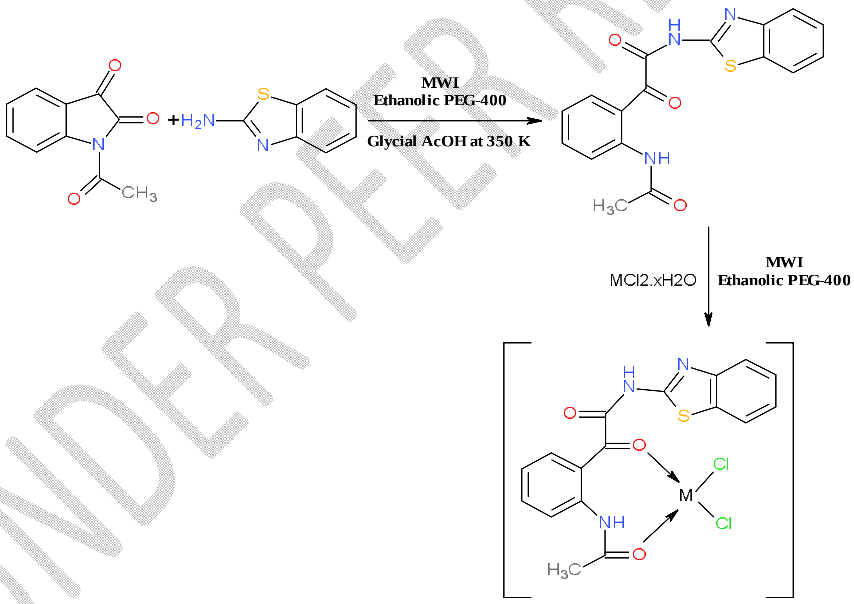
CORROSION INHIBITION ACTIVITY OF TRANSITION METAL(II) COMPLEXES OF A BIDENTATE LIGAND FOR MILD STEEL IN ACIDIC MEDIUM PERTINENT TO GREEN CHEMISTRY

ABSTRACT

A new bidentate amide ligand 2-(2-acetylaminophenyl)-N-benzothiazol-2-oxo-acetamide (apba) and its complexes with Co^{2+}, Ni^{2+} and Cu^{2+} have been synthesized using microwave-assisted synthesis (MAS) under mild conditions with excellent yields (up to 85%) in shorter reaction times (in 5-10 min).All compounds have been characterized by spectro-analytical techniques.The corrosion inhibitory effects of the investigated ligand and its metal (II) complexes on mild steel were studied in 1.0 M HCl at different concentrations using the 'weight loss method' which revealed the high inhibition efficiency of the complexes compared to the free ligand.The data show that the inhibitory efficiency obtained by the investigated compounds increased as the concentration of the compounds increased and follow the order Co>Ni>Cu>ligand.

Graphical Abstract



Keywords: Corrosion inhibition; Mild steel; Microwave-assisted synthesis; Bidentate ligand; Transition metal complexes

INTRODUCTION

Synthetic scientists in the fascinating world of science and technology have adopted environmentally benign methodologies for the synthesis of desired products for a sustainable future. These eco-friendly synthetic approaches are designed to synthesise products that possess negligible or no toxicity to human health or the environment [1-2]. Microwave-assisted synthetic chemistry is an alternative well-established approach of sustainable chemistry that follows the choice of *green solvents* and *energy efficiency* standards of the twelve principles of green chemistry for attractive green synthesis [3-5]. This synthetic approach is safe because it avoids chemical wastes, saves energy, and prevents accidents. Furthermore, it is an environmentally sustainable and cost-effective technology because it increases the purity of products and their percentage yield, reduces the reaction time, and allows easy workup [6-8].

Nitrogen heterocycles, especially indole derivatives, have been used widely in material science along with pharmaceuticals and biological fields for several years. Transition-metal complexes of N-heterocycles play a central role in biochemical, analytical, and pharmaceutical sciences. Various heterocyclic compounds, especially benzothiazole derivatives of isatin (indole-2,3-dione), have versatile and substantial research interest due to their pharmaceutical activities [9]. The isatin derivatives and their transition metal complexes play an important role in several industries, including the oil and petroleum industries [10-11].

Mild steel alloys have outstanding mechanical and chemical properties for use in several technical and production processes, including the oil and petrochemical industries. In petrochemical processing and oil-well operations, acids (mainly hydrochloric acid) have been used to clean-up operations and remove mineral oxides and mineral deposits, which have corrosive effects. Iron steel alloys have many problems, including corrosion which requires prevention or protection via corrosion inhibitors. Corrosion inhibitors (CI) are chemical additives that are used at low concentrations [12]. CIs can delay, minimize, or inhibit corrosion processes on metal surfaces when added to a corrosive medium. CIs may be inorganic inhibitors(ICIs) or organic inhibitors (OCIs). Although ICIs have the best performance, they generate highly toxic by-products in the environment during corrosion inhibition of metals. OCIs are more viable inhibitors of metals without environmental detriment. These OCIs are natural or synthetic compounds with structural characteristics (heteroatoms, e.g., N, O, S and P, with non-bonding electrons and or π-electron systems) that provide them with the ability to interact with vacant d orbitals of metal / alloyatoms [13]. These forms a chemically and mechanically stable molecular layer on the surface of the metals / alloys and forms a barrier between the alloys and corrosive solutions through an adsorption mechanism by blocking the active sites, thus preventing; or inhibiting the corrosion process. Owing to their high efficiency, environmentally sustainable organic inhibitors have beenwidely used to protect against corrosion of iron steel alloys [14-17].

A literature survey revealed that very little research has been conducted on benzothiazole derivatives of satin as ligands and their transition metal(II) complexes with application as corrosion inhibitors in the iron steel alloy industry [18-21]. The present research article describes the synthesis of a new bidentate amide ligand 2-(2-acetylaminophenyl)-N-benzothiazol-2-oxo-acetamide *(apba)*, Co^{2+}, Ni^{2+} and Cu^{2+} complexes through microwave-assisted synthesis (MAS); their characterisation and structure elucidation and their low-cost corrosion inhibition activity through weight loss measurements (chemical method).

EXPERIMENTAL STUDY

Materials and Methods

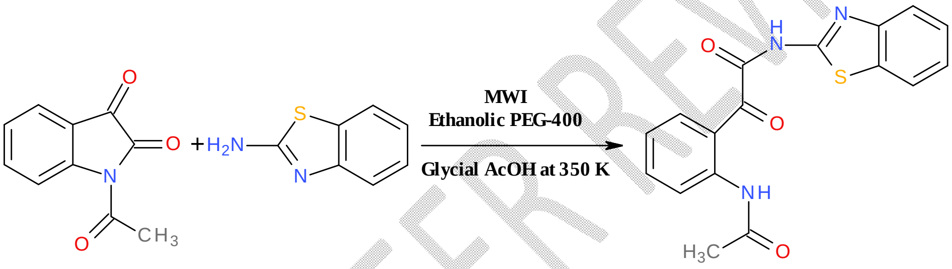
All the chemicals / reagents used in this research project were of Anal R grade and were purchased from different commercial sources such as Sigma Aldrich, and the metal salts used were from LobaChemie.

A modified microwave oven model 2001 ETB with a rotating tray and a power source of 230 V, a microwave energy output of 800 W and a microwave frequency of 2450 MHz was used in which the synthetic reactions were performed via on/off cycling to control the temperature via a thermocouple. The completion of the synthetic reactions was monitored by TLC and melting point measurements. TLC was carried out on silica gel plates, and the plates were scanned under 254 nm UV light.

