol. The ligand likely plays a crucial role in stabilizing the metal ion by Preventing its precipitation or decomposition. Modulating the reactivity by enhancing the reactivity of the metal ion towards phenol. Facilitating electron transfer through acting as a ligand or electron transfer mediator between the metal ion and the phenol substrate. Investigating the effect of different ligands on the catalytic activity of the metal ions would provide valuable insights into the role of the ligand in the reaction mechanism. Understanding the specific role of each metal ion in the oxidation process is crucial for optimizing the reaction conditions.

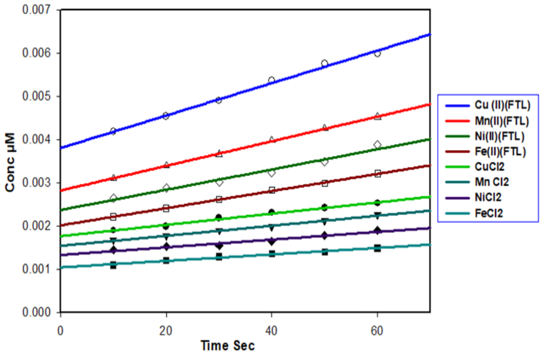


Fig. 3. Oxidation rate of phenol using metal salts and metals complexes with H_2O_2

Enhanced catalytic efficiency across all cases, the metal complexes with FTL as the ligand show significantly higher oxidation rates compared to their corresponding metal salts[55]. This demonstrates that the FTL ligand effectively enhances the catalytic activity of the metals. Selectivity and stability the improvement in the observed rates suggests that the FTL ligand not only increases the efficiency but potentially also the selectivity and stability of the metal catalysts. Ligand effects the FTL ligand likely facilitates better interaction between the metal center and the substrates (phenol and hydrogen peroxide), thereby accelerating the oxidation process. Overall, the data clearly shows the superior performance of metal-FTL complexes over their simple metal salt counterparts, making them more effective catalysts for the phenol oxidation process.

The compound was tested with various metal complexes, and it was found that the complex with copper (Cu(II) FTL) gave the best results. The copper complex exhibited significantly higher catalytic efficiency in the oxidation of phenol compared to other metal complexes such as Mn(II), Ni(II), and Fe(III). This superior performance is demonstrated by the highest observed rate among the tested complexes, indicating that copper is particularly effective in enhancing the oxidation process.

The effect of concentration of metal complex on oxidation of phenol

The concentration of metal complexes plays a crucial role in the oxidation of phenol[56]. Generally, increasing the concentration of the metal complex can enhance the oxidation rate up to a certain point. Beyond this optimal concentration, the reaction may reach saturation or even inhibition due to excessive catalyst presence. There is an optimal concentration at which the oxidation rate is maximized. Beyond this point, further increases in concentration may not significantly enhance the reaction rate and could potentially inhibit the process. The optimal concentration helps in minimizing the amount of catalyst required, reducing costs and waste. The study (Fig. 4) explored the impact of various concentrations of the copper complex [Cu(II) FTL] on the oxidation of phenol in the presence of 0.17 mM H_2O_2. Up to 100 μM, the observed rate of phenol oxidation increased linearly with the concentration of the copper complex, indicating a direct relationship between the catalyst concentration and the reaction rate. Beyond this concentration, the reaction rate began to plateau, suggesting the system reached a saturation point. Kinetic Parameters V_{max} (Maximum Rate)1.33x10^{-5} mMS^{-1}, K_m (Michaelis Constant) 37.6 mM and K_cat 3.5x10^{-7} S^{-1}. These parameters indicate that the oxidant is directly bound to the active metal center, optimizing the catalytic efficiency[57].

