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Research Article

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Synthesis, structural study, corrosion inhibition studies, and antibacterial activities of bis(di-5-bromosalicylaldehyde)biphenyl-3,3'-dimethoxy-4,4'- diamine and its transition metal complexes

A. M. Hassan¹, A. M. Nassar¹, M. A. Shoeib² and A. N. El kmash^{1*}

¹Chemistry Department, Faculty of Science (boys), Al-Azhar University, Cairo, Egypt ²Central of Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt

ABSTRACT

Bis(di-5-Bromosalicylaldehyde)biphenyl-3,3'-dimethoxy-4,4'-diamine (H_2L^1) and its Co(II), Ni(II), Cu(II), and Zn(II) complexes have been synthesized and characterized by elemental analysis, magnetic moment, UV-Vis., IR, ¹H NMR,¹³C NMR and ESR spectral techniques. Also, the thermal properties were examined by TGA. The corrosion inhibition of compounds has been investigated by weight loss, potentiodynamics polarization, and SOM on mild steel in (0.5M) HCl. The adsorption of compounds was founded to obey the Langmuir adsorption isotherm model and show mixed type inhibition behavior. The antibacterial activity of compounds was measured against SRB. The antibacterial results showed a good antibacterial activity of the synthesized compounds.

Keywords: Schiff base complexes & Corrosin inhibitors & Biocides.

INTRODUCTION

A corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes or prevents corrosion [1]. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [2]. The choice of the inhibitor is based on two considerations: first it could be synthesized conveniently from relatively cheap raw materials, secondly, it contains the electron cloud on the aromatic ring or, the electronegative atoms such as nitrogen and oxygen in the relatively long chain compounds [3]. Most commercial inhibitor formulations include an aldehyde and amines in their structure [4]. Schiff bases, named after Hugo Schiff (1864-1915), and their transition metal complexes continue to be of interest even after over a hundred years of study [5-8]. Schiff base with –CH=N– linkage (azomethine) have both the above features combined with their structure which make them effective potential corrosion inhibitors [9, 10]. Various micro-organisms effects on metal are known as biochemical corrosion rate, inducing stress corrosion and pitting corrosion [12]. Several Schiff bases and transition metal complexes have been investigated as corrosion inhibitors and as biocides [13-15].

In this work, we synthesized, and structural studies of Schiff base; Bis(5-Bromosalicylaldehyde)biphenyl-3,3'dimethoxy-4,4'-diamine (H_2L^1) and its Cobalt(II), Nickel(II), Copper(II), and Zinc(II) complexes and studied the effect of compounds on the corrosion of mild steel in 0.5M HCl. The gravimetric and electrochemical techniques such as weight loss, and potentiodynamic polarization measurements were used in this study. The scanning optical microscope was used to explain adsorption of inhibitors on surface of metal. Some isotherm was used to describe the adsorption behavior of the compounds understudied. Also, antibacterial activity against SRB of compounds was studied.