The melting points of the undertaken compounds were determined by the Gallenkamp M F B 600-01 melting point apparatus and were uncorrected. The purity of the products was determined via TLC. Elemental analyses of the compounds were performed on a Carlo Erba 1106 elemental analyser. The electronic spectra of the compounds in the UV-visible region (200-1100 nm) in DMSO were recorded on a Shimadzu 160 UV-Vis spectrophotometer. Infrared spectra of compounds as KBr discs were recorded on a Shimadzu FTIR-8400S spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker Varian-400 MHz NMR spectrometer in DMSO-d_6 solvent employing TMS as an internal standard. The chemical shifts are expressed in the δ-scale downfield scale from the TMS, and the proton signals are indicated as *s* = singlet, *d* = doublet, *t* = triplet, *q*= quartet, and *m* = multiplet. EPR spectra of the Cu(II) complex were recorded as polycrystalline samples at room temperature via an E4-EPR spectrometer with DPPH as the g-marker. Molar conductance measurements were performed using a 10^{-3} M solution of the complexes in DMF on an Elico-CM 82 conductivity bridge at room temperature. Magnetic susceptibility measurements were performed on a Gouy balance at room temperature using Hg[Co(SCN)$_4$] as the calibrant. Diamagnetic corrections were applied in compliance with the Pascal constant.

Microwave-assisted synthesis of ligand

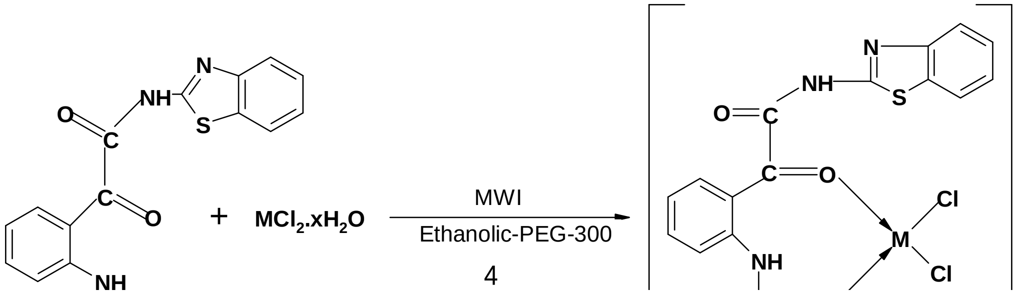
A 1:2 molar ratio of N-acetylisatin (1 mmol) and 2-aminobenzothiazole (3mmol) was thoroughly mixed in a grinder and then the mixture was irradiated in a microwave oven at 350 K by adding 4-5 ml of its ethanolic-PEG-400 solution in the presence of glacial acetic acid as a catalyst with intensive stirring and chilled at 273 K. The synthetic reaction was completed in a short time (about 10 minutes) with higher yields. The resulting yellow product was the crystallized with ether and ultimately dried under reduced pressure over anhydrous CaCl$_2$ in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 72%) (Scheme-1).



Scheme-1:*Green synthesis of ligand (apba)*

Microwave-assisted synthesis of metal(II) complexes

The ligand (apba) and metal salt [MCl$_2$.xH$_2$O] were mixed at a 1:1 (ligand : metal salt) ratio in a grinder. The reaction mixture was then irradiated in a microwave oven, and 4-5 mL of ethanolic-PEG-400 was used as the solvent. The synthetic reaction was completed in a short time (6-10 min.) with relatively high yields. The resulting-coloured product was subsequently recrystallized with ether and ultimately dried under reduced pressure on anhydrous CaCl$_2$ in a desiccator. The progress of the reaction and purity of the products was monitored by TLC using silica G (yield: 75-80%).



Scheme-2:*Green synthesis of metal(II)-complexes, where M = = Co, Ni, & Cu.*

Corrosion inhibition studies

The corrosion inhibition activity of green synthesized ligand and its transition metal complexes was evaluated on mild steel specimens by weight loss measurements as follows:

Concentration range of compounds and acid

The aggressive 1.0M HCl was prepared by diluting the analytical grade 37% HCl with double distilled water. Inhibitor solutions with concentrations of 200 ppm, 300 ppm, 400 ppm, and500 ppmwere prepared by dissolving the required amount of the ligand and its transition metal (II) complexes separately in 50 ml of 1.0 M HCl respectively. The blank solution was prepared as 50 ml of 1.0 M HCl without inhibitor.

Mild steel coupons

All corrosion inhibition tests were carried out at 298K temperatures using mild steel in the form of a rectangular coupon of 2 × 2 × 0.05 $cm^3$with the following chemical composition (by weight): C = 0.16%, Si = 0.10%, Mn = 40.0 %, P = 0.013%, S = 0. 2%, and iron balance. These coupons were polished with emery paper ranging from a coarse grade of 200 to 1000 grit.The sample coupons were thoroughly washed with doubly distilled water, then in absolute ethanol and degreased with acetone, dried at room temperature, and stored in a moisture-free desiccator before their use in corrosion studies.

Weight loss measurements

The weights of the specimens' coupons before and after immersion were determined via a 4-digit analytical balance using a Shimadzu balance, model AY62 during weight loss measurements.The coupons were dipped in a 100 ml beaker containing a 1.0 M HCl deaerated solution with and without the additives of the investigated ligand and its complexes at 24 hours intervals at 303Krespectively.After the corrosion test, the samples were carefully washed in double-distilled water, dried and then weighed. The loose segments of the film were removed from the corroded samples by rinsing. The weight loss was taken as the difference between the initial and final weights of the coupons. Triplicate experiments were performed in each case and the mean value of the weight loss is reported here.

The surface coverage (θ) and the inhibition efficiency (%IE) were calculated by using the following equations:

$\theta = (W^* - W) / W^*$ (i)

$\% IE = \theta \times 100$ (ii)

Where W* and W refers to the weight loss of sample material in uninhibited and inhibited 1M HCl solution, respectively.

The corrosion rate (CR) was calculated using the following equation:

CR = Weight loss (in mg) / (surface area x Immersion period) (iii)

Morphology of Surface

The surface morphology of corrosion product on mild steel samples after 24 hours immersion in 1.0 M HCl solution with 500 ppm of the investigated ligand and metal (II) complexes and without inhibitors was studied by SEM (scanning electron microscope) using JEOL-JSM-6460LV model scanning electronic microscope with an accelerating voltage of 20kV.

RESULTS AND DISCUSSION

Physio-analytical studies

The formation of a new bidentate ligand namely 2-*(2-Acetylamino-phenyl)-N-benzothiazol-2-yl-2-oxoacetamide (apba)* by condensation of N-acetylisatin with 2-aminobenzothiazole occurred with ring cleavage at C_2 of the heterocyclic ring of the acetylisatin. The presence of various donor atoms and the stereochemistry of the ligand increased its complexing behaviour and consequently the formation of transition metal complexes. The formation of ligand as well as its transition metal (II) complexes under microwave irradiation is an approach for green chemistry and all structures were confirmed by the 1H NMR, 13C NMR and IR spectral and physico-analytical studies. The spectro-analytical studies of the ligand are as follows:

Yield: 89%; **colour**: yellow; **m.p.**: 432-433K; **IR** (KBr, cm^{-1}): 3245 ν(N-H), 1706 ν(C=O, keto), 1675 ν(C=O, amide), 1534 ν(C=N, thiazole ring), 1102 ν(C-N, thiazole ring), 755 ν(C-S, thiazole ring). **^{1}H NMR**(DMSO-d_6, δ, ppm): 2.078 (s, 3H, -CH_3), 7.021 (d, 1H, Ar-H), 7.270 (d, 2H, Ar-H), 7.647 (t, 4H, Ar-H), 7.881 (d, 1H, Ar-H), 10.604 (s, 2H, NH).**^{13}C NMR**(DMSO-d_6, δ, ppm): 24.40 (C of -CH_3), 117.89 -139.17(C of Ar), 152.13 (C of Ar), 169.51 (C of thiazole ring), 189.89 (C of C=O, keto of thiazole&Ar), 165.28 (C of amide), 167.104 (C of acetamide).**Analytical** calculated (found) (in %) for $C_{17}H_{13}N_3O_3S$, (339.26):C = 60.17 (59.84), H = 3.83 (4.09), N = 12.38 (12.25).