Table 4: Oxidation of Phenol by Different Concentrations of Cu(II)(FTL) and 0.17 mM H_2O_2

Concentration of Cu (II)FTL$_2$ μM	Observed rate V_o mMS^{-1}	Standard rate
40	6.153 x10^{-6}	0
60	8.205 x10^{-6}	6.487x10^{-6}
80	9.615 x10^{-6}	2.557x10^{-6}
100	1.026 x10^{-5}	4.815x10^{-6}
140	1.090 e^{-5}	4.320x10^{-6}
180	1.128 x10^{-5}	3.320x10^{-6}
220	1.201 x10^{-5}	6.239x10^{-6}
500	1.289 x10^{-5}	5.162x10^{-6}

The data in Table 4 indicates that the observed rate of phenol oxidation increases with the concentration of Cu(II)FTL up to a certain point, after which the rate plateaus and even slightly decreases. This trend suggests a complex interaction between the catalyst concentration and the reaction kinetics. Initial Increase in Reaction Rate At lower concentrations of Cu(II)FTL (40-80 μM), the observed rate of phenol oxidation increases significantly. This can be attributed to the availability of more catalytic sites, which enhances the reaction rate. The presence of Cu(II) ions facilitates the generation of reactive oxygen species (ROS) from H_2O_2, which are responsible for the oxidation of phenol. Plateau and Decrease in Reaction Rate: Beyond 80 μM, the observed rate does not increase proportionally with the concentration of Cu(II)FTL. At higher concentrations (100-500 μM), the rate plateaus and even shows a slight decrease. This behavior can be explained by the saturation of catalytic sites and possible inhibitory effects at higher catalyst concentrations. Excess Cu(II) ions may lead to the formation of inactive complexes or the scavenging of ROS, thereby reducing the overall reaction rate. Comparison with Standard Rates The standard rates provided in Table 3 serve as a benchmark for evaluating the efficiency of the Cu(II)FTL catalyst. The observed rates at lower concentrations (40-80 μM) are significantly higher than the standard rates, indicating the effectiveness of Cu(II)FTL in catalyzing the oxidation of phenol. However, at higher concentrations (100-500 μM), the observed rates are closer to or even lower than the standard rates, suggesting a decline in catalytic efficiency. Mechanistic Insights The oxidation of phenol by Cu(II)FTL and H_2O_2 likely involves a Fenton-like mechanism, complex of Cu(II) ions were more active to induce dissociation of hydrogen peroxide (H_2O_2) to peroxoanion (-OOH) and hydrogen ions (H^+) in the reaction mixture. Which are highly reactive and capable of oxidizing phenol to catechol and hydroquinone due to ortho and para substitution of hydroxyl group in the phenol[58,59] (Scheme 3).

The efficiency of this process depends on the concentration of Cu(II) ions and the availability of H_2O_2. At optimal concentrations, the generation of hydroxyl radicals is maximized, leading to efficient phenol oxidation. However, at higher concentrations of Cu(II), the formation of inactive complexes or the scavenging of hydroxyl radicals can reduce the reaction efficiency[60].

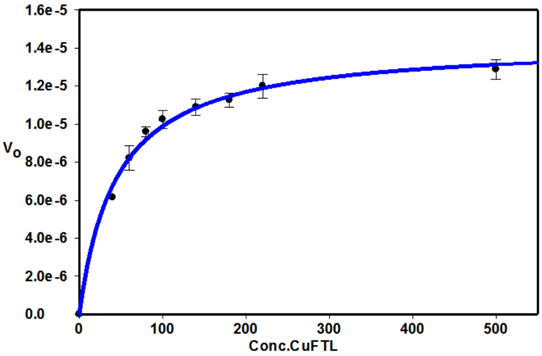


Fig. 4. Oxidation of 1mM of phenol by different concentration of $[Cu(II)(FTL)(OH)_2]$and 0.17mM of H_2O_2

The effect of concentration of phenol.