EXPERIMENTAL SECTION

The analytical reagent grade (AR) o-Dianisidine, 5-Bromo salicylaldehyde, CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, ZnCl₂.2H₂O are Merck chemicals was used and organic solvents used (methanol, ethanol, diethyl ether and acetone) were HPLC or extra pure grades and were used without further purification. The electrolyte solution was 0.5 M HCl, prepared from analytical grade HCl and distilled water. All corrosion tests were performed at room temperature. The mild steel working electrode specimens have the following composition, C=0.066%, Mn=0.3%, P=0.01%, S=0.02%, Cr=0.026%, Cu=0.02%, and Fe=99.5% and using 2 cm² coupons of same sample material. The weight loss and Polarization measurements were performed on mild steel in deaerated 0.5 M HCl solution with and without Schiff base and its complexes additives within the concentration range 1, 3, 5, and 7×10^4 Mol/dm³. The Stock solutions of the Schiff base and its complexes were made in 10:1 ratio water: DMSO mixture by volume to ensure solubility. Weight loss experiments were carried out in an electronically at room temperature. After recording the initial weights of mild steel specimens on a Mettler Toledo, Japan AB 135-S/FACT, single pan analytical balance, (with a precision of 0.01mg), they were kept in different isolated chamber (perfectly insulated from each other) for 48hours of exposure time in different concentration 1, 3, 5, 7×10^{-4} Mol/dm³. A uniform thin film of compounds was adsorbed onto the metal coupons after 48 hours of exposure. Then these coupons were taken out from the chamber and washed initially under the running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with triple distilled water and acetone and dried with hot air blower and then weighed again. The electrochemical behavior of the mild steel sample in inhibited and noninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 0.5 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -250 to +500 mV versus corrosion potential at a scan rate of 1 mV s⁻¹. The optical microscope images were taken to establish the interaction of inhibitors with metal surface in acid medium. The surface images of carbon steel samples were examined by optical microscope after the sample is immersed in 0.5 M HCl for 48 hours in absence and in the presence of inhibitors. The stabilized mixed culture of sulfate reducing bacteria (SMC-SRB) was isolated by the National Research Center (NRC) from received internal sludge sample of the failure shipping pipe line into sterile screw capped vials (1.5×5 cm) containing modified Postgate medium B .The bottle was incubated for 7 days at 30°C. Blackening of the bottle meant a positive growth for SRB. This step was repeated at least 10 times to obtain a SMC-SRB. Postage medium B was expressed in g/L was used for the following purposes isolation, enrichment of SRB and biological assay using most probable number (MPN) technique. The mic of prepared compounds against SMC-SRB activity were determined by preparing postage medium B containing the following concentrations (100, 300 and 700 ppm). The inoculation was done by inoculating one ml of a four days enriched old culture of SMC- SRB into sterile capped bottles containing each biocide amended medium. Incubation of biocides and control (without biocides) tubes was done at 30°C for 7 days at pH=7. The antibacterial activity of compounds against SMC-SRB was detected by using MPN technique.

Instruments:

Elemental analysis (%C, %H, and %N) was determined in the Micro analytical Laboratory, The regional center for mycology and biotechnology, Al-Azhar University. Magnetic susceptibility measurements were carried out at room temperature on a Sherwood Scientific Magnetic Balance at El-Mansoura University, Egypt. Electronic spectra were measured in the ultraviolet (UV–Vis) range (195–1100 nm) using a Perkin-Elmer lambda 35 UV–Vis Spectrometer at the Central laboratories, Tanta University. Infrared (IR) spectra were recorded using KBr pellets on a Perkin-Elmer 1430 Spectrometer for the region (200–4000 cm⁻¹) at the Central laboratories, Tanta University. The proton neucular magnetic resonance (¹H NMR) and (¹³C NMR) spectra were recorded on GEMINI-300BB NMR 500 MHz Spectrometer at the Chemical laboratories, the main laboratories of the war chemical. The electron spin resonance (ESR) spectra were recorded on Bruker EMX spectrometer working in expand 9.7 GHz with 100 KHz frequency and microwave power 1MW and modulation amplitude 4Gauses at the Central laboratories, Tanta University. The mass spectra were recorded on GC-MSA-QP 5050A Shimadzu at the Micro analytical Laboratory, the regional center for mycology and biotechnology, Al-Azhar University.

Potentiodynamics polarization measurement was carried out using Autolab-PGSTAT302N-HP and using a glassy carbon working electrode, platinum wire auxiliary electrode and an Ag/AgCl as reference electrode and Scanning Optical Microscope (SOM) using ZEISS, Axiovert 40 mat microscope at Central metallurgical research and development institute (CMRDI), Helwan, Egypt.

Synthesise of Schiff base H₂L¹ ligand (1):

The Schiff base ligand H_2L^1 was synthesized by adding drop wise 25mL ethanolic solution of 5-Bromo salicylaldehyde (2.020gm, 0.010 mol) to 25mL hot ethanolic solution of o-dianisidine (1.22gm, 0.005mol) in round flask and refluxing the mixture for 3 hours. The volume of solution reduced to half volume and allowed to cool at room temperature. The orange colour precipitate was collected, washed several times with ethanol, diethyl ether

and finally air dried. The purity of the ligand was checked by TLC technique. M.p. 255 °C, M. Wt. 611.0, Yield (83.5%), Anal. Calc. for $C_{28}H_{22}N_2O_4Br_2$: C, 55.1; H, 3.6; N, 4.6 %, Found: C, 54.98; H, 3.64; N, 4.73 %; main IR Peaks (KBr, cm⁻¹): v(OH)3428, v(C=N)1615.