The green synthesized metal (II) complexes were microcrystalline coloured solid and stable in air. These isolated solids were insoluble in water, partial soluble in hot methanol & ethanol but soluble in DMF and DMSO. These complexes decompose above their respective melting points. The experimental molar conductance of the isolated metal complexes in DMF show values in range 32.12 to 39.05 Ω^{-1} cm^2 mol^{-1}indicating their non-electrolytic nature [22]. The physico-analytical data of the isolated metal complexes are presented in table-1.

Table-1

Physical measurements and analytical data of the investigated complexes of the ligand

Symbol	**Mol. Formula**	**Colour**	**M. P. (K)**	**% Yield**		**% Elemental Analysis Found (calculated)**				
				Conventional Method	**Green Method**	**% C**	**% H**	**% N**	**% M**	**% Cl**
C_1	$[CoLCl_2]$	Pink	496	29	42	44.40 (44.3)	3.50 (3.7)	8.05 (8.2)	11.50 (11.4)	13.90 (13.8)
C_2	$[NiLCl_2]$	Greenish white	524	44	65	43.50 (43.6)	2.90 (2.8)	8.75 (8.8)	12.50 (12.4)	15.10 (15.0)
C_3	$[CuLCl_2]$	Greenish yellow	464	20	45	43.20 (43.0)	2.90 (2.7)	8.95 (8.9)	13.50 (13.4)	15.10 (15.0)

Infrared spectra and Coordination Modes

The mode or site of linkage of green synthesized ligand to the corresponding metal ions in the metal (II) complexes is described by the infrared spectral analysis. The important vibrations and the tentative assignments of the significant IR spectral bands of the ligand and its Co(II), Ni(II) and Cu(II) complexes are presented in Table 2.The IR spectrum of the studied ligand has bands of secondary amide group of 2-aminobenzothiazole and not the frequency of amino group. The single band at 3245 cm^{-1} corresponding to N-H stretching mode of amide group with its bending vibration band at 1610 cm^{-1} appeared in the spectrum. The spectrum contains aromatic and aliphatic C-H bands at 3060 and 2935 cm^{-1} respectively. The aromatic C=C vibration bands ($\nu_{C=C}$) appeared at 1405, 1455 and 1585 cm^{-1} respectively. The vibrational bands corresponding to C=O ($\nu_{C=O}$) vibration of keto and amide groups was observed at 1705 and 1675 cm^{-1} respectively. Three bands of thiazole ring attributed to C=N ($\nu_{C=O}$), C-N (ν_{C-N}) and C-S-C (ν_{C-S-C}) vibration were appeared at 1535, 1100 and 755 cm^{-1} respectively.

The investigated transition metal (II) complexes exhibited an enhancement of the N-H stretching vibration frequencies ($\nu_{N\text{-}H}$) of the ligand, which may be due to the absence of H-bonding and non-linkage or non-coordination with metal ions.Changes in amide vibration ($\nu_{C=O}$) to lower frequencies in all complexes refer to the coordination of the amide group with metal (II) ions [23].Similarly, the infrared spectra of the complexes exhibited additional shifts in keto ($\nu_{C=O}$) vibration at lower frequencies, which indicated the coordination of the keto group with the metal ions (II) [24].Obviously, the ligand acts as a neutral bidentate (O O) ligand (O of the keto group and O of the amide group) in the complexes.The new IR bands appearing at lower frequencies are assigned to M-O and M-Cl stretching vibrational modes in the complexes.

Table-2

IR spectral bands (cm^{-1}) and tentative assignments of ligand and its complexes

Symbol	$\nu_{N\text{-}H}$	$\nu_{C=O}$ **(keto)**	$\nu_{C=O}$ **(amide)**	**Thiazole ring**			$\nu_{M\text{-}O}$	$\nu_{M\text{-}Cl}$
				$\square_{C=N}$	$\square_{C\text{-}N}$	$\square_{C=S}$		
Ligand	**3245**	**1705**	**1675**	**1536**	**1102**	**755**	**-**	**-**
C_1	**3268**	**1680**	**1646**	**1525**	**1090**	**755**	**472**	**332**
C_2	**3280**	**1685**	**1648**	**1528**	**1100**	**753**	**479**	**295**
C_3	**3275**	**1682**	**1647**	**1530**	**1096**	**762**	**514**	**232**

Electronic spectral analysis and structure of complexes

The electronic absorption spectral data of the investigated ligand and its transition metal (II) complexes and spectroscopic parameters with molar conductance and magnetic moments are presented in table 3.

The electronic spectrum of the ligand in DMF solvent exhibited a high intensity sharp band at 294 nm with a shoulder at 328 nm which were assigned to $\pi \rightarrow \pi^*$ transitions of the conjugated system along with a low intensity band at 366 nm which was assigned to $n \rightarrow \pi^*$ transition.

The electronic spectrum of Co(II) complex exhibited a sharp absorption band at 985 nm and a multiplet absorption bands at 514, 557, 596 and 636 nm with the average of 572 nm. These two absorption bands are assigned to ${}^4A_2 \rightarrow {}^4T_1$ (F) (ν_2) and ${}^4A_2 \rightarrow {}^4T_1$ (P) (ν_3) respectively. The multiplet bands may be a result spin-orbital coupling. These two transitions are quite usual in tetrahedral Co(II) complexes. By applying the band ratio ν_3/ν_2 (1.72) and band energies on Tanabe Saugano diagram of Co(II) complexes, the values D_q/B (1.1), B =(581 cm^{-1}) and 10Dq (6391 cm^{-1}) were calculated using Band-fitting equations.The energy of ν_1 which was assigned to $^4A_2 \rightarrow ^4T_2$(F)transition was calculated from the diagram and found to be (6441 cm^{-1}). The value of nephelauxetic ratio (β) 0.598 (less than unity) indicates a covalent character in the metal ligand bond [25]. These ligand field parameters suggest tetrahedral geometry for Co(II) complexes.

The spectrum of the Ni (II) complex exhibited a low intensity band appeared at 985 nm and this was attributed to the transition $^3T_1$ (F) → $^3A_2$ (F) (ν_2) and low intensity multiplet absorption band at 635, 667 and 710 nm with the average of 669 nm which assigned to the $^3T_1$ (F) → $^3T_1$ (P) (ν_3) transition. The band appeared at 329 nmwas attributed to charge transfer transition. By applying band ratio ν_3/ν_2 (1.47) and band energies on Tanabe-Saugano diagram of Ni(II) complexes, the values Dq/B (0.75), B (746.25) cm^{-1} and 10Dq (5596 cm^{-1}) were calculated. The value of β = 0.75 indicates a covalent character of the complex [26]. The energy of ν_1 was calculated from the diagram and found to be 4264 cm^{-1} and was assigned to $^3T_1$ (F)→$^3T_2$ (F) transition.These ligand field parameters suggest tetrahedral geometry for Ni(II) complexes [27].