The kinetics of phenol oxidation using 100 µM Cu(II) FTL as a catalyst and 0.17 mM H_2O_2 demonstrate a model compound or mimetic enzyme kinetics. This system exhibits nonlinear behavior, reaching saturation at high phenol concentrations[61]. The process involves phenol binding to the Cu(II) FTL catalyst, forming an intermediate complex, which subsequently leads to the transformation of the phenol substrate into products. Phenol binds to the Cu(II) FTL catalyst, forming an intermediate complex (Scheme 3). This intermediate then facilitates the transformation of the bound phenol into the oxidation products. The kinetics of this reaction are quantitatively described by the Michaelis-Menten equation, commonly used for enzyme catalysis. $(k^{-1} + k\_cat)/k_1$.- Phenol Dissociation Constant (K_m) Expressed as First Order Catalytic Rate Constant (k_cat) = $2.7x10^{-7}S^{-1}$ Michaelis Constant (K_m): 44.7 mM. Nonlinear Behavior The rate of phenol oxidation increases with phenol concentration but eventually reaches a saturation point at higher concentrations, indicating that all active sites of the Cu(II) FTL complex are occupied. Kinetic Parameters The values of k_cat and K_m provide insights into the efficiency and capacity of the catalytic system under these conditions[62]. These findings highlight the importance of optimizing phenol concentration for maximizing the efficiency of the catalytic oxidation process using Cu(II) FTL Figure 5.

Table 5: Oxidation different concentrations of phenol by 100 µM of $CuFTL_2$ and 0.17 mM H_2O_2

Concentration of Phenol µM	Observed rate V_omMS^{-1}	Standard rate
40	$5.138x10^{-6}$	$2.051x10^{-7}$
60	$7.034x10^{-6}$	$3.547x10^{-7}$
80	$8.123x10^{-6}$	$2.761x10^{-7}$
100	$8.606x10^{-6}$	$4.904x10^{-7}$
140	$9.187x10^{-6}$	$2.761x10^{-7}$
180	$9.594x10^{-6}$	$2.761x10^{-7}$
2400	$1.002x10^{-5}$	$3.648 x10^{-7}$
3000	$1.051 e^{-5}$	$5.162x10^{-7}$
4000	$1.078x10^{-5}$	$1.297x10^{-6}$

The data The data in Table 5 indicates that the observed rate of phenol oxidation increases with the concentration of phenol up to a certain point, after which the rate plateaus and slightly increases. This trend suggests a complex interaction between phenol concentration and reaction kinetics. At lower concentrations of phenol (40-100 µM), the observed rate of phenol oxidation increases significantly. This can be attributed to the availability of more substrate molecules, which enhances the reaction rate. The presence of Cu(II) ions facilitates the generation of reactive oxygen species (ROS) from H_2O_2, which are responsible for the oxidation of phenol. Beyond 100 µM, the observed rate does not increase proportionally with the concentration of phenol. At higher concentrations (140-4000 µM), the rate plateaus and shows a slight increase. This behavior can be explained by the saturation of catalytic sites and possible inhibitory effects at higher substrate concentrations. Excess phenol may lead to the formation of inactive complexes or the scavenging of ROS, thereby reducing the overall reaction rate. The standard rates provided in Table 4 serve as a benchmark for evaluating the efficiency of the Cu(II)FTL catalyst. The observed rates at lower concentrations (40-100 μM) are significantly higher than the standard rates, indicating the effectiveness of Cu(II)FTL in catalyzing the oxidation of phenol. However, at higher concentrations (140-4000 μM), the observed rates are closer to or even lower than the standard rates, suggesting a decline in catalytic efficiency. The oxidation of phenol by Cu(II) FTL and H_2O_2 likely involves a Fenton-like mechanism, where Cu(II) ions react with H_2O_2 to generate hydroxyl radicals (•OH), which are highly reactive and capable of oxidizing phenol. The efficiency of this process depends on the concentration of phenol and the availability of H_2O_2. At optimal concentrations, the generation of hydroxyl radicals is maximized, leading to efficient phenol oxidation. However, at higher concentrations of phenol, the formation of inactive complexes or the scavenging of hydroxyl radicals can reduce the reaction efficiency[63].