Synthesise of the metal complexes:

The cobalt(II), Nickel(II), copper(II), and Zinc(II) complexes of Schiff base H_2L^1 were synthesized by adding drop wise of 25ml methanolic solution of metal(II) chlorides(0.010mol) to 25ml hot methanolic solution of Schiff base H_2L^1 ligand (3.05gm, 0.005mol) separately, in (2:1) molar ratio of (M:L) in a round bottom flask and reaction mixture reflux for 3hr. The metal complexes were filtered, washed several times with methanol, diethyl ether, and finally dried at room temperature.

The complex, Co₂L(H₂O)₂(Cl)₂.2H₂O (2):

Dark brown solid. M.p.285 °C; M. Wt. 868.8; Anal. Calc for $C_{28}H_{28}Co_2N_2O_8Br_2Cl_2$: C,38.67; H,3.22; N,3.22; Co, 13.56 %; Found: C,38.74; H,3.27; N, 3.29; Co, 13.3 %; main IR Peaks(KBr, cm⁻¹): v(C=N) 1563.

The complex, $Ni_2L(H_2O)_2(Cl)_2H_2O(3)$:

Dark brown solid. M.p.270 °C; M. Wt.850.28; Anal. Calc for $C_{28}H_{26}Ni_2N_2O_7Br_2Cl_2$: C,39.5; H,3.05; N,3.28; Ni,13.8 %; Found: C, 39.56; H, 3.0; N, 3.38; Ni, 13.3 %; main IR Peaks(KBr, cm⁻¹): v(C=N) 1561.

The complex, $Cu_2L(H_2O)_2(Cl)_2.H_2O(4)$:

Black solid. M.p.290 °C; M. Wt. 859.98; Anal. Calc for $C_{28}H_{26}Cu_2N_2O_7Br_2Cl_2$: C,39.07; H,3.02; N,3.25; Cu, 14.77%; Found: C, 39.15; H, 2.99; N, 3.3; Cu, 14.3 %; main IR Peaks(KBr, cm⁻¹): v(C=N) 1563.

The complex, Zn₂L(H₂O)₂(Cl)₂.2H₂O (5):

Brown solid. M.p.>300°C; M. Wt. 881.66; Anal. Calc for $C_{28}H_{28}Zn_2N_2O_8Br_2Cl_2$: C,38.1; H,3.17; N,3.17; Zn, 14.83 %; Found: C, 38.2; H, 3.2; N, 3.22; Zn, 14.2 %; main IR Peaks(KBr, cm⁻¹): v(C=N) 1564.

RESULTS AND DISCUSSION

The present Schiff base H_2L^1 ; Fig. (1) was prepared by refluxing in ethanol (1:2) molar ratio of o-dianisidine with 5-Bromo salicyaldehyde, respectively. The structure of formed Schiff base was established by IR, ¹H NMR, mass, and UV–Vis spectra as well as elemental analysis. All complexes were prepared by direct reaction between one mole of Schiff base ligand H_2L^1 to two moles of corresponding salts.



Fig. (1): The proposed Structure of Schiff base ligand H_2L^1

Characterization of Schiff base ligand (H₂L¹):

The infrared spectrum of the Schiff base ligand H_2L^1 in the region 200–4000 cm⁻¹ shows a medium absorption band at 1615 cm⁻¹ assigned to the v(C=N) azomethene stretching vibrations, indicating the formation of the Schiff base linkage. Furthermore, the absence of C=O and NH₂ stretching vibration in the spectra of the ligand related to aldehyde and amine, respectively, indicate the occurrence of Schiff base condensation [16]. The spectrum shows a broad medium intensity band occurs at 3428cm⁻¹ due to vOH, the phenolic vC-OH stretching vibration is appeared at 1282cm⁻¹, and the two bands are evidence to the presence intramolecular hydrogen bond [17] as shown in the structure of ligand; **Fig.(1)**. The two weak intensity bands at 3035 and 2959 cm⁻¹ corresponding to v(C–H) ar., and v(C–H) aliph.stretching vibration. The (Ph–N) gives medium intensity band at 1175 cm⁻¹.