The spectrum of the Cu(II) complex C_3, exhibited three low intensity bands appeared two doublets at 807 nm & 785 nm , (the average value 796 nm) and (689 nm & 646 nm), (the average value 667 nm) and a single band at 553 nm which were assigned to ($^2B_{1g} \rightarrow ^2A_{1g}$) ν_1, ($^2B_{1g} \rightarrow ^2B_{2g}$) ν_2 and ($^2B_{1g} \rightarrow ^2E_g$) $\nu_3$respectively of square planar Cu(II) complex [28].

Obviously, the profile of the π→π* transition band was changed in all metal (II) complexes and the electronic absorption spectra exhibited hypsochromic shifts of ligand band (π→π*) appeared to (281 & 299), (277 &300) and (281 & 302) nm respectively in Co(II), Ni(II) and Cu(II) complexes respectively.

Conductance and magnetic susceptibility measurements

The molar conductance values of metal complexes were calculated at room temperature taking DMF as a solvent and the results are displayed in Table-3.

The magnetic moment value of 4.34 B.M. for Co(II) complex undoubtedly suggests its tetrahedral geometry. The value of molar conductivity in DMF was (35.5) $Smol^{-1}cm^2$ for it, indicating its non-electrolytic nature.The magnetic moment of the complex (μ_{eff} 2.82 B.M) comes in agreement with those of tetrahedral Ni(II) complexes. The molar conductivity value in DMF (32.2 $Smol^{-1}cm^2$) showed the non-electrolytic nature of the complex.The magnetic moment (μ_{eff} 1.81 B.M) indicates a paramagnetic character of the square planar geometry of the synthesized complex [29]. The molar conductivity value in DMF (39.10 $\mathrm{Smol^{-1}cm^{2}}$) shows that the complex was non-electrolyte.

Table 3

Conductivity, magnetic moment, and electronic spectral bands & spectral parameters of metal complexes

Symbol	**Molar Conductivity** ($\mathrm{S\ mol^{-1}.cm^{2}}$)	**Magnetic Moment** (**μ_{eff}BM**)	**Electronic Bands (nm)**	**Electronic transitions**	**D_q/B**	**B** (**cm^{-1}**)	**β**	**10 D_q** (**cm^{-1}**)
Ligand	-	-	294 &328 366	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	-	-	-	-
[$CoLCl_2$]	35.5	4.34	985 (ν_2) 572 (ν_3)	$^4A_2\rightarrow{}^4T_1$ (F) $^4A_2\rightarrow{}^4T_1$ (P)	1.1	581	0.598	6391
[$NiLCl_2$]	32.2	2.82	983 (ν_2) 669 (ν_3)	$^3T_1$ (F) → $^3A_2$ (F) $^3T_1$ (F) → $^3T_1$ (P)	0.75	746	0.725	5595
[$CuLCl_2$]	39.1	1.81	796 (ν_1) 667 (ν_2) 553 (v3)		-	-	-	-

EPR Spectral Analysis

EPR spectrum of Cu(II) complex was recorded at room temperature as polycrystalline sample, on X band at frequency of 9.1 GHz under the magnetic-field strength of 3000 G. The Cu complex analysis provides $g_{\parallel}$ = 2.148, $g_{\perp}$ = 2.067, g_{av} = 2.094 and G = 2.20. Similarly, the g-tensor values observed for complex are $g_{\parallel}$ = 2.241, $g_{\perp}$ = 2.074, g_{av} = 2.12 and G = 3.25. These g-values have been used to derive the ground state. The unpaired electron lies in $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state with $g_{\parallel} > g_{\perp} > 2$, while the unpaired electron lies in the d_{z^2} orbital giving $^2A_{1g}$ as the ground state with $g_{\perp} > g_{\parallel} > 2$ in square planar complexes. In the present cases, the $g_{\parallel} > g_{\perp} > 2$, therefore the unpaired electron is likely to be in the $d_{x^2-y^2}$ orbital indicates square planar geometry around the Cu(II) ion [30]. The possibility of the dimeric form was ruled out as no signal was observed in the spectrum at half field. This is also supported by the magnetic moments of Cu complexes (1.81BM) which confirm the mononuclear nature of the complex.

Proposed Geometries of Complexes

From the observationsobtained from spectro-analytical data, the suggested stereo-chemical structures of the synthesized complexes can be proposed as follows:

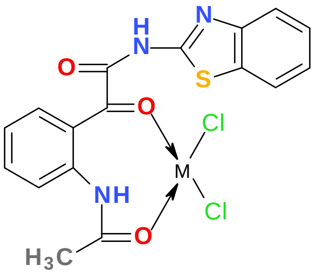


Figure-1:*Proposedsquare planarstereochemical structure of the synthesized complexes*

Corrosion inhibition activity by Weight loss measurements

The gravimetric method, i.e., weight loss measurement, is a highly reliable and simple technique to study the anticorrosive or corrosion inhibition nature of the compounds. The percentage of inhibition efficiency (% IE), the corrosion rate (CR) and surface coverage (θ) calculated from the weight loss measurements for 24 h are presented in Table 4 and are plotted in Figure 2 and 3.

Figure-2:*Plot of weight loss (in mg) for mild steel versus concentrations (in ppm) in 1.0 M HCl in the absence and presence of ligand (BAPA) and its Co, Ni and Cu complexes*

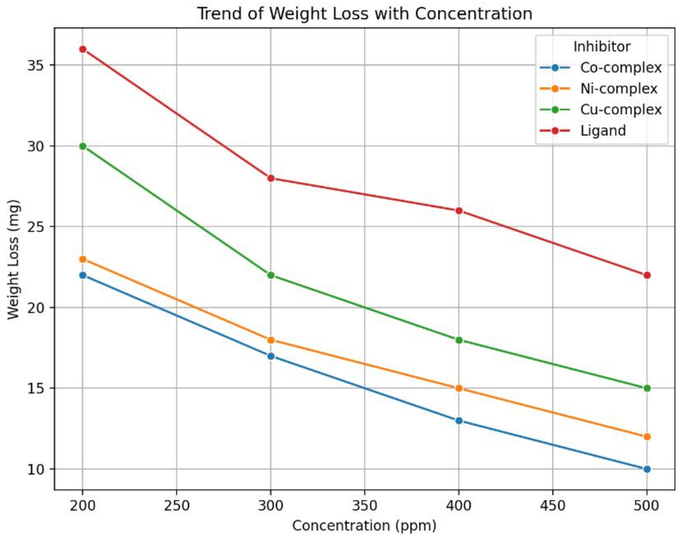


Figure-3:*Plot of inhibition efficiency(% IE) versus concentrations (in ppm) in 1.0 M HCl in the absence and presence of ligand (apba) and its Co, Ni and Cu complexes*

