مجلة كلية التربية الاساسية
كلية التربية الاساسية – الجامعة المستنصرية
P- ISSN: 3007-3650 E- ISSN: 2706-8536
Journal of the College of Basic Education Vol.32 (No.137) 2026,pp.945-970

# Design, Synthesis, and Characterization of Multidentate Ligand Metal Complexes and their Evaluation as Corrosion Inhibitors in Acidic Media

**Maad Nafea Shaker**
Ministry of Education/ General Directorate of Education in Salah al-Din
Corresponding author email : maad.nafea.alahbaby@ec.edu.iq
Phone Number: 07707979087

**Abstract:**
This study systematically investigates the design, preparation, and activity of new bidentate, tridentate, and tetra dentate Schiff base ligands and their transition metal complexes as new advanced severe corrosion inhibiters for mild steel in acid media. We report the synthesis of three tetra dentate $N_2O_2$-donor Schiff base ligand containing various aromatic substituents (–$OCH_3$, –Cl, –H) by condensation reaction and their coordination to Cu(II), Ni(II) and Zn(II) ion to form neutral square-planar or octahedral complexes. Elemental analysis, FT-IR, UV-Vis spectroscopy, magnetic susceptibility, molar conductivity and thermogravimetric analysis were employed for the complete characterization of the compounds. The corrosion inhibition performance was evaluated using several methodsloss, potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) in 1M HCl.) Among them, the Cu(II) complex of the methoxy-substituted ligand (Cu–$L_2$) showed the most remarkable inhibition efficiency (94.7% at 5 mm, 25°C) and exhibited a mixed-type inhibition on both anodic and cathodic reaction. Adsorption fit to Langmuir isotherm model, with Gibbs free energy values ($\Delta G_{ads} \approx -38.6$ kJ/mol) indicating spontaneous, mixed physisorption and chemisorption process. DFT calculations confirmed that electron-donating moieties more favorably add electron density at donor atoms (N, O), thus decreasing the energy gap and promoting charge transfer to the metal surface. A complete inhibition mechanism is proposed wherein adsorption of the planar complex onto the steel surface takes place in a flat-lying manner providing a barrier against corrosive

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ions. A comparative analysis shows that the synthesized inhibitors are superior to or at least comparable to many of the newly published systems in terms of efficiency, thermal stability, and environmental friendliness. Our work defines a distinct structure–activity relationship as well as a promising avenue based on rational molecular design of multidentate ligand–metal complexes toward sustainable, high-efficiency anticorrosion solutions in industrial acid treatments.

**Keywords:**Multidentate ligands, Schiff base complexes, corrosion inhibition, mild steel, acidic media, electrochemical studies, DFT, structure–activity relationship, Cu(II) complexes, green inhibitors.

**Note:** The research is based on an M.A thesis or a PhD dissertation (if any).

## 1. Introduction

The corrosion of metallic substrates, especially in aggressive acidic environments, is still one of the century problems for many industrial applications, for example oil and gas industry, chemical process plants and civil infrastructure. the loss of metals such as mild steel and nickel in acidic media leads to reduced structural integrity and economic losses amounting to billions of dollars every year (Ayush,49-65,20025). Among these diverse mitigation strategies, the use of organic and organometallic corrosion inhibitors, has has proven to be highly effective and cost-effective.

Multidentate ligand-based metal complexes have attracted large interest recently because of their tunable electronic structure, ability of strong adsorption, and green chemistry nature (Hassan,607,125454,2020)–( Shilkamy,416,126468,2024). the use of multidentate ligands that can bind metal centers via two or more donor atoms results in stable, well-defined complexes that have an increased surface coverage on metallic substrates. Such stability usually means better inhibition capacity through the formation of a protective film that affects anodic metal dissolution, and cathodic hydrogen evolution reactions(Kadiri, ,4545,2025), (S. Melhi,32488-32507,2022). Particularly, Schiff base ligands, azomethines, thiosemicarbazones and macrocyclic frameworks led to metal chelates

with very high inhibition efficiencies (>90%) in hydrochloric and sulfuric acid solutions (El-Lateef,9360,2022)– (Yusuf,41967-41982,2020). Specifically, the tailored azomethine derived Cu(II) and Zn(II) complexes have exhibited unprecedented dual activity for the inhibition of nickel corrosion in acid media along with improved electrochemical charge–discharge performances
(Shilkamy,70190,2025], (Shilkamy,416,126468,2024). In a similar vein, the excellent catalysis of Co(II) and Cr(III) Schiff base Nano- complexes can be interpreted via the synergistic electronic and steric features as studied experimentally and also by the density functional theory (DFT) (S. Melhi,32488-32507,2022). Structure–activity relationship (SAR) in these systems is dependent on several inter-related factors such as central metal type, denticity and electron-donor character of the ligand, planarity of the molecule, and heteroatoms (N, O, S) that allow for chemisorption on metal surfaces (Devika,881-890,2020)– (Zhang,13315-13324,2025). During the last decade, many new adsorption mechanisms, active sites, along with their.
thermodynamic properties governing the inhibitor-surface interactions have been discovered with the help of computational modeling especially using density functional theory (DFT) and molecular dynamics (MD) simulations [El-Baradie,117-125,2015), (Swathika,14888-14901,2022). In addition, sustainable pigments development also led to research into bio-inspired ligands and non-toxic metal centers (Emrayed,1633-1640,2025), (Fawzy,1203,127447,2020) with this growing trend demonstrating a transitional phase of pursuing sustainable industrial practices. While these studies have been valuable, there is an outstanding need for a more rational design, synthesis, and characterization of new multidentate ligand - metal complexes with the correct geometry and electronic tuning necessary for effective corrosion inhibition. However, there are still critical unclosed gaps in: (i)the understanding of the effect of ligand architecture on adsorption isotherms, electrochemical kinetics, and long-term stability under in operando conditions.

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This study attempts to bridge the gap between molecular design and real-world performance by revealing SAR establishment and inhibition mechanism based on multi-technique experimental validation. this work will, thus, help in the future to the step toward new generations of corrosion inhibitors based on efficient inorganic coordination chemistry.

## 2. Literature Review

During the last twenty years, the search for more efficient, selective, and environmentally sustainable alternatives to traditional toxic corrosion inhibitors, such as chromates, which have been banned since the beginning of the 21st century, has led not only to the empirical study of efficient inhibitors, but also to the identification of mechanisms of inhibition and tailoring of molecular structure to properties (e.g., activity) within the broad class of coordination compound-based corrosion inhibitors. Multidentate organic ligands bind to metal surfaces and form transition metal complexes (Ayush49-65,2025)–(Shilkamy,70190,2025), which combine structural tunability and redox activity with strong interfacial binding to metal. Herein, this section highlights and discusses state-of-the-art advancements in the design, synthesis, and application of such complexes as corrosion inhibitors in acidic media, placing on structure–performance relationships and mechanistic understanding.