The ¹H NMR spectrum of the Schiff base ligand shows signals lying at range 14.1 ppm are due to the resonance hydroxyl groups, the signals of OH groups lying at the higher field side can be attributed to the contribution of the OH group intramolecular and intermolecular hydrogen bonds, and the addition of D₂O to the previous solution results in disappear the signal due to proton exchange [18]. Also, the multiple signals lying in the range of 6.6–7.8 ppm [19] are due to resonance of aromatic protons; **Fig. (2a, b)**. The methoxy groups appear signal at 3.9 ppm [20]. The resonance of imine proton was downfield shifted to 9.02 ppm due to shielding effect of the hydroxyl group. The ¹³C NMR spectrum of Schiff base showed signals at 162.12ppm(C2-ipso), 160.05(C7-H), 153ppm(C13-ipso),

141.6ppm(C11-ipso), 135.2ppm(C8-ipso), 133.1ppm(C4,C6-H), 132.4ppm(C9-H), 119.4ppm(C3,C10-H), 119.1ppm(C1-ipso), 116.8ppm(C5-H), 109.5ppm(C12-H), and 55.9ppm(C14-H) as shown in **Fig.(3**).

The electronic spectrum of the ligand displays bands at 309 and 395 nm are attributed to intraligand π - π * and n- π * transitions for the benzene ring and azomethine group [21].

The mass spectrum of the free Schiff base ligand **Fig.(4)** shows its molecular ion peak at m/e = 611 which matching with a formula weight (Scheme 1).



Fig. (2-a): The ¹HNMR Spectrum of (H₂L¹) in (DMSO)



Fig. (2-b): The ¹HNMR Spectrum of (H₂L¹) in (DMSO+D₂O)



Fig. (3): Number of carbon atoms in Schiff base ligand $H_2 L^1 \label{eq:harden}$



Fig. (4): The Mass Spectrum of (H₂L¹)

Characterization of complexes:

Infrared spectra (IR):

The infrared spectra were collected in a **table** (1) of the complexes and data give us some information about the bonding in the complexes. The band in the IR spectrum of the ligand at 1615 cm⁻¹ is found to be shifted to lower frequencies (1581-1584) cm⁻¹ in the spectra of the complexes, indicating coordination via the azomethine nitrogen [22], in addition, the new bands in the far infrared spectra of the complexes in the range (510-525) cm⁻¹ assigned to the vM-N. Deprotonation of of all hydroxyl functions is confirmed by the lack of phenolic v -C-O and shift lower wave number about (1257-1262) cm⁻¹ but appeared in free ligand at1282cm⁻¹, indicating the Participation with the metal ion as -O- [23], on the other hand very broad bands observed in the spectra of the complexes in the range (3407-3443) cm⁻¹ considerable support the presence of lattice and coordinated water molecules in the complexes [24-26]. The weak bands appeared in the far IR spectra between (586-587) cm⁻¹ astributed to vM-O. The far infrared spectra of the complexes show weak bands in the range (460-485) cm⁻¹ ascribable to vM-Cl.

Assign. Comp.	v(H ₂ O)	v(CH) ar.	v(CH) aliph.	v(C=N)	v(C-O) phenolic	v(Ph-N)	v(M-O)	v(M-N)	v(M- Cl)
2	3407	3041	2960	1583	1262, 1248	1135	587	524	460
3	3423	3040	2936	1581	1260, 1247	1145	586	511	485
4	3443	3045	2933	1583	1258, 1247	1138	586	525	485
5	3427	3047	2938	1584	1257, 1247	1140	586	510	483

Ultraviolet- Visible (UV-Vis.) Spectra:

The electronic spectrum of Co(II) complex (2) shows the low intensity shoulders at 590 and 656. The former bands are probably due to ${}^{4}A_{2}$ (F) $\rightarrow {}^{4}T_{1}$ (P) and ${}^{4}A_{2}$ (F) $\rightarrow {}^{4}T_{1}$ (F) which indicates the tetrahedral geometry of this complex. The magnetic moment (4.2 B.M) confirms the tetrahedral geometry of the ligand around Co⁺² ions [27]. The spectrum of the Ni(II) complex (3) shows a very broad band at 504 nm containing the ${}^{3}T_{1}(F)\rightarrow {}^{3}T_{1}(P)$ corresponding to the tetrahedral configuration of this complex. The magnetic moment (3.2 B.M) indicates the tetrahedral geometry of the ligand around Ni⁺² ions [28]. The spectrum of Cu(II) complex (4) gave a broad band at 496 nm, hence, the copper complex appears to be ${}^{2}B_{1g}\rightarrow {}^{2}A_{1g}$ in tetrahedral geometry and the μ_{eff} value (2.0 B.M) is corresponding to the square planar geometry arrangement of the ligands around the Cu⁺² ions [29]. Finally, the electronic absorption spectrum of Zn(II) complex (5) showed the charge transfer band at 425 nm, the diamagnetic behavior due to d¹⁰ configuration of Zn⁺² ions [30].