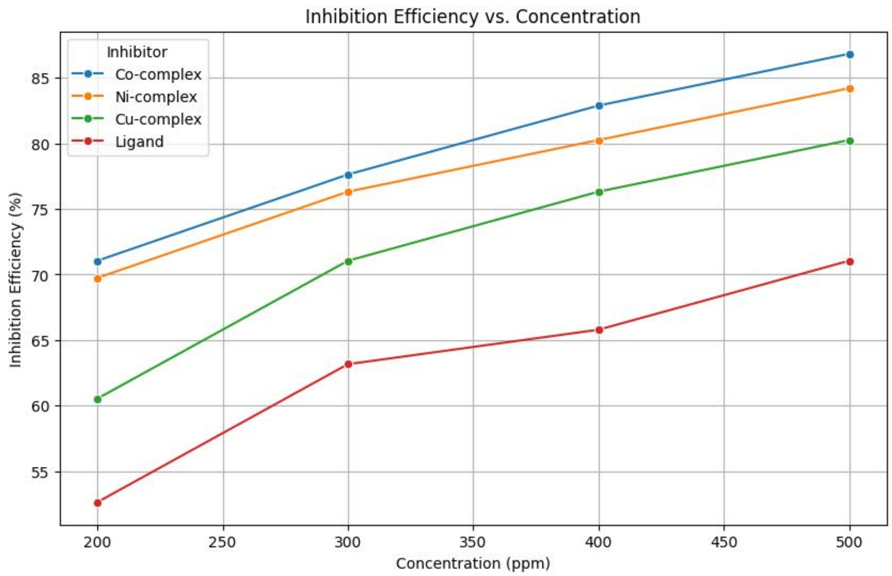


Table 4

Weight loss data for inhibition of corrosion on mild steel exposed to 1.0 M HCl solution for 24 h with different concentration of investigated compounds

Inhibitor	**Concentration (in ppm)**	**Weight loss (in mg)**	**% IE**	**θ**	**CR (mg cm^{-2}h^{-1})**
Blank (1M HCl solution)	-	76	-	-	6.93
Co-complex	200	22	71.05	0.71	2.01
Co-complex	300	17	77.63	0.78	1.55
Co-complex	400	13	82.89	0.83	1.18
Co-complex	500	10	86.84	0.87	0.91
Ni-complex	200	23	69.74	0.70	2.09
Ni-complex	300	18	76.32	0.76	1.64
Ni-complex	400	15	80.26	0.80	1.37
Ni-complex	500	12	84.21	0.84	1.09
Cu-complex	200	30	60.53	0.60	2.74
Cu-complex	300	22	71.05	0.71	2.00
Cu-complex	400	18	76.32	0.76	1.64
Cu-complex	500	15	80.26	0.80	1.37
Ligand	200	36	52.63	0.53	2.89
Ligand	300	28	63.16	0.63	2.54
Ligand	400	26	65.79	0.66	2.38
Ligand	500	22	71.05	0.71	2.00

According to the data, an increase in the concentration of inhibitors results in a reduction in weight loss. This indicates that weight loss diminishes as the inhibitor concentration rises. Clearly, a significant number of inhibitor molecules adsorb onto the mild steel surface, covering a large area and inhibiting further corrosion as the inhibitor concentration increases.

The dataset illustrates the link between concentration and inhibition efficiency (% IE) for ligand and its metal complexes. The data indicates that as the concentration of the investigated compounds rises from 200 to 500 ppm, the inhibition efficiency steadily increases.

The metal complexes exhibit greater corrosion inhibition efficiency compared to the free ligands, likely due to their planarity and larger molecular size, increasing the inhibition efficiencies in the following order: [$CoLCl_2$] > [$NiLCl_2$] > [$CuLCl_2$] > Ligand. Furthermore, the inhibitory nature of Co-complex was assigned to the adsorption over the metal surface and demonstrated highest inhibition power than the ligand and other metal complexes due to its higher binding equilibrium constant value (K) indicating the interaction of the inhibitor with the mild steel surface. Moreover, the results show that the level of surface coverage and the efficiency of corrosion inhibition increased with a higher concentration of the inhibitor solution. This correlates with an increase in mass and charge transfer to the MS surface, leading to the adsorption of inhibitor molecules onto the metal, thereby reducing metal dissolution. This suggests that corrosion inhibition is a result of adsorption of inhibitor on the metal surface and the investigated compounds act as adsorption inhibitors [31-33].

Adsorption isotherm, Corrosion Kinetics and Thermodynamic Parameters

The compounds demonstrated high corrosion inhibition efficiencies due to the firm adsorption of inhibitor molecules on the surface of mild steel. The chemisorption of these molecules can be anticipated through the unfilled *d*-orbitals of iron atoms interacting with the *p*-orbitals of heteroatoms in the studied inhibitors. Consequently, the adsorption process follows the Langmuir adsorption isotherm characterized by a negative free energy of adsorption, ΔG^0_{ads}. The strong corrosion-inhibiting properties of these complexes are further supported by the adsorption of inhibitor molecules at the metal/solution interface, displacing water molecules [35].

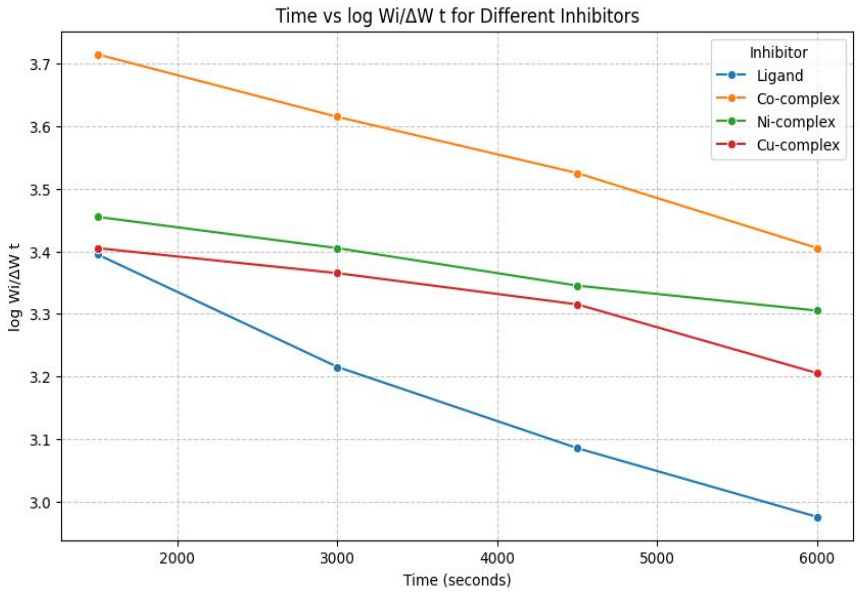
$$\mathrm{Org}_{(sol)} + x\,H_2O_{\ (ads)} \rightarrow \mathrm{Org}_{(ads)} + x\,H_2O_{(sol)}$$

Where the size ratio (x) represents the number of replaced water molecules by the investigated inhibitor molecules.