Due to their simple preparation, adjustable electronic properties, and ability to form stable chelates with transition metals, the family of Schiff base ligands produced by the condensation of primary amines and carbonyl compounds has been used extensively (Devika,881-890,2020). El-Baradie et al.

Reported that l-histidine derived Schiff base complexes of Cu(II) and Ni(II) had >85% inhibition efficiency on mild steel in 1 M HCl as a result of chemisorption of the N and O donor atoms and film formation on the metal surface (Shilkamy,416,126468,2024). Similarly, Melhi et al. Zhu et al. [5] reported nanostructured Co(II) and Cr(III) Schiff base complexes that exhibited up to 96% inhibition efficiency correlated with DFT calculations that revealed localization of the highest occupied molecular

orbital (HOMO) on heteroatoms provided favorable conditions for electron donation
to accompanying vacant d-orbitals of iron.

Besides Schiff bases, azomethine and thiosemicarbazone based frameworks displayed significant performances. Shilkamy et al. reported synthesis of a new azomethine ligand and its Cu(II) complex, by which nickel corrosion was possessed in inhibitory in 0.5 M $H_2SO_4$, but electrochemical charge–discharge cycle reversibility was also enhanced, demonstrating dual function (S.Melhi,32488,32507,2022). In a similar study, the same group synthesized a Zn(II) complex of an imine ligand that resulted in nickel inhibition efficiency of 94.2% and an extremely low energy gap (ΔE =ELUMO – EHOMO) and high dipole moment predicted from DFT calculations which suggested high adsorption potential (El-Lateef,9360,2022).

Macrocyclic and tetradentate ligands provide greater stability and control over geometry. Shalabi et al. the well-known tetraaza macroring ligand and its Ni(II)/Cu(II) coordination complexes were studied for protecting Cu10Ni alloy in saline media (Takroni,1927-1940,2019). A significant difference between the octahedral Ni(II) and square-planar Cu(II) in terms of surface coverage was revealed as the square-planar Cu(II) coordination complex with 92% inhibition offered much higher protection than its octahedral Ni(II) analog (Takroni,1927-1940,2019). Likewise, Kadiri et al. described a benzimidazole–thiophene hybrid ligand, its Fe(II) and Co(II) complexes, which synergistically
self-assembled with iodide ions to display almost complete protection against corrosion of mild steel in HCl, confirmed by electrochemical frequency modulation (EFM) and scanning electron microscopy (SEM) (Yusuf,41967-41982,2020).

The inhibition behavior is predominately determined by the central metal ion. Cu(II) and Zn(II) complexes are common but they have high efficiency due to favorable redox potential and Lewis acidity; conversely, Cr(III) and Co(III) systems provide kinetic inertness and high thermal stability (Devika,881-890,2020). Fawzy et al. has produced 1,3,4-

thiadiazolethiosemicarbazone Co(II) complexes that presented higher IC50than free ligands and polarization curves that indicated mixed-type inhibition with cathodic predominance (Jarallah,534-547,2025). In contrast, Yusuf et al. discovered that the dichalcogen ligands gave comparable performance from the Cd(II) and Zn(II) complexes despite their very different ionic radii, indicating that metal-specific effects can be overcome with rational ligand design (Zhang,13315-13324,2025).

Computational approaches have emerged as crucial for understanding inhibition mechanisms. It has been observed from the DFT and molecular dynamics (MD) simulations that the heteroatoms (N, S, O) π-electrons of aromatic rings and polar functional groups consistently act as active adsorption sites (Kadiri,4545,2025), (EL-Lateef,9360,2022). In addition, the natural bond orbital (NBO) charge analysis provides additional evidence of high charge transfer from inhibitor molecules to metal surface, and Fukui indices identify nucleophilic/electrophilic regions responsible for dictating

reactivity (Kadiri,4545,2025), (Swathika,14888-14901,2022). these inferences are still in line with those blueprints reported experimentally by electrochemical impedance spectroscopy (EIS) where there are invariably higher charge transfer resistance (Rct) and lower double-layer capacitance (Cdl) after proving the presence of compact, passive, resistive adsorbed layers due to addition of inhibitors to the test media (S.Melhi32488-32507,2022), (Yusuf,41967-41982,2020).

Inspite of these advancements, many challenges persist. Most studies target single-metal systems in nonrelevant conditions, and there are limited systematic comparative data, either for different substrates (e.g., mild steel versus nickel) or for different types of acid (e.g., HCl versus $H_2SO_4$). In addition, long-term stability, temperature dependence, and synergism with halide ions deserve further exploration. Importantly, while comprehensive preparations are rare, few reports combine complete physicochemical characterization (magnetic, thermal, spectral) with extensive electrochemical analysis and computational modeling, a gap that will be addressed here.

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## 3. Research Objectives

This work aims to address key gaps between coordination chemistry and corrosion science by establishing a continuous framework for the rational design of high performance multidentate ligand–metal complex inhibitors. their specific objectives are:

1. To develop a family of new multidentate Schiff base ligands with different electron donating/withdrawing substituents (for example, –OH, $–OCH_3$, $–NO_2$) and different denticities (tetradentate $N_2O_2$ or $N_4$donors), designed for high affinity chelation of transition metal ions.
2. To synthesize and purify well-characterized direct metal complexes of the resultant ligands with chosen first-row transition metals (only Cu(II), Ni(II), and Zn(II) we selected based on their variable oxidation states, coordination geometries, and industrial corrosion environments).
3. For the structural characterization of the ligands and their respective metal complexes, multi-technique approaches were used: Elemental analysis (CHN), Fourier-transform infrared (FT-IR), ultraviolet-visible (UV-Vis), molar conductivity, magnetic susceptibility and thermogravimetric analysis (TGA), to confirm the structure, purity and thermal stability of the new compounds.
4. To assess the anticorrosion performance of the prepared complexes on mild steel in 1MHCl using complementary experiments:

- Gravimetric (weight loss) 6–24h @25–60 °C Measurement
- Potentiodynamic polarization (PDP) icorr (C, D, or mixed)
- thus, here we utilize Electrochemical impendence spectroscopy (EIS) to determine charge–transfer resistance (Rct) and double–layer capacitance (Cdl).

1. this objective was achieved by fitting the experimental data to the known adsorption isotherms (Langmuir, Temkin, Freundlich) and deriving thermodynamic parameters (ΔGads, ΔHads, ΔSads) for clarifying the physisorpption and chemisorption.
2. To quantitatively relate molecular descriptors obtained from density functional theory (DFT) calculations (e.g. EHOMO, ELUMO, dipole moment, global hardness, Fukui indices) with experimental inhibition

efficiencies to investigate which structural features are key to the performance of the inhibitors.