From the above spectral data, the proposed structures as in Fig. (5) have been assigned for the metal complexes.



Fig. (5): The proposed Structure of complexes (2-5)



Scheme (1): The mass fragmentation pattern of Schiff base ligand H₂L¹

¹H NMR and ¹³C NMR spectra:

The ¹H NMR spectrum of the zinc complex (**5**) as showed in **Fig. (6-a)** recorded in DMSO-d6 at room temperature. In the spectrum of the zinc complex the hydroxyl phenolic proton signals observed at δ 14.1 ppm in the spectrum of the free ligand was found to be absent, confirming the subsequent involvement of deprotonated hydroxyls in chelation to the metal ions [31]. The broad signal appeared at δ 3.5 ppm, which not found in the spectrum of the free ligand due to resonance of protons of coordinated water molecules. The addition of D₂O to the previous solution showed the absence of the signal due to proton exchange **Fig. (6-b)**. The ¹³C NMR spectrum of zinc complex showed chemical shift to higher value at 162.8ppm (C2-ipso) and 160.6ppm (C7-H) in comparison with signal of

free ligand suggest that coordination through oxygen of phenolic (-C-OH) and nitrogen of azomethine (C=N) group, and no change in signals of other carbon atoms.

Electron Spin Resonance (ESR) spectra:

The electron spin resonance (ESR) spectrum of Cu(II) complex (4); **Fig.(7**) in solid state gives axial signal shape and having symmetric bands with two g value, $g_{\parallel} = 2.16$, $g_{\perp} = 2.04$. These values suggest a tetrahedral stereochemistry for the complex. The average g value equal 2.08 were calculated according to the equation g_{av} $=1/3[g_{\parallel} + 2g_{\perp}]$. Complex (4) exhibits $g_{\parallel} < 2.3$, suggesting covalent characters of the copper- ligand bonding in this complex [32]. From the observed trend $g_{\parallel} > g_{\perp} > 2.0023$, it is clear that the unpaired electron lies predominantly in $d_x^2 \cdot g^2$ orbital, giving 2B_{1g} as the ground state [33]. The exchange interaction (axial) parameter (G), calculated as G = $(g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$, and found for the present copper(II) complex is 4.2, suggests that the local tetragonal axes are aligned parallel and the exchange interactions between copper centers in the solid state are negligible [34-35]. The ESR spectral parameter of Cu(II) in complex having tetrahedral geometry around Cu(II) ions. These data are well consistent with other reported values [36].



Fig.(6-a): ¹HNMR spectrum of Zn(II) complex(5) with DMSO



Fig.(6-b): ¹HNMR spectrum of Zn(II) complex (5)with DMSO and D₂O



Fig.(7): ESR spectrum of Cu(II) complex(4)

TGA:

The thermo gravimetric analysis (TGA) curves for complexes (2 and 3); **Figs.(8-9**), respectively, were obtained at a heating rate of 10° C/min and flowing nitrogen atmosphere over a temperature range of 25–800°C and the proposed decomposition data were recorded in **table (2)**. The decomposition temperature and the weight losses of the complexes were calculated from TGA data.

Table (2): Thermal gravimetric analysis of compounds 2 and 3

Compound No.	Stages	Temp. range (°C)	Calculated %	Found %	Assignment
	First Step	40-103	12.30	11.20	2 Crystalline $H_2O + Cl_2$
	Second Step	103-192	9.20	10.00	2 Coordinated $H_2O + N_2O$
2	Third Step	192-337	13.80	14.20	Decomposition of organic part of ligand $(C_7H_4) + O_2$
	Fourth Step	337-631	52.80	52.60	Decomposition of organic part of ligand $(3C_7H_5) + Br_2 + O_2$
	Residue	40-632	12.90	12.10	1.5 CoO
	First Step	40-218	6.30	6.80	1 Crystalline H ₂ O + 2 Coordinated H ₂ O
3	Second & Third Step	218-472	30.20	29.30	Decomposition of Organic part of ligand($2C_7H_4$) + O_2
	Fourth Step	472-660	51.40	52.00	Decomposition of Organic part of ligand($2C_7H_5$) + Br_2 + Cl_2 + N_2
	Residue	40-660	12.20	11.90	1.4 NiO