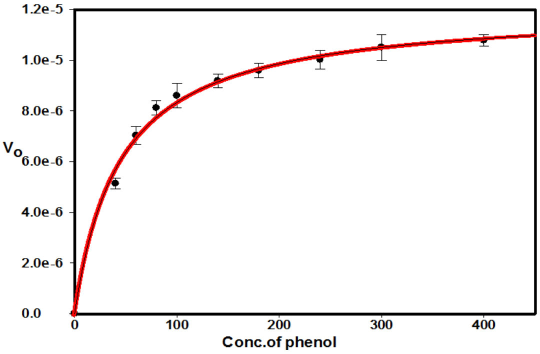


Fig. 5. Oxidation of different concentration of phenol by 100*μ*M of [Cu(II)(FTL)(OH)$_2$] and 0.17mM of H_2O_2

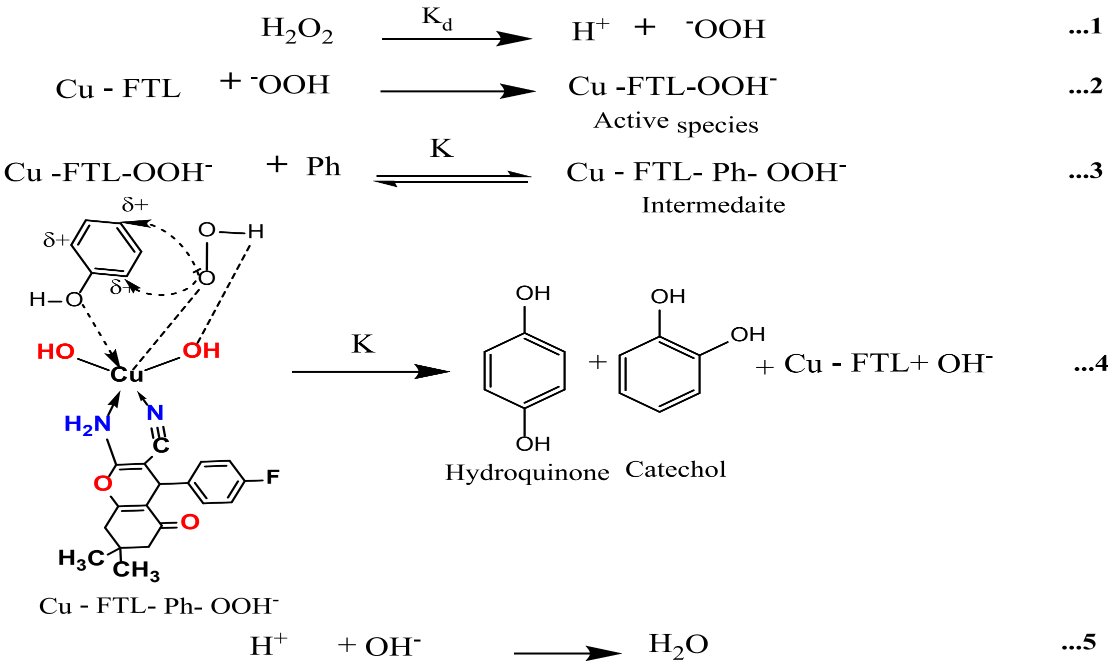
Exploring the Dual-Substrate Mechanism of Phenol Oxidation with H_2O_2.

The concentration of H_2O_2 (hydrogen peroxide) plays a crucial role in the oxidation of phenol, influencing the rate and efficiency of the reaction. The saturation pattern observed at high concentrations in the oxidation of phenol as a function of H_2O_2 Fig. 6 suggests a bi-substrate binding mechanism (Scheme 3). This implies that both phenol and H_2O_2 directly bind to the active metal center of the Cu(II) FTL complex, acting as substrates in the reaction. Bi-Substrate Binding Mechanism in this context, the bi-substrate binding mechanism means that both phenol and H_2O_2 are simultaneously interacting with the catalyst[64]. This interaction can be quantitatively described using the Hannes equation, which is similar to the Michaelis-Menten equation but adapted for bi-substrate systems. Phenol and H_2O_2 as Substrates both phenol and H_2O_2 are essential for the reaction, and their concentrations influence the overall reaction rate. Saturation Point At high substrate concentrations, the reaction rate reaches a maximum (V_{max}), beyond which it does not increase significantly, indicating that the active sites of the catalyst are fully occupied. By understanding and applying the Hannes equation, we can better describe and predict the kinetics of the phenol oxidation reaction in the presence of the Cu(II) FTL complex and H_2O_2. This approach helps in optimizing the reaction conditions for maximum efficiency and effectiveness.