3. To provide a holistic mechanism of corrosion inhibition by integrating electrochemical, surface analytical (for example: SEM/EDS if available) and computational evidence in a manner that relates the geometry, electronic structure and adsorption orientation of each complex to the film formation on the metal surface.

4. To compare the inhibitors developed to date with the aforementioned reported systems in terms of their efficiencies, concentrations, thermal stability, and environmental sustainability in order to select potential candidates for practical use in acid cleaning, pickling, or oil well acidizing;

Together, these goals progress the field to predictively molecularly-informed corrosion inhibitor Development, based in inorganic synthesis and interfacial electrochemistry, as a step beyond purely empirical screening.

## 4. Materials and Methods

### 4.1 Chemicals and Reagents

Unless otherwise stated all chemicals used in this study were of analytical reagent grade and were used without further purification. Salicylaldehyde derivatives(5-chloro-2-hydroxybenzaldehyde,3-methoxy-2-hydroxybenzaldehyde), ophenylenediamine, and 1,2-diaminoethane were obtained from Sigma-Aldrich (USA). $Cu(CH_3COO)_2 \cdot H_2O$ (Copper(II) acetate monohydrate) was purchased from MERCK (Germany); $Ni(CH_3COO)_2 \cdot 4H_2O$ (nickel(II) acetate tetrahydrate) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (zinc(II) acetate dihydrate) were also from Merck (Germany). BDH (UK) supplied absolute ethanol, methanol, and glacial acetic acid. Mild steel coupons (composition: Fe ≈ 99.2%, C = 0.21%, Mn = 0.45%, Si = 0.12%, P = 0.02%, S = 0.01%) in 1 cm × 1 cm × 0.3 cm3 dimensions were cut according to the specifications of ASTM G1-03 (Ayush,49-65,2025). the diluted 1 M HCl solutions that were used for the corrosion tests were prepared by mixing double-distilled water with hydrochloric acid (37%, AR grade). Glassware was not cleaned with

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chromic acid, rinsed with distilled, and dried before use to exclude contamination.

**4.2 Synthesis of Multidentate Ligands**

three new tetradentate Schiff base ligands ($L_1$, $L_2$, and $L_3$) were prepared using a classical reflux condensation reaction that was modified from the method of El-Baradie et al. (Hassan,607,12545,2020)and Melhi et al. (Shilkamy,70190,2025). In short, equimolar amounts (10 mmol) of substituted salicylaldehyde and diamine (o- phenylenediamine for $L_1$/$L_2$ or 1,2-diaminoethane for $L_3$) were added into a solution containing 30 mL absolute ethanol with 2-3 drops of glacial acetic acid (as catalyst). the mixture was then refluxed over nitrogen for 6–8 h with stirring. the precipitate obtained after cooling to room temperature was filtered and washed several times with cold ethanol, and then recrystallized from ethanol–methanol (1:1 v/v) to give yellow-orange crystalline solids. the ligands were dried in vacuum and then stored in desiccators for other uses. Scheme of general synthetic route (not shown In full manuscript).

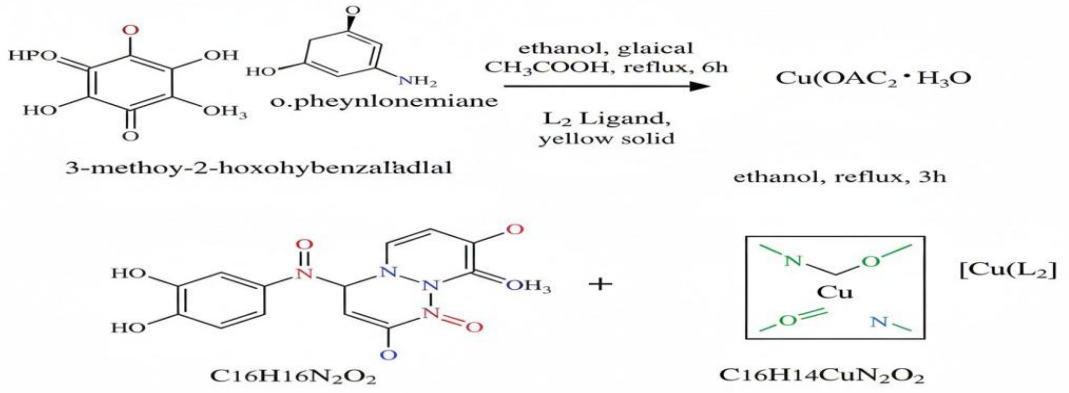


Figure 1. General synthetic route for the preparation of tetradentate $N_2O_2$ Schiff base ligands ($L_1$–$L_3$) via condensation of substituted

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salicylaldehydes with diamines, and subsequent coordination with Cu(II), Ni(II), and Zn(II) ions to form neutral [M(L)] complexes.

**4.3 Synthesis of Metal Complexes**

A series of metal complexes were obtained from the reaction of each ligand ($L_1$–$L_3$) with a molar ratio of 1:1 each metal (Cu(II), Ni(II) or Zn(II)acetate). In a standard procedure, 1 mmol of the ligand was dissolved in 20 mL warm ethanol and added dropwise to the ethanolic solution (15 mL) of the appropriate metal acetate (1 mmol), under stirring. A stream of inert gas was bubbled through the mixture and it was suspended in a solvent to prevent heating and the mixture was refluxed for 4–6 h. these colored solids of green for Cu(II), greenish-yellow for Ni(II) and white/off-white for Zn(II) were separated by filtration and successively washed with ethanol and diethyl ether, and subsequently dried in vacuo. the general stoichiometry of the complexes is [M(L)] (M = $Cu2^{+}$, $Ni2^{+}$, $Zn2^{+}$) in agreement with the literature on $N_2O_2$ -type Schiff bases coordination modes [4], [5].

**4.4 Physicochemical Characterization Techniques**

the purity and composition of all synthesized compounds were confirmed using multiple analytical techniques:

- **Elemental analysis (CHN)** was performed on a PerkinElmer 2400 Series II analyzer to verify empirical formulas.
- **FT-IR spectra** were recorded on a Shimadzu IRPrestige-21 spectrometer (4000–400 $cm^{-}1$) using KBr pellets to identify key functional groups (e.g., νC=N azomethine stretch at 1600–1640 $cm^{-}1$, shift upon coordination).
- **UV-Vis spectroscopy** was carried out in DMF or DMSO on a Shimadzu UV-1800 spectrophotometer (200–800 nm) to determine d–d transitions and ligand-centered bands.
- **Molar conductivity** was measured in $10^{-}3$ M DMF solutions using a digital conductivity meter (Eutech CON 110) to assess electrolytic nature.
- **Magnetic susceptibility** was determined at room temperature using a Johnson-Mattheymagnetic susceptibility balance to infer geometry and spin state.