Fig.(8): TGA of Co(II) complex(2)

.....(1)

.....(3)



Fig.(9): TGA of Ni(II) complex(3)

Corrosion inhibition efficiency: Weight Loss Technique:

The corrosion rate (CR) in mils per year (MPY) and percentage corrosion inhibition efficiency (IE% = μ_w %) were calculated using the equations (1) and (2) respectively [37].

Where, W = Weight loss (gm), D = Density of mild steel (7.85 gm/cm³), A = Area of specimen (sq.cm), T = Exposure time (hours).

$$\mu_{\rm w}\% = ((C_{\rm R}^0 - C_{\rm R}^{\rm i}) / C_{\rm R}^0) \times 100 \qquad \dots \dots (2)$$

Where, C_R^0 and C_R^i are the corrosion rate in the absence and presence inhibitors, respectively. From the evaluated weight loss, surface coverage (θ) was calculated using equation (3):

$$\boldsymbol{\theta} = (\mathbf{C}^{0}_{\mathbf{R}} - \mathbf{C}^{i}_{\mathbf{R}} / \mathbf{C}^{0}_{\mathbf{R}})$$

The values of percentage inhibition efficiency (μ_{WL} %), corrosion rate (CR) and surface coverage (θ) obtained from weight loss method at different concentrations of all compounds at 293 K are summarized in **Table (3)**.



Chart (1): The inhibition efficiency of Schiff base and its complexes (1-5)

From the data, the Schiff base and its complexes show appreciable corrosion inhibition for carbon steel in 0.5M HCl medium. The effect of inhibitor concentration on inhibition efficiency in the presence of different concentration of the Schiff base and its complexes were shown that the maximum inhibition efficiency at 7×10^{-4} Mol/dm³ in 0.5M HCl solution. The Co (II) complex (2) exhibited the greatest impact on corrosion inhibition among the other compounds as appear in the **chart** (1). It was found that the efficiency order, followed by compounds are 2 > 5 > 1 > 3 > 4.

Potentiodynamic polarization:

The electrochemical behavior of the mild steel sample in inhibited and non-inhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion current densities (*i*corr). From the polarization curves obtained, **Figs. (10-14)**, the corrosion current (*i*corr) was calculated by curve fitting using the equation (4) and (5):

$$I = i_{\rm corr} \left[\exp\left(\frac{2.3\Delta E}{b_{\rm a}}\right) - \exp\left(-\frac{2.3\Delta E}{b_{\rm c}}\right) \right]$$

... (4)

Compound	Concentration(M)	C.R(mm/y)	θ	IE%
Blank	0.5M HCl	0.0035	-	
	1*10-4	0.00087	0.792	79.26
III. (1)	3*10-4	0.00076	0.817	81.77
$H_2L;(1)$	5*10-4	0.00046	0.890	89.03
	7*10-4	0.00037	0.900	90.02
	1*10-4	0.00074	0.824	82.43
	3*10-4	0.00071	0.829	82.95
2	5*10-4	0.00036	0.914	91.41
	7*10-4	0.00026	0.930	93.06
	1*10-4	0.00172	0.591	59.11
2	3*10-4	0.00096	0.743	74.37
5	5*10-4	0.00079	0.788	78.86
	7*10-4	0.00046	0.889	88.96
	1*10-4	0.00099	0.762	76.22
4	3*10-4	0.00081	0.782	78.23
4	5*10-4	0.00071	0.807	80.71
	7*10-4	0.00046	0.875	87.58
	1*10-4	0.00173	0.530	53.03
5	3*10-4	0.00106	0.712	71.26
5	5*10-4	0.00065	0.822	82.23
	$7*10^{-4}$	0.00029	0.919	91.94

Table (3): The corrosion rate, surface coverage and inhibition efficiency values for the corrosion of mild steel in aqueous solution of 0.5 M HCl in the absence and in the presence of different concentrations of different inhibitors from weight loss measurements

The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship:

$$\mu_{\rm P} \% = \frac{i_{\rm corr}^0 - i_{\rm corr}^i}{i_{\rm corr}^0} \times 100$$

Where, i_{corr}^0 and i_{corr}^i are the corrosion current density in the absence and presence of inhibitor, respectively. The electrochemical polarization parameters of steel corrosion in 0.5M HCl in the presence and absence of various concentrations of Schiff base and its complexes and the corresponding corrosion efficiency by using Nova 1.10 program are given in **table (4)**.