A plot of initial weight over difference weight of mild steel coupon at time t ($\log W_i / \Delta W_t$) versus time (in second) for each compound undertaken at a concentration of 500 ppm show straight lines which complemented that the reaction follows first order kinetic equation (iv) and the corresponding rate constant were calculated from plot (figure-4):

$$\log W_i / \Delta W_t = -k / 2\text{-}303\, t - \log W_i \qquad \text{(v)}$$

Figure-4: Plot of ($\log W_i / \Delta W_t$) versus time (in second) for each compound at a concentration of 500 ppm

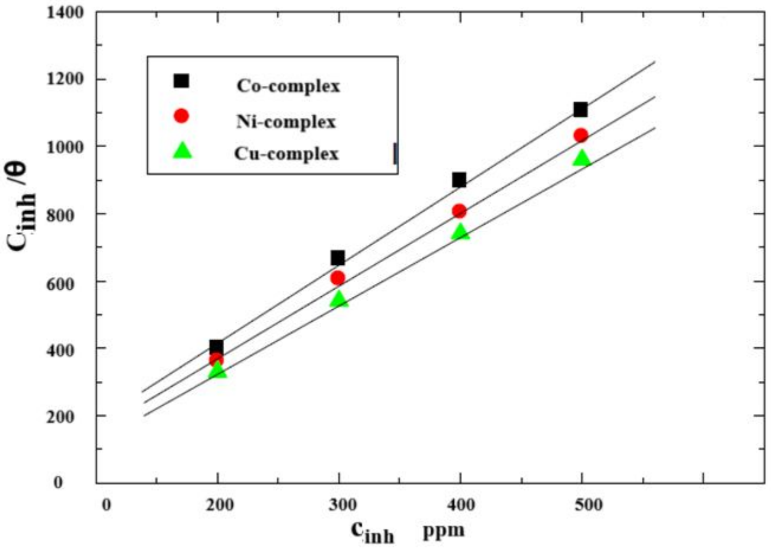


The data obtained from the weight loss measurements are more likely to fit with the Langmuir adsorption isotherm which follows the relation:

$$\text{Langmuir Adsorption Isotherm,} [\mathbf{C_{inh}} / \boldsymbol{\theta}] = 1 / K_{ads} + \mathbf{C_{inh}} \qquad \text{(v)}$$

Where $C_{inh}$is the inhibitor concentration, K_{ads} is the adsorptive equilibrium constant of the adsorption isotherm process and θ is the degree of surface coverage. A plot of (C_{inh} / θ) against C show the clear slope of Langmuir adsorption isotherm for the four green synthesized inhibitors at 303K almost close to unity (Figure-5). The calculated high values of the equilibrium constants, (K_{ads}) for the investigated inhibitors obtained from the intercept lines from figure-5 (given in table-5), indicate the strong adsorption force between the undertaken inhibitors and the surface of the mild steel(MS).

Figure-5:*Langmuir adsorption isotherm for MS in 1 M HCl without and with inhibitors*



The standard Gibbs free energy of adsorption (ΔG^0_{ads}) can be calculated from K_{ads}according to the following relation (vi):

$$\Delta G_{ads} = -RT \ln (55.5\ K_{ads}) \qquad \text{(vi)}$$

Where (55.5) is the molar concentration of water in solution (mole/litre), T is the absolute temperature, and R is the universal gas constant with value 8.314 J mol-1K-1.The calculated values of ΔG0ads for the investigated ligand and its metal (II) complexes are less than -40 kJ mol-1which indicated spontaneous adsorption of inhibitors on mild steel surfaces and through chemically adsorption type and leads to formation of coordination bond between inhibitor molecules and the d orbital of the iron atom [36-37].The enthalpy of adsorption (ΔHads) and entropy of adsorption (ΔSads) can be calculated using the following equations:

$$\ln K_{ads} = (\Delta H_{ads} / RT) + \text{constant} \qquad \text{(vii)}$$

$$\Delta G = \Delta H_{ads} - T\Delta S_{ads} \qquad \text{(viii)}$$

The values of ΔH_{ads}were obtained from a plot of ln K_{ads} against 1/T with slope $\Delta H_{ads}/R$.

The calculated negative values of ΔHads and ΔSads (as presented in Table 5) suggest the exothermic nature of the adsorption of inhibitors onto mild steel surfaces, probably clarifying the possibility of the formation of an iron complex on the metal surface.

Table 5

Thermodynamic parameters using Langmuir adsorption isotherm on mild steel surface in 1.0M HCl containing inhibitors at 30^{0}C

Inhibitors	R^2	K_{ads}(KJ/mol)	ΔG_{ads} (KJ/mol)	ΔS_{ads} (J/mol. K)	ΔH_{ads}(KJ/mol)
Ligand	0.9999	10.8867	-34.154	-83.48	-45.76
Co-complex	0.9997	19.1224	-40.067	-73.98	-60.47
Ni-complex	0.9996	14.6157	-37.675	-66.65	-53.58
Cu-complex	0.9996	11.4386	-36.534	-81.86	-48.86

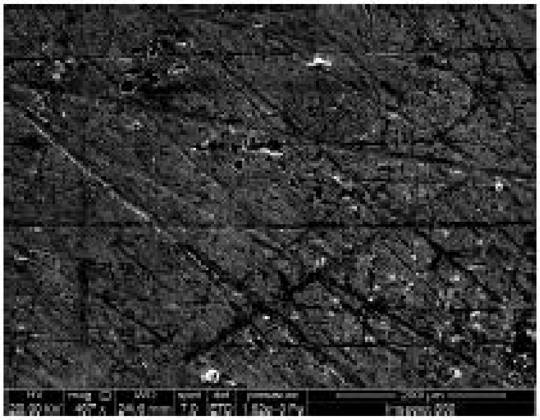
Table 5 indicates that the inhibitors used have negative free Gibbs adsorption energy values, which suggests the spontaneous nature of the adsorption process on the mild steel surface. The adsorption thermodynamic parameters of the investigated compounds are in the order of [$CoLCl_2$] > [$NiLCl_2$] > [$CuLCl_2$] > Ligand (apba) and ΔG_{ads} values are higher than -20 KJ/mol (physio sorption) and nearly - 40 KJ/mol (chemisorption). Therefore, the investigated compounds have the potent to interact with mild steel through semi-chemisorption [38].

Inhibition Mechanism

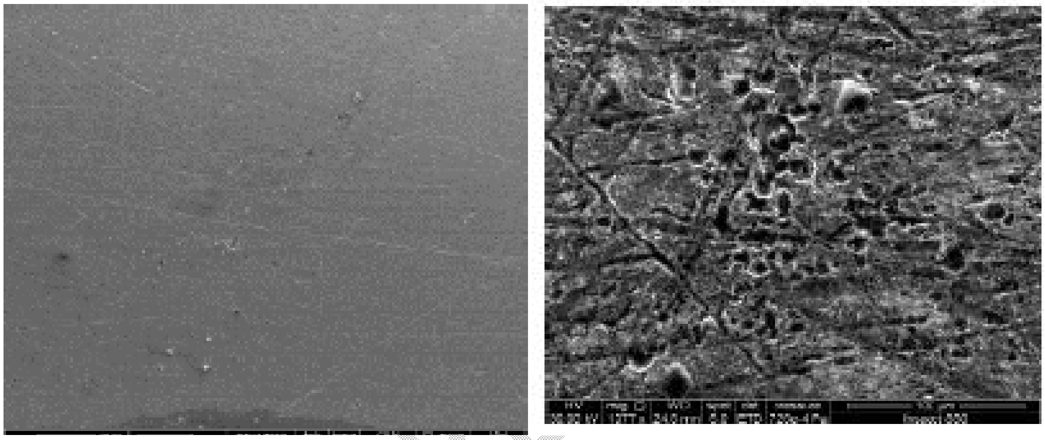
The role of structure and functional groups influences whether coordination compounds hinder or promote corrosion. The process of inhibitor's adsorption is affected by (a) the nature of the metal surface, (b) chemical structure of the organic inhibitor, (c) the type of aggressive electrolyte and (d) the interaction between organic molecules and the metallic surface. The coordination compounds that exhibit significant surface activity and low solubility in solutions are effective in preventing corrosion. The compounds examined show a strong capability to inhibit the corrosion of mild steel in 1 M HCl, which can be attributed to the presence of π-electrons in the aromatic rings and *p*-electrons in electronegative elements (N, O, and S) within the framework of the tested inhibitors. By measuring the electric charge of the metal surface relative to the solution, electrostatic forces can determine the possibility of cation adsorption.The investigated inhibitors anti-corrosion properties in HCl are explained by the presence of cationic species and chloride ions on the steel surface, which has positive charges of acid media [39].