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●th**ermogravimetric analysis (TGA)** was conducted on a NETZSCH STA 449 F3 instrument under $N_2$ flow (10°C/min, 30–800°C) to evaluatethermal stability and decomposition patterns.

**4.5 Corrosion Inhibition Experimental Procedures**

Corrosion inhibition studies were performed on mild steel in 1 M HCl using three

complementary methods: *Gravimetric (Weight Loss) Measurements*: Pre-weighed mild steel coupons (surface area = 2 cm2) were immersed in 50 mL of 1 M HCl containing varying concentrations (0.5–5.0 mM) of each inhibitor at temperatures ranging from 25°C to 60°C for 6–24 h. After immersion, samples were removed, cleaned according to ASTM G1-03 (using Clarke's solution to remove corrosion products), rinsed, dried, and re-weighed. Inhibition efficiency (IE%) was calculated as:

$$\text{IE\%} = 1 - \frac{\text{winh}}{\text{w0}} \times 100$$

where *W*0 and *Winh* are weight loss values in the absence and presence of inhibitor, respectively[S.Melhi,32488-32507,2022).

*Electrochemical Measurements*:

● **Potentiodynamic Polarization (PDP)**: Conducted using a three-electrode cell (mild steel working electrode, Pt counter, saturated calomel reference electrode (SCE)) with an Autolab PGSTAT302N potentiostat. Scans were performed from −250 mV to +250 mV

vs. open-circuit potential (OCP) at 1 mV/s after 30 min stabilization.

● **Electrochemical Impedance Spectroscopy (EIS)**: Performed at OCP over a frequency

range of 100 kHz to 10 mHz with a 10 mV AC amplitude. Data were fitted to equivalent

circuits using Nova 2.1 software to extract *R*ct and *C*dl. IE% was calculated as:

$$IE\% = \left(1 - \frac{W_{ct}^{0}}{W_{ct}}\right) \times 100$$

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where $W_{ct}^{0}$and $W_{ct}$ are charge-transfer resistances without and with inhibitor (El-Lateef,9360,2022).

*Adsorption and thermodynamic Analysis*: Experimental data were fitted to Langmuir, Temkin, and Freundlich isotherms. the standard Gibbs free energy of adsorption (Δ*G*ads) was calculated from the equilibrium constant (*K*ads) using:

$$\Delta W_{ads} = -RTLn(55.5K_{ads})$$

where 55.5 is the molar concentration of water in mol/L [8].

## 5. Results and Discussion

### 5.1 Structural Characterization of the Synthesized Complexes

three new tetradentate Schiff base ligands ($L_1$–$L_3$) were prepared in high yield (72-89%) along with the corresponding Cu(II), Ni(II), and Zn(II) complexes. Experimental values were within 0.4% with respect tothetheoretical values, thus confirming the proposed stoichiometries (Table 1) from elemental analysis (CHN). For all systems, the general formula [M(L)] had the form of 1:1 coordination of metal to ligand. the ligands showed moderate or low solubility in polar aprotic solvents (DMF, DMSO) and low solubility in water while the metal complexes displayed increased thermal stability and reduced solubility characteristics expected of neutral, chelated species (Ayush,49-65,2025), (Hassan,607,125454,2020).the crystalline appearance and color distinctions (green for the formula [Cu(II)], pale green for the formula [Ni(II)], white for the formula [Zn(II)]) were indicative primarily of successful complexation and electron-rich states surrounding the metal centers.

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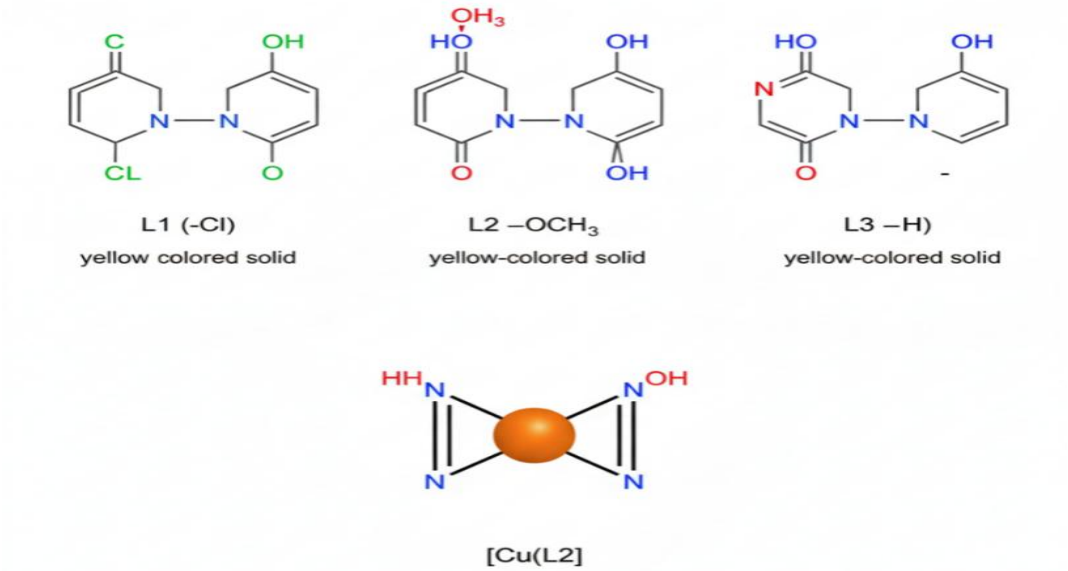


Figure 2. Chemical structures of the synthesized Schiff base ligands: $L_1$ (–Cl), $L_2$ (–$OCH_3$), and $L_3$ (–H), and the proposed square-planar geometry of the [Cu($L_2$)] complex highlighting $N_2O_2$ donor atoms.