The obtained results show that the inhibition efficiency increase in the case of all used compounds when the inhibitor concentration increases. The results obtained from the polarization measurements are in good agreements with those obtained from the weight loss method and render to it. Also, addition of studied compounds effected both anodic and cathodic reactions. Therefore, those compounds could be classified as mixed type (anodic/cathodic) inhibitors. From the data, The corrosion rsistance of mild steel samples is having the following efficiency order is as 2 > 5 > 1 > 3 > 4 [38-39].

The results indicate that the weight loss of the carbon steel sample was decreased in comparison with absence of Schiff base and its complexes (inhibitors) because these compounds were formed prevented layer on the surface of

... (5)

metal due to presence of azomethine group (C=N), hydroxyl groups, and aromatic rings in the compounds, in addition, the increasing efficiency of complexes compared to the Schiff base due to the larger size and molecular planarity of complexes.



Fig.(10):Polarization curves for mild steel in presence of different concentrations of Schiff base H₂L¹(1)



Fig.(11): Polarization curves for mild steel in presence of different concentrations of (2)



Fig.(12): Polarization curves for mild steel in presence of different concentrations of (3)



Fig.(13): Polarization curves for mild steel in presence of different concentrations of (4)



Fig.(14): Polarization curves for mild steel in presence of different concentrations of (5)

Adsorption isotherm:

The increase in the inhibition efficiency of carbon steel in 0.5M HCl solution, with increasing compound concentration can be explained on the basis of additives adsorption. In the present medium, the additives were showed the linear plots for C/ θ versus Conc. and suggesting to obey the Langmuir adsorption isotherm as seen in **Fig. (15)**, according to the following equation (6):

$$\theta / (1 - \theta) = KC$$

..... (6)

Where θ is the surface coverage, C is the concentration of inhibitors, and K the adsorption equilibrium constant and represent to the degree of adsorption (i.e., the higher value of K indicate that inhibitor is strongly adsorbed on the metal surface); the K obtained from the reciprocal of the intercept of Langmuir plot lines and the slope of these lines is near unity, meaning that each inhibitor molecule occupies one active site on the metal surface.

Comps.	Conc.	ba	bc	Ecorr.	Icorr.	C.R.(mm/y)	I.E.%
1	Blank	39.0	44.9	-479.0	150.4	1.166	
	1*10-4	28.0	32.1	-465.7	45.8	0.355	69.5
	3*10-4	21.9	16.3	-462.1	39.1	0.303	74.0
	5*10 ⁻⁴	22.4	22.0	-467.5	33.6	0.260	77.6
	7*10 ⁻⁴	22.4	23.5	-468.5	24.7	0.191	83.6
	Blank	39.0	44.9	-479.0	150.4	1.166	
	$1*10^{-4}$	30.0	28.8	-476.6	39.7	0.307	73.6
2	3*10 ⁻⁴	15.0	6.6	-446.2	35.4	0.274	76.4
	5*10 ⁻⁴	23.4	24.0	-469.5	30.3	0.235	79.8
	7*10 ⁻⁴	21.9	16.95	-467.9	21.9	0.170	85.4
	Blank	39.0	44.9	-479.0	150.4	1.166	
	1*10-4	21.4	16.2	-473.4	50.7	0.393	66.3
3	3*10-4	13.6	6.9	-459.4	41.4	0.320	72.4
	5*10 ⁻⁴	16.2	11.9	-474.6	37.3	0.289	75.2
	7*10 ⁻⁴	19.0	19.1	-471.8	30.3	0.235	79.8
	Blank	39.0	44.9	-479.0	150.4	1.166	
4	$1*10^{-4}$	16.8	20.0	-455.9	74.2	0.575	50.6
	3*10-4	31.2	29.0	-466.5	42.9	0.332	71.4
	5*10 ⁻⁴	14.1	11.1	-431.4	41.1	0.318	72.6
	7*10 ⁻⁴	41.1	42.9	-461.1	33.2	0.257	77.9
5	Blank	39.0	44.9	-479.0	150.4	1.166	
	1*10-4	17.9	10.4	-481.1	51.9	0.402	65.4
	3*10-4	20.9	17.3	-478.6	42.1	0.326	72.0
	5*10 ⁻⁴	18.8	13.2	-472.2	36.4	0.282	75.8
	7*10 ⁻⁴	36.2	27.5	-461.7	23.3	0.181	84.5