Study of Surface Morphology

The SEM micrographs obtained after corrosion test from exposed and unexposed MS in 1.0M HCl for 24 hours in the existence and inexistence of 500 ppm of the green synthesized ligand and its transition metal (II) complexes are presented here in figure-6. The graphs shows that corrosion rate reduced extremely in the presence of inhibitors and a good preventative film adsorbed on the steel surface [40]. This film acted as a barrier and was accountable for the inhibition of corrosion.Comparing the SEM images of the uninhibited and inhibited steel samples after 24 hours immersion in 1 M HCl medium at 303K revealed the anti-corrosive properties of the examined derivatives.Mild steel in 1.0M HCl solution experienced a lower corrosion rate compared to ligand (apba) in the presence of M-complexes, which reflects the better corrosion mitigation propensity of these over ligand (apba).

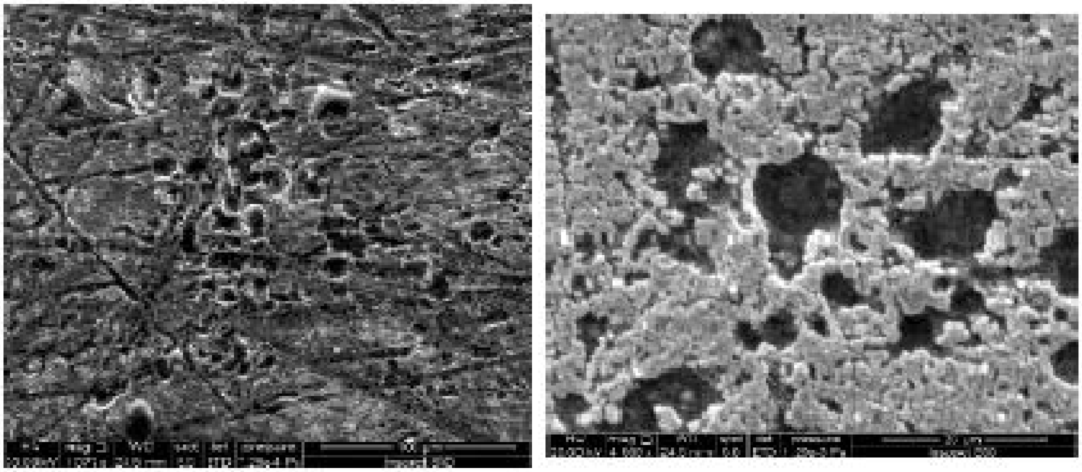


Without inhibitors



With ligand (apba)

With Co-complex



With Ni-complex

With Cu-complex

Figure-6:*Scanning electron micrographs of mild steel without inhibitors and with investigated inhibitors in 1.0M HCl solution*

CONCLUSIONS

The present article describes the synthesis of a bivalent amide ligand (O O 'donor') and its Co(II), Ni(II) and Cu(II) complexes using the environmentally friendly microwave-assisted reaction in a green solvent relevant to the principle of green and sustainable chemistry. The investigated compounds were characterized by spectro-analytical techniques. The main goal was to investigate the anticorrosion behavior of these compounds on mild steel in 1.0 M HCl using experimental technique such as weight loss measurements. The following conclusions may be estimated from this research project:

1. A new bidentate amide (O,O' donor) ligand (apba) and its 3d-transition metal (II) coordination compounds were synthesized using the microwave-promoted reaction in PEG-400 solvent.
2. The ligand and its Co(II), Ni(II) and Cu(II) complexes were characterized by elemental analyses, physico-spectroscopic techniques and the study revealed the square planar geometry of the coordination compounds.
3. The weight loss measurement method was used to investigate the corrosion inhibition activity of the investigated ligand (apba) and its metal complexes.
4. The experimental data show that ligand as well as its metal complexes show efficient corrosion inhibitor property.
5. Inhibition efficiency increases with the increase of the concentration s of the investigated compounds.
6. The metal complexes exhibit greater corrosion inhibition efficiency compared to the free ligand, likely due to their planarity and larger molecular size, increasing the inhibition efficiencies in the following order: [$CoLCl_2$] > [$NiLCl_2$] > [$CuLCl_2$] > Ligand.
7. The thermodynamic and adsorption parameters indicated spontaneous adsorption of inhibitors on mild steel surface and through chemically adsorption type and follows Langmuir adsorption isotherm. leads to formation of coordination bond between inhibitor molecules and the d orbital of the iron atom.
8. The SEM micrographs revealed the existence of protective film of inhibitors on mild steel surface which inhibits metal deterioration in the aggressive acid medium.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Authors hereby declare that no generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

DATA AVAILABILITY STATEMENT

The data that have been used are present here.

ETHICAL STATEMENT

The authors declare that the research for the manuscript submitted does not involve human or animal research subjects.

REFERENCES

1. R. Schmink, and N. E. Leadbeater, Microwave Heating as a Tool for Sustainable Chemistry: An Introduction, *Microwave Heating as a Tool for Sustainable Chemistry*; CRC Press: Boca Raton, FL, USA; pp. 1–24 (**2011**).
2. A. K. Mahato, B. M. Sahoo, B. K. Banik, and B. C. Mohanta, Microwave-assisted synthesis: Paradigm of green chemistry. *J. Indian Chem. Soc.*, 95, 1327–1339 (**2018**).
3. Á. Díaz-Ortiz, and J. R. Carrillo, *Microwaves in green and sustainable chemistry*. In Microwave Chemistry; Cravotto, G., Carnaroglio, D., Eds.; De Gruyter: Berlin, Germany; pp. 167–183 (**2017**).
4. P. Anastas, and N. Eghbali, *Green Chemistry: Principles and Practice*. Chem. Soc. Rev., 39, 301–312 (**2010**).
5. C. O. Kappe, My Twenty Years in Microwave Chemistry: From Kitchen Ovens to Microwaves that aren’t Microwaves. *Chem. Rec.*, 19, 15–39 (**2019**).
6. E. Gabano, and M. Ravera, Microwave-Assisted Synthesis: Can Transition Metal Complexes Take Advantage of This “Green” Method? *Molecules*; 27, 4249- (**2022**).