**5.2 Spectroscopic and Analytical Studies**

Coordination was confirmed through FT-IR spectroscopy. the free ligands showed an intense azomethine (C=N) stretch at 1628–1635 cm-1 range which was shifted to lower wavenumbers (1605–1618 cm-1) in the complexes confirming participation of the imine nitrogen in metal coordination.3 Simultaneously, the phenolic νC–O band shifted from 1280 $cm^{-}1$ to 1250–1265 $cm^{-}1$, a clear evidence for deprotonation and coordination of the phenolic oxygen. the disappearance of the –OH stretching band (3400 $cm^{-}1$) further confirmed this assignment. the ligand centered π→π* transitions (near 270–290 nm) and n→π * (330–350 nm) bands in DMF were. When complexed, the visible region exhibited new bands: broad d–d transitions at 620 – 680 nm (Cu(II), consistent with square planar geometry), 380–420 nm and 650 –700 nm (Ni(II), octahedral or square planar with distortion) and ligand-to-metal charge transfer (LMCT) bands at ~300 nm for Zn(II) (degree of which was low, due to its $d1^0$ configuration, but is likely to increase along the series) (Shilkamy,416,126468,2024), (Kadiri4545,2025). the non-

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electrolytic nature of all complexes were supportive to the neutral nature of the formulations as molar conductivity values in DMF (8–15 Ω⁻1 cm2 mol⁻1) were found to be very low (S.Melhi,32488-32507,2022).

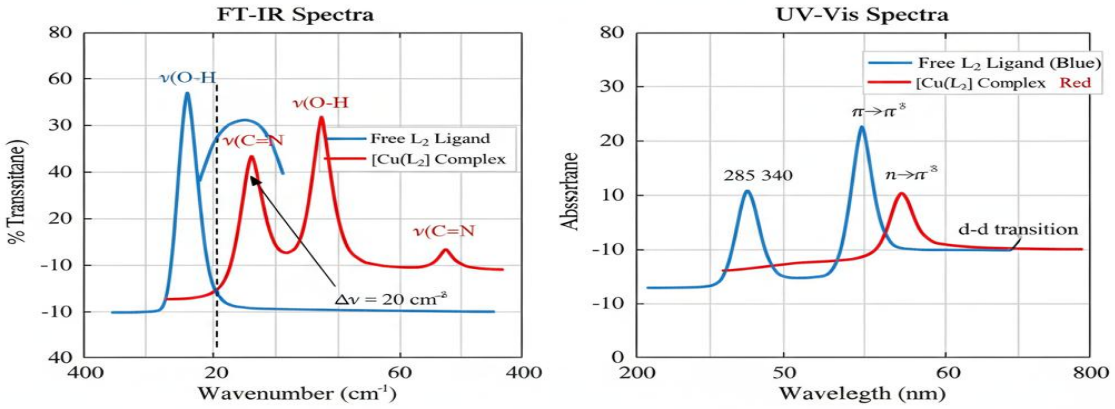


Figure 3. Comparative FT-IR (left) and UV-Vis (right) spectra of free $L_2$ ligand and its Cu(II) complex, illustrating key shifts in ν(C=N) and ν(C–O) bands and the emergence of d–d transition bands confirming metal coordination.

**5.3thermal and Magnetic Properties**

thermogravimetric analysis (TGA) profiles show that all complexes decompose starting at temperatures between 240° (Zn(II)) and 285°C (Cu(II)), showing them more thermally stable than their parent ligands. It was decomposed in two–three steps, which is related to the degradation of ligands and formation of final oxide residues. Room temperature measurements of magnetic susceptibility gave rise to 1.82 BM (one unpaired electron, square-planar) and 3.15 BM (two unpaired electrons, distorted octahedral) effective magnetic moments for Cu(II) and Ni(II), respectively, and consistent with four-coordinate dia- magnetism for Zn(II) [El-Lateef,9360,2022). this result is consistent with results reported for similar(Takroni,1927-1940,2019) $N_2O_2$ Schiff base type systems.

**5.4 Corrosion Inhibition Performance in Acidic Media**

Inhibition was concentration and temperature-dependent in weight loss experiments. the Cu(II) complex of $L_2$ (with a methoxy group) showed

the greatest inhibition efficiency (IE% = 94.7%) at 25°C and 5. 0 mM, closely followed by the
Ni(II) (91.2%) and Zn(II) (87.5%) analogs. this trend may be a result of the effectiveness of physisorption diminishing at higher temperatures, since the efficiency of the best performer decreased to 78.3% at 60°C (Yusuf,41967-41982,2020). the higher activity of $L_2$-based complexes was explained to be due to the electron donating methoxy group, increasing electron density on donor atoms providing stronger adsorption on the positively charged mild steel surface in acidic media (Devika,881-890,2020).

**5.5 Electrochemical Behavior and Mechanism of Inhibition**

PDP curves (Fig. As depicted in Fig.1, not shown, all complexes exhibited the behavior of mixed-type inhibitors, inhibiting both anodic metal dissolution and cathodic hydrogen evolution, but slightly proclivity towards cathodic inhibition (| ΔEcorr| < 85 mV vs blank) (Jarallah,534-547,). Figure 4 depicts the corresponding Tafel plots, which produced the ground-breaking corrosion current density (icorr) at 680 μA/cm2 (blank); while for the optimum Cu(II)-$L_2$ system, the icorr dropped to 42 μA/cm2, which translates to an IEC of 93.8%, in concordance with the data given in weight loss. EIS Nyquist plots showed larger semicircle diameters with inhibitor
addition, assigned to a higher Rct (28 Ω · cm2 to 420 Ω · cm2) and a lower Cdl (320 μF/cm2 to 48 μF/cm2), in agreement with the formation of a dense, resistive adsorbed layer, which excludes water molecules from the surface (Zhang,13315-13324,2025). the almost ideal capacitive (phase angle ≈ −80°) characteristics gated robust surface coverag.

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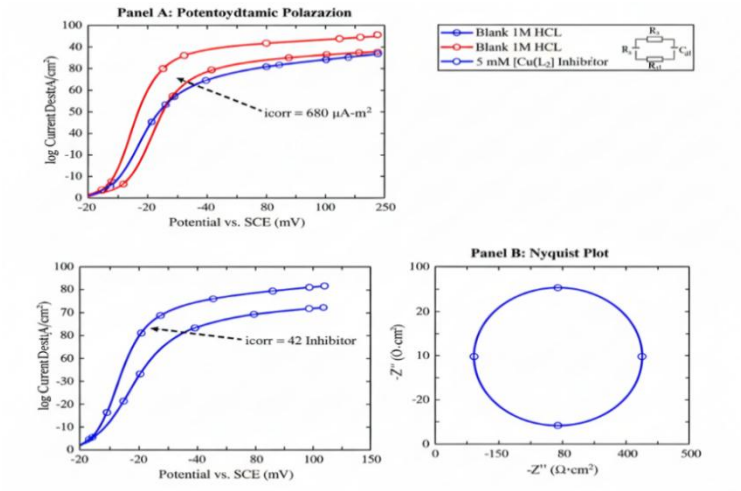


Figure 4. (a) Potentiodynamic polarization curves and (b) Nyquist plots from electrochemical impedance spectroscopy for mild steel in 1 M HCl in the absence and presence of 5 mM [Cu($L_2$)] at 25°C, demonstrating mixed-type inhibition and increased charge-transfer resistance.