Table(4): Polarization parameters of Schiff base and its complxes



Fig.(15): Langmuir isotherm of H_2L^1 and its complexes at 20°C on carbon steel surface

Scanning Optical Microscope:

The optical images of carbon steel sample **Fig.(16-a)** shows degradation of carbon steel in the absence of inhibitors. The degradation appears more at grain boundaries, since these regions are most susceptible to corrosion, and may be responsible for the high rate of corrosion. The optical images **Figs.(16 b-f)** of the carbon steel after corrosion in acid medium containing inhibitors shows adsorbed layer of inhibitor.

Antibacterial activity:

Enrichment of SRB and biological assay were carried out using the most probable number (MPN) techniques [40]. The incubation period was worked for seven days at 30°C. The results of antibacterial activity of Schiff base ligand H_2L^1 and its complexes against sulfate reducing bacteria (SRB)-stabilized mixed culture were collected in a **table** (5). The antibacterial activity tests were carried out in three concentrations 100, 300, and 700 ppm and showed good antibacterial activity. The most active compound comparison to other is 5 which record 10 Cell/ml at 100 ppm, followed by 4 and 2 compound which record 10^4 , 10^2 ,0 and 10^4 , 10^3 ,10 Cell/ml, respectively. From the results, The antibacterial activity was increased with increasing concentration of compounds.

All compounds showed good antibacterial activitiy with low growth of bacteria at concentration 700 ppm.

The antibacterial activity of compounds due to the interaction of biocides with surface cell causing the destroy of the micro structure of the cell wall and the cytoplasmic membrane[41]. Finally, The good antibacterial activity of metal complexes than Schiff base ligand due to chelation theory [42], which suggest the chelation process increases

the delocalization of the π -electrons over the whole chelate ring, which results in an increase in the lipophilicity of the metal complexes. Consequently, the metal complexes can easily penetrate into the lipid membranes and block the metal binding sites of enzymes of the microorganisms. These metal complexes also affect the respiration process of the cell and thus block the synthesis of proteins, which restrict further growth of the organism.



Fig. (16): Optical microscope images of carbon steel sample in acid medium without inhibitor(a), and with inhibitors $H_2L^1(b)$, 2 (c), 3(d), 4(e), and 5 (f)

Table (5): The antibacterial activity of compounds (1-5), and control against SRB

Comps.	100 ppm	300ppm	700ppm
Control		>10 ⁵	
1	>10 ⁵	10 ⁴	10^{2}
2	10^{4}	10^{3}	10
3	>10 ⁵	10 ⁴	10 ²
4	10^{4}	10 ²	Zero
5	10	N.D*	N.D*

*N.D: Not detected due to low amount of sample.

CONCLUSION

In this study, we prepared a new Schiff base H_2L^1 and its Co (II), Ni (II), Cu (II), and Zn (II) complexes containing nitrogen and oxygen donor atoms due to formation of azomethine group. The structure of Schiff base and its complexes were determined by elemental analysis, magnetic moment, mass, UV, IR, ¹H NMR, ¹³C NMR and ESR spectra. The chemical structure agreement with proposed structure of compounds. The Schiff base and its complexes tested as corrosion inhibitors and fined as mixed type inhibitors as evident from the weight loss and potentiodynamics polarization techniques. The inhibitors efficiencies of compounds increase with increasing concentration of compounds. The order of inhibition efficiency follows the following pattern 2>5>1>3>4, due to increasing of molecular weight of compounds.

The inhibitors obey Langmuir adsorption isotherm. Also, the optical microscope images revealed protection of metal surface in the HCl medium by the adsorption of inhibitors on surface of metal. The synthesized compounds appeared good antibacterial activity against SRB which can be cause corrosion. Finally, the synthesized compounds can be used in double purpose as corrosion inhibitors and as biocides.

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