7. G. Cravotto, and P. Cintas, *Microwave chemistry: History, development, and legacy*. In Microwave Chemistry; G. Cravotto, and D. Carnaroglio, Eds.; De Gruyter: Berlin, Germany; pp. 1–17 (**2017**).
8. K. P. Srivastava, U. S. Yadav, and Pragya Singh, Microwave-assisted Synthesis, Characterization and Antimicrobial Evaluation of Transition Metal (II) Complexes of Unsymmetrical Tetradentate (ONON Donor) Schiff Base. *Orient. J. Chem*., **37** (4), 972-978 (**2021**). http://dx.doi.org/10.13005/ojc/370426
9. T. Abe, A. Miyazawa, Y. Kawanishi, and H. Konno, Microwave-Assisted Synthesis of Metal Complexes, *Mini-Rev. Org. Chem*., 8, 315–333 (**2011**).
10. N. Bhojak, D. D. Gudasaria, N. Khiwani, and R. Jain, Microwave Assisted Synthesis Spectral and Antibacterial Investigations on Complexes of Mn(II) with Amide Containing Ligands. *E-J. Chem*., 4, 785626 (**2007**).
11. P. R. Roberge, *Handbook of corrosion Engineering*, McGraw-Hill, (**2000**).
12. O. L. Riggs Jr., "*Corrosion Inhibitors*" (2nd Edition), C. C. Nathan, NACE, Houston, TX, (**1973**).
13. Suraj B. Ade; Corrosion inhibition analysis of mild steel in various acid medium by amide (-$CONH_2$) group of organic compounds, *World Journal of Pharmaceutical Research*, 11, 3, 1525 (**2022**).
14. Vinod P. Singh, Pooja Singh, Ashish K. Singh,Synthesis, structural and corrosion inhibition studies on cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 2-acetylthiophene benzoyl hydrazone, *InorganicaChimicaActa*, 379, 56–63 (**2011**).
15. M. R. Ezhilarasi, B. Prabha, and T. Santhi, Corrosive inhibitive effect of pyrazole compounds towards the corrosion of mild steel in acidic medium, *Rasayan Journal of Chemistry*, 8 (1),71-83 (**2015**).
16. Reda. S. Abdel Hameeda, M. Alfakeerc, and M. Abdallahd, Inhibiting Properties of Some Heterocyclic Amide Derivatives as Potential Nontoxic Corrosion Inhibitors for Carbon Steel in 1.0 M Sulfuric Acid; *Surface Engineering and Applied Electrochemistry*, 54, (6), 599–606 (2018). DOI: 10.3103/S1068375518060054
17. R. S. Abdel Hameed and A. H. Shamroukh; Synthesis, characterization, and evaluation of some acyclic S-nucleosides of pyrazolo[3,4-d] pyrimidine-thiones as corrosion inhibitors for carbon steel in hydrochloric acid;*Int. J. Corros. Scale Inhib.*, 6, (3), 333–348 (**2017**). DOI: 10.17675/2305-6894- 2017-6-3-8
18. Y. Elkhotfi, H. Boubekraoui, I. Forsal, and E. M. Rakib; Inhibition Action of 1H-1,2,4-triazol-4-amine, 3, 5-diphenyl-N- (phenyl methylene) on Ordinary Steel

Corrosion in an Acidic Medium; *PortugaliaeElectrochimicaActa*, 40 (3) 141-156 (**2022**). DOI: https://doi.org/10.4152/pea.2022400301

19. A. S. Fouda, M. A. Diab, and S. Fathy, Role of Some Organic Compounds as Corrosion Inhibitors for 316L Stainless Steel in 1 M HCl, *Int. J. Electrochem. Sci.*, 12, 347 – 362 (**2017**).
20. Wurood Ali Jaafar and Ruwaidah S. Saeed, Synthesis, characterization and corrosion inhibition study of new heterocyclic compounds and Schiff base with Co(II), Ni(II), Cu(II) and Hg(II) complexes, *Sys Rev Pharm*, 11 (10), 134-143 (**2020**).
21. D. Greenwood, R. Snack and J. Peurtherer;*Medical microbiology: A guide to microbial infections: Pathogenesis, immunity, laboratory diagnosis and control*, 15th edn., (**1997**).
22. W. J. Geary, The use of conductivity measurements in organic solvents for the characterization of coordination compounds, *Coordination Chemistry Reviews*, 7(1):81–122 (**1971**).
23. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York, NY, USA, (**2009**).
24. L. J. Bellamy, *The Infrared spectra of Complex Molecules*, Chapman & Hall, London, UK, (**1975**).
25. B. N. Figgis, *Introduction to ligand fields*, Wiley Eastern Ltd. New Delhi, (**1976**).
26. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, (**1984**).
27. G. B. Bagihalli, P. G. Avaji, P S Badami, and S A Patil, Synthesis, spectral characterization, electrochemical and biological studies of Co(ii), Ni(II), and Cu(II) complexes with thiocarbohydrazone, *J. Coord. Chem.*,61 (17), 2793-2806 (**2008**). DOI: https://doi.org./10.1080/00958970801975109
28. Cezar Spinu and Angela Kriza;Co(II), Ni(II) and Cu(II) complexes of bidentate Schiff Bases, *Acta Chim. Slov.*, 47, 179−185 (**2000**).
29. R. L. Carlin and A. J. Van Dryneveledt;*Magnetic properties of transition metal compounds*, Springer-Verlag, New York, (**1997**).
30. B. J. Hathway, and D. E. Billing, The Electronic Properties and Stereochemistry of Mono-Nuclear Complexes of the Copper(II) Ion. *Coordination Chemistry Reviews*, 5, 143-207 (**1970**).https://doi.org/10.1016/S0010-8545(00)80135-6
31. Pradnya D. Desai, Chetan B. Pawar, Madhavi S. Avhad, and Aarti P. More; Corrosion inhibitors for carbon steel: A review; *Vietnam J. Chem.*, 61(1), 15-42 (**2023**). DOI: https://doi.org./10.1002/vjch.202200111

32. Jagadeesan Saranya, Murugaiyan Sowmiya, Palanisamy Sounthari, Kandhasamy Par ameswari, Subramanian Chitra, and Kittusamy Senthilkumar; N-heterocycle as corrosion inhibitors for mild steel in acidic medium, *Journal of Molecular Liquids*, 216, 42-52 (**2016**). DOI: https://doi/10.1016/j.molliq.2015.12.096
33. Chandrabhan Verma, and M.A. Quraishi; Recent progresses in Schiff bases as aqueous phase corrosion inhibitors: Design and applications, *Coordination Chemistry Reviews*, 446, 214105 (**2021**). DOI: https:// doi.org/10.1016/j.ccr.2021.214105
34. Sujata Kumari Gupta, Raj Kumar Mehta, and Mahendra Yadav; Schiff bases as corrosion inhibitors on mild steel in acidic medium: Gravimetric, electrochemical, surface morphological and computational studies, *Journal of Molecular Liquids*, 368B, 120747 (**2022**). DOI: https://doi.org/10.1016/j.molliq.2022.120747
35. C. Verma, J. Haque, M.A. Quraishi, and E.E. Ebenso; Aqueous Phase EnvironmentalFriendly Organic Corrosion Inhibitors Derived from One Step Multicomponent Reactions: A Review; *Journal of Molecular Liquids*, **(2019)** 275, 18-40. https://doi.org/10.1016/j.molliq.2018.11.040
36. M. Mahdavian and M. M. Attar; Electrochemical behaviour of some transition metal acetylacetonate complexes as corrosion inhibitors for mild steel; *Corros. Sci*, (**2009**), 51, 409–414.
37. B. Yiheyis, D. Nithyakalyani and K. Ananda; Synthesis, Structural Characterization, Corrosion inhibition and in vitro antimicrobial studies of 2-(5-Methoxy-2-Hydroxybenzylideneamino) Phenol Schiff Base ligand and its transition metal complexes, *International Journal of Chem Tech Research*, (**2014),** 6 (11), 4569-4578.
38. P. V. Singh, P. Singh and A.K. Singh; Synthesis, structural and corrosion inhibition studies on cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 2-acetylthiophene benzoylhydrazone; *Inorg. Chim. Acta*, **(2011),** 379, 56–63. DOI: https://doi.org/10.1016/j.ica.2011.09.037
39. Ali M. Hassan, Bassem H. Heakal, Ahmed Younis, M. A. Bedair, Zaghloul. I. Elbialy and M. M. Abdelsalam; Synthesis of Some Triazole Schiff Base Derivatives and Their Metal Complexes under Microwave Irradiation and Evaluation of Their Corrosion Inhibition and Biological Activity; *Egypt. J. Chem.* (**2019**), Vol. 62, No. 9. pp. 1603- 1624.DOI: https://doi.org/10.21608/ejchem.2019.10834.1699