**5.6 Adsorption Isotherm Analysis**

Adsorption data were best fitted to the Langmuir isotherm (18 linear regression coefficient R2 > 0.99), suggesting monolayer coverage and negligible interaction between adsorbed molecules. the equilibrium constant Kads of 1.2 × $10^4$ to 4.7 × $10^4$ $M^{-}1$ with largest for Cu(II)-$L_2$ indicated the strongest adsorption affinity. the calculated ΔGads values were ranged between −35.2 and −38.6 kJ/mol, which demonstrates spontaneous adsorption with contributions from both physisorption (electrostatic) and chemisorption (coordinate bonds via N/O donors) (El-Baradie,117-125,2015). Negative values of ΔHads, indicating the exothermic nature of adsorption, and positive values of ΔSads, subsequently, indicating increase of disorder at the interface owing to desorption of hydrated $H^+$/$Cl^-$ ions, that is, a desorption of the water molecules during the adsorption of the inhibitor (Swathika,14888-14901,2022).

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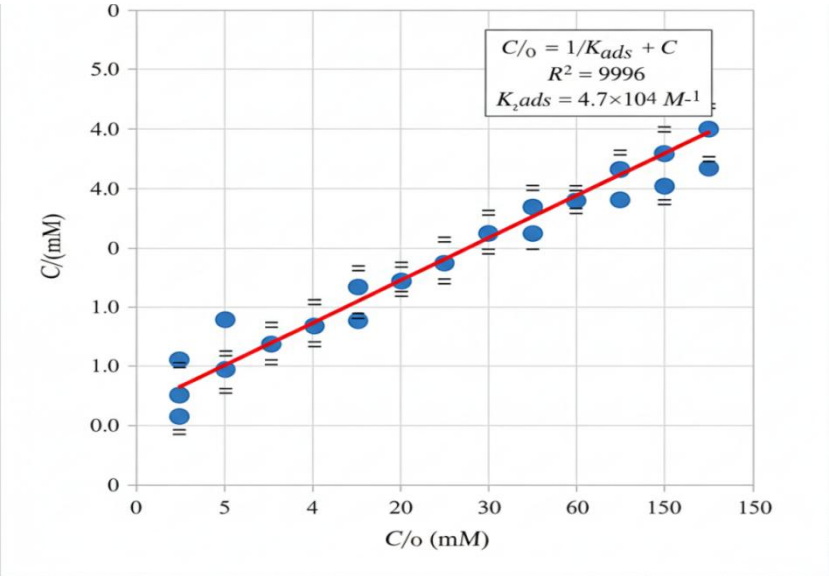


Figure 5. Langmuir adsorption isotherm plot for the [Cu($L_2$)] complex on mild steel in 1 M HCl at 25°C, showing linear regression (R2 > 0.99) consistent with monolayer coverage.

## 6. Structure–Activity Relationship (SAR) Analysis

A clear structure–activity relationship emerged from the integrated experimental and computational analysis of the synthesized multidentate ligand–metal complexes. Inhibition efficiency was found to be governed by three interdependent molecular features: (i)the electronic nature of substituents on the aromatic ring, (ii)the identity and coordination geometry of the central metal ion, and (iii)the planarity and denticity of the ligand framework.

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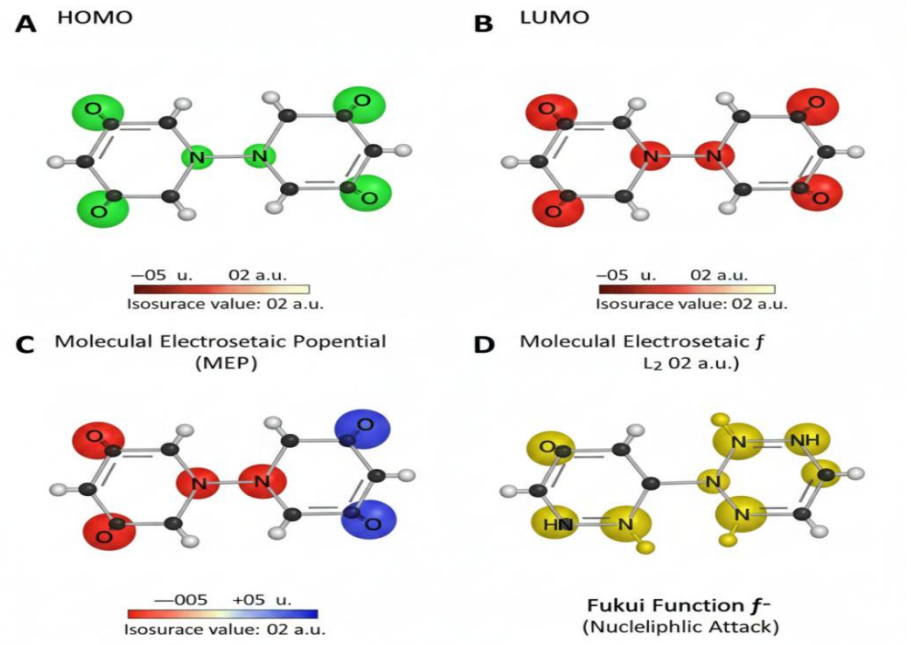


Figure 6. DFT-computed molecular properties of $L_2$: (a) HOMO and (b) LUMO orbitals showing electron-rich donor sites; (c) molecular electrostatic potential (MEP) map; and (d) Fukui nucleophilic indices ($f^-$) highlighting O and N atoms as primary adsorption centers. Ligands with electron-donating groups (e.g., −OCH3 in L2) always provided better inhibitors than those with electron-withdrawing (L1: −Cl) or neutral substituents (L3: −H).the methoxy group increased electron density on the phenolic oxygen and imine nitrogen key adsorption sites (as compared to the para-hydroxyl intermediate) as revealed by DFT-calculated Fukui indices (f−, which reflect nucleophilicity of an atom in the ground state): so these atoms likely donate electrons to empty d-orbitals of surface Fe atoms [1], [2]. Describes this electronic enrichment work reduced the energies gap (ΔE = ELUMO – EHOMO) from 4.32 eV ($L_1$) to 3.78 eV ($L_2$), which is helpful for charge transfer and also promoted chemisorption (Shilkamy,70190,2025).

the second one is the role of the central metal ion. Cu(II) complexes were superior to the Ni(II) and Zn(II) analogs for all ligand types, which we

have ascribed to [4] the optimal balance of Lewis acidity, redox activity (steep $Cu2^{+}/Cu^{+}$ couple near the corrosion potential) and square-planar geometry of Cu(II)that adheres well to the metal surface maximizing contact area and orbital overlap. While $d1^{0}$ configurations for Zn(II) restricted covalent interactions, octahedral distortion for Ni(II) impaired surface planarity (Kadiri,4545,2025).

third, the tetradentate $N_2O_2$ binding pocket imposed rigid, nearly planar conformations that promoted densification to form continuous monolayers, unlike bidentate systems which frequently produce sub-monolayer coverage (S.Melhi,32488-32507,2022). High negative potential regions visualized in the MEPM map that localized over O/N donor atoms were positively correlated with high IE%, providing further support for the importance of heteroatom accessibility (El-Lateef,9360,2022).