Table 6: Kinetic Analysis of Phenol Oxidation with H_2O_2 Using Dual-Substrate Hannes Plot

Concentration of H_2O_2 mM	K_m	K_cat
0.068 mM	455.3	$1.063e^{-7}$
0.120 mM	435.1	$1.201e^{-7}$
0.136 mM	428.3	$1.34e^{-7}$
0.170 mM	414.5	$1.43e^{-7}$
0.204 mM	393.4	$1.59e^{-7}$
0.230 mM	358.6	$1.691e^{-7}$

The data shows the observed reaction rates (V_{obs}) for the oxidation of phenol at various concentrations (200-4000 μM) and different H_2O_2 concentrations (0.068 mM to 0.230 mM). At each H_2O_2 concentration, the reaction rate generally increases with increasing phenol concentration. This suggests that the reaction rate is positively correlated with the concentration of the substrate (phenol). For a given phenol concentration, the reaction rate generally increases with increasing H_2O_2 concentration, indicating that H_2O_2 is a necessary reactant for the oxidation process. To gain a deeper understanding of the reaction kinetics, further analysis is needed. Here are some potential approaches by Plot the observed reaction rate against the phenol concentration ([phenol]) at each H_2O_2 concentration[65]. This will help determine if the reaction follows Michaelis-Menten kinetics. Create double reciprocal plots at each H_2O_2 concentration. This will allow you to determine the Michaelis-Menten parameters for each H_2O_2 concentration.



Scheme 3. Mechanism for oxidation of phenol in presence of copper complex

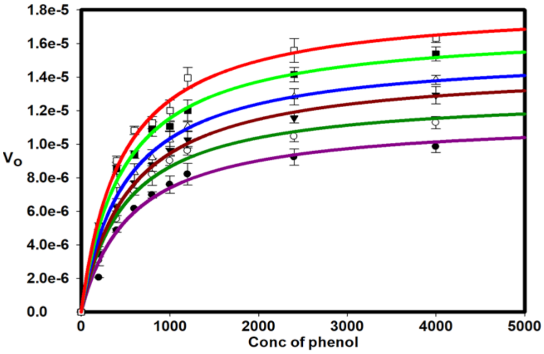


Fig. 6. Hannes Plot for bi-substrate binding oxidation of phenol as a function of H_2O_2 by 100 μM of CuFTL

CONCLUSION

This work focuses on the synthesis, characterization, and catalytic application of a novel copper(II) complex, Cu(II)(FTL), where FTL represents the 2-amino-4-(4-fluorophenyl)pyrazole ligand. Spectroscopic characterization confirmed the formation of the complex, revealing coordination of the copper(II) ion through the nitrogen atoms of the pyrazole's amino and [specify which nitrogen, e.g., N1 or N2 if applicable, or "ring nitrogen"] groups. This complex was then investigated as a catalyst for the green oxidation of phenol using hydrogen peroxide (H_2O_2) as the oxidant. Kinetic studies of the phenol oxidation, catalyzed by 100 μM Cu(II)(FTL) in the presence of 0.17 mM H_2O_2, yielded a Michaelis constant (K_m) of 44.7 mM and a turnover number (k_cat) of $2.7 \times 10^{-1} S^{-1}$. For comparison, the kinetic constants for the uncatalyzed oxidation by H_2O_2 alone were determined to be K_m = 37.6 mM and k_cat = 3.5×10^{-1} S^{-1}. The observed increase in K_m in the presence of the catalyst suggests a lower binding affinity of the catalyst for phenol compared to H_2O_2, which is consistent with a proposed mechanism where H_2O_2 is the primary substrate activated by the copper center. The relatively low k_cat values suggest a slow turnover rate, potentially due to [mention possible reasons, e.g., slow product release, stable intermediate formation]. Further investigation of the reaction mechanism and optimization of the catalytic system are warranted. This study demonstrates the potential of Cu(II)(FTL) as a catalyst for environmentally benign phenol oxidation."

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Conflict of interest

The author declare that we have no conflict of interest.

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