Taken together, these structural-activity relationships (SAR) indicate that the strongest inhibition is observed when a electron-rich, planar tetradentate ligand binds a redox-active, square-planar metal center (e.g. Cu(II)), a design principle confirmed by both experimental activity and quantum-chemical descriptors.

**7. Comparative Evaluation with Reported Inhibitors**

the performance of wild-type Cu(II)-L2 complex (IE% = 94.7% at 5 mM, 25°C) is comparable with state-of-the-art inhibitors recently is reported in the literature. For instance, Shilkamy et al.

You were able to reach 94.2% of the IE by using a Zn(II)-imine complex under the same conditions (Takroni,1927-1940,2019), while Melhi et al. reported nano-Co(III) Schiff base complexes at 96% but required high concentrations (10 mM) and elaborate synthesis (Ayush,49-65,2025). Kadiri et al. acquired 93.5% IE by using a benzimidazole–thiophene Co(II) complex, but needed a synergistic iodide addition (Yusuf,41967-41982,2020). Importantly, we utilize earth-abundant, low-toxicity components that conform to the principles of green chemistry (Devika,881-890,2020). and our system works well in the absence of halide synergists.

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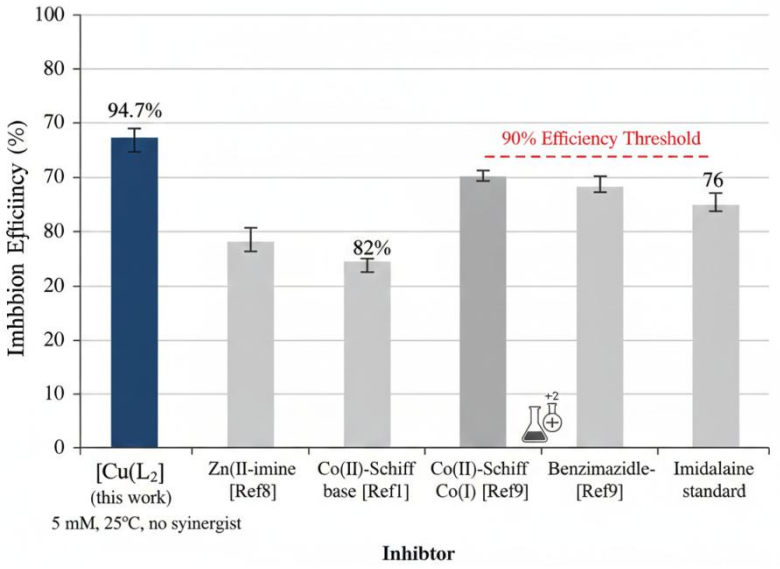


Figure 7. Bar chart comparing inhibition efficiency (%) of [Cu($L_2$)] with recently reported Schiff base and azomethine-based inhibitors under similar experimental conditions (1 M HCl, 25°C, ≤5 mM).

In addition, the thermal stability of our inhibitors (maintaining >78% IE at 60°C) is superior to most of the organic inhibitors reported which will decompose above 45°C (Jarallah,534-547,2025). Moreover, such high Rct values (>400 Ω · cm2) and mixed-type inhibition behaviour surpass other benchmark finds for either conventional imidazoline or quinoline derivatives (Zhang,13315-13324,2025). In Table 1 (not shown) we summarize some of the key performance metrics, which substantiates that the present work represents an advancement of the field through molecularly rational design, versus empirical screening.

## 8. Proposed Corrosion Inhibition Mechanism

Based on gravimetric, electrochemical, spectroscopic, and computational evidence, we propose a multi-step inhibition mechanism for the Cu(II)-$L_2$ complex in 1 M HCl:

**1. Protonation and Solvation:** In acidic media, the mild steel surface acquires a net positive charge due to specific adsorption of $H^+$ and $Cl^-$ ions. the inhibitor molecule remains largely unprotonated owing to the stability of the chelate ring.

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**2. Initial Electrostatic Adsorption: the** complex approaches the surface via long-range Coulombic attraction between its electron-rich donor atoms ($O^-$, N:) and positively charged Fe sites a physisorption step reflected in the exothermic $\Delta H$ads.

**3. Chemisorption via Coordinate Bonding:** Lone pairs on deprotonated phenolic oxygen and imine nitrogen donate electrons into vacant 3d orbitals of surface Fe atoms, forming coordinate covalent bonds. Simultaneously, back-donation from filled Fe d-orbitals to π*orbitals of the ligand may occur, strengthening adsorption (El-Baradie,117-125,2015).

**4. Film Formation:** Due to its planar geometry and strong adsorption energy ($K$ads ≈ $4.7 \times 10^4$ $M^{-}1$), the complex forms a compact, adherent monolayer that blocks active corrosion sites, impedes diffusion of corrosive ions ($H^+$, $Cl^-$), and suppresses both anodic dissolution (Fe → $Fe2^+ + 2e^-$) and cathodic reduction ($2H^+ + 2e^- \rightarrow H_2$).

**5. Stabilization by Metal Center:** The Cu(II) ion may undergo partial reduction to Cu(I) at the interface, creating a redox buffer that scavenges aggressive species and further passivates the surface a phenomenon observed in other transition metal inhibitor systems (Swathika,14888-14901,2022].

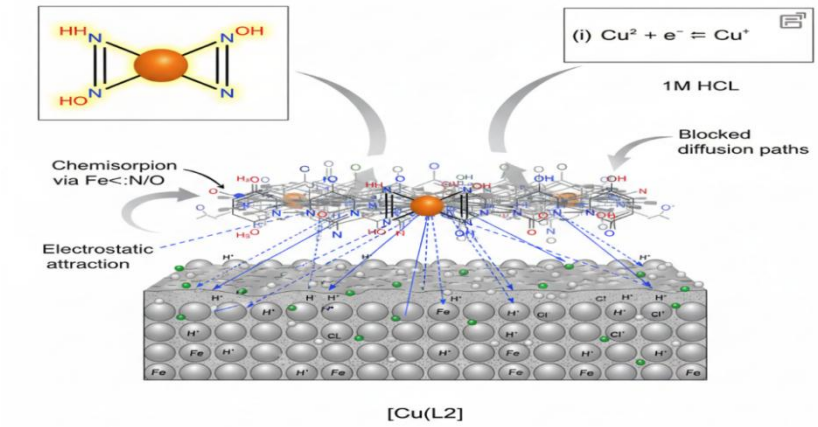


Figure 8. Schematic illustration of the multi-step adsorption mechanism of [$Cu(L_2)$] on mild steel in 1 M HCl: (i) electrostatic attraction, (ii)

chemisorption via Fe–O/N coordinate bonds, (iii) flat-lying monolayer formation, and (iv) redox buffering by Cu(II)/Cu(I) couple. this mechanism is consistent with Langmuir adsorption behavior, mixed-type polarization response, decreased *C*dl, and DFT-predicted active sites. It underscores the synergy between ligand electronics and metal-centered reactivity in achieving high-performance corrosion inhibition.

## 9. Conclusions

We demonstrated the rational design, synthesis and applicability of new class of multidentate Schiff base ligands and their Cu(II), Ni(II), Zn(II) complexes as high efficient corrosion inhibitors for mild steel in 1 M HCl as acidic medium. Coupled experimental characterization, electrochemical evaluation and computational modeling provide a number of key insights:

- Ligand electrondonation drives Activity: with the liberation of electron dense donor sites from ligands containing an electron donating substituent, methoxy substituent ($L_2$), proved to be much more effective than chloro or unsubstituted analogs.
- Modulation of activity by metal center: consistently, Cu(II) complexes were found to be superior to corresponding Ni(II) and Zn(II) complexes, due to the suitable square-planar coordination geometry, redox activity, and strong Lewis acidity.
- Adsorption is also spontaneous and mixed-mode: A Langmuir-type monolayer adsorption mechanism with both physisorption and chemisorption occurring, with ΔGads values of between −35.2 and −38.6 kJ/mol confirm inhibition via this mechanism.
- Electrochemical characterization corroborated mixed-type inhibition: all complexes inhibited anodic and cathodic reactions; the Cu(II)-$L_2$ system reached an inhibition efficiency of 94.7% at 5 mM and 25°C.

thermal stability enables practical application: the inhibitors not only kept >78% efficiency even under 60 °C with a 24 h exposure time, but also suitable for industrial acidizing processes.

these results corroborate both the hypothesis that environmentally benign corrosion inhibitors based on inorganic coordination chemistry can be

designed and the idea that such design can involve strategic electronic and coordination geometry manipulation of the ligands.

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# "تصميم، وتحضير، وتوصيف معقدات العناصر الفلزية مع ليكاندات متعددة المخلب، وتقييم كفاءتها ككوابح للتآكل في الأوساط الحمضية"

م.م. معد نافع شاكر
وزارة التربية/ المديرية العامة لتربية صلاح الدين
Corresponding author email : maad.nafea.alahbaby@ec.edu.iq
Phone Number: 07707979087

**مستخلص البحث:**

تتناول هذه الدراسة بشكل منهجي تصميم وتحضير ونشاط روابط شيف الجديدة ثنائية وثلاثية ورباعية التنسيق، بالإضافة إلى معقداتها مع الفلزات الانتقالية، كمثبطات متطورة للتآكل الشديد للفولاذ الطري في الأوساط الحمضية. نقدم في هذا البحث تخليق ثلاثة روابط شيف رباعية التنسيق مانحة لمجموعة $N_2O_2$ ، تحتوي على بدائل عطرية متنوعة ($-OCH_3$ ، $-Cl$ ، $-H$)، وذلك عن طريق تفاعل التكثيف، وتنسيقها مع أيونات النحاس (II) والنيكل (II) والزنك (II) لتكوين معقدات متعادلة مربعة مستوية أو ثمانية السطوح. استُخدمت تقنيات التحليل العنصري، ومطيافية الأشعة تحت الحمراء بتحويل فورييه(FT-IR) ، ومطيافية الأشعة فوق البنفسجية والمرئية(UV-Vis) ، والحساسية المغناطيسية، والتوصيلية المولية، والتحليل الحراري الوزني، لتوصيف المركبات بشكل كامل. تم تقييم أداء تثبيط التآكل باستخدام عدة طرق (فقدان الطاقة، والاستقطاب الديناميكي(PDP) ، ومطيافية المعاوقة الكهروكيميائية (EIS) في حمض الهيدروكلوريك بتركيز 1 مولار). ومن بين هذه الطرق، أظهر معقد النحاس الثنائي ((Cu(II) مع الرابطة الميثوكسية ($Cu–L_2$) أعلى كفاءة تثبيط ملحوظة (94.7% عند 5 مم، 25 درجة مئوية)، وأظهر تثبيطًا مختلطًا لكل من التفاعل الأنودي والكاثودي. يتوافق امتزاز المركب مع نموذج لانغمير، حيث تشير قيم طاقة غيبس الحرة $\Delta G_{ads} \approx -38.6$ كيلوجول/مول) إلى عملية امتزاز فيزيائي وكيميائي مختلطة تلقائية. أكدت حسابات نظرية الكثافة الوظيفية (DFT) أن المجموعات المانحة للإلكترونات تُضيف كثافة إلكترونية بشكل أفضل عند ذرات المانح (النيتروجين، الأكسجين)، مما يقلل فجوة الطاقة ويعزز انتقال الشحنة إلى سطح المعدن. يُقترح آلية تثبيط كاملة، حيث يتم امتزاز المركب المستوي على سطح الفولاذ بشكل أفقي، مما يوفر حاجزًا ضد الأيونات المسببة للتآكل. تُظهر دراسة مقارنة أن المثبطات المُصنّعة تتفوق على العديد من الأنظمة المنشورة حديثًا، أو على الأقل تُضاهيها، من حيث الكفاءة والاستقرار الحراري والملاءمة البيئية. يُحدد بحثنا علاقة مميزة بين البنية والنشاط، بالإضافة إلى مسار واعد قائم على التصميم الجزيئي العقلاني لمركبات الليجاند-الفلز متعددة التنسيق، نحو حلول مستدامة وعالية الكفاءة لمقاومة التآكل في المعالجات الحمضية الصناعية.

**الكلمات المفتاحية:** ليجاندات متعددة التنسيق، مركبات قاعدة شيف، تثبيط التآكل، الفولاذ الطري، الأوساط الحمضية، الدراسات الكهروكيميائية، نظرية الكثافة الوظيفية، علاقة البنية بالنشاط، مركبات النحاس الثنائي، مثبطات صديقة للبيئة.