Synthesis, Characterization and the Corrosion Inhibition Study of Two Schiff Base Ligands Derived From Urea and Thiourea and Their Complexes with Cu(II) and Hg(II) Ions

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Abstract. The research includes synthesis of [L1] and [L2] Schiff base ligands by the reaction of vanillin with urea and thiourea respectively in 2:1 mol ratio. The two ligands were reacted with CuII ion in 1:2 mol ratio and HgII ion in 1:1 mol ratio. The prepared compounds have been identified by FTIR, U.V-Vis, 1H-NMR (L1, L2 and HgII complex) spectroscopies, microelemental analysis (C.H.N.S), magnetic susceptibility measurements, atomic absorption, chloride content along with conductivity and melting point measurements. According to applied characterization methods, the proposed general formulas of CuII and HgII complexes were [Cu2LnCl4] and [HgLnCl]Cl, respectively, (where n= 1, 2). The ability of corrosion inhibition with two ligands and their copper complexes has been studied in diluted hydrochloric acid media.

Keywords: Schiff Base Ligand, Metal Complex, Urea, Thiourea, Corrosion Inhibition.

1. Introduction
Compounds comprising carbonyl and thion groups have an important position between organic reagents to be used as potential donor ligands with transition metal ions [1, 2]. Thiourea and urea derivatives were considered potentially very versatile ligands, its oxygen, nitrogen and sulfur donor atoms provide a multitude of coordinating possibilities [3]. Schiff bases and their metal complexes owns a wide range of applications as anticarcinogenic, pharmaceutical and antimicrobial reagents, beside the industrial and analytical uses[4-7]. Cu, Hg metals are present as essential elements in tracing amounts in biological systems; also they play an important role in bioinorganic chemistry [8]. Because of the main concerns of corrosion in the durability of materials structure; therefore, many studies were always carried out to develop an effective and economic means of corrosion control. To select an appropriate inhibitor for a certain system may be actually complicated, due to the great variety of corrosion related applications [9]. The corrosion inhibitor adsorbed on the surface of metals as a protective layer, the strength of the adsorption bond depends on the type of the functional group donor atom, the electron density and the polarizability of the functional group. Corrosion inhibitor normally contains oxygen, sulfur and nitrogen atoms. Multiple bonds in the corrosion inhibitor molecules that may facilitate the adsorption on the metal surface [10,11]. Recently Al-Obaidi prepared several mixed ligands complexes of Cu(II) and Zn(II) using benzylidene thiourea obtained by the
condensation of benzaldehyde and thiourea as the primary ligand and acetamide or thioacetamide as an additional ligand[12].

2. Experimental
Melting points have been measured using an electro thermal apparatus (Stuart). FT-IR spectra were obtained using FT-IR test scan Shimadzu (FT-IR)- 8300 series spectro photometer in the range (400-4000 cm \(^{-1}\)); spectra were registered as potassium bromide discs at College of Education for Pure Science Ibn- Al- Haitham / Baghdad University. The electronic spectra of the compounds were achieved using (U.V-Vis) spectrophotometer UV-1800, using quartz cell of (1.0) cm length, in the range (1100-200 nm) with concentration (10\(^{-5}\)) M of samples in DMSO solvent at 25\(^{\circ}\)C. Chloride content were determined by potentiometric titration method on (686-titro proceccor-665 dosinat metrome Swiss), while metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu (AA 680) in Ibn Sina Company, Ministry of Industry, Baghdad-Iraq. Electrical conductivity measurements of prepared complexes carried out at (25\(^{\circ}\)C) using (10\(^{-3}\)–10\(^{-5}\)) M solutions of the samples in DMSO solvent using Eutech 150 conductivity meter in central laboratory of College of Education for Pure Science Ibn- Al- Haitham / Baghdad University. \(^1\)H-NMR spectra for two ligands and two Hg\(^{II}\) complexes were recorded in DMSO-d\(_6\) solution using Brucker, model: ultrashield 400 MHz, origin: Switzerland, at Kashan University, Iran. Microelemental Analysis (C.H.N.S) recorded using, Euro EA 300, at College of Education for Pure Science Ibn- Al- Haitham / Baghdad University. Magnetic moments at 298K were determined with a magnetic susceptibility balance (Sherwood Scientific). Samples were recorded at College of Sciences, Al-Mustansiriyah University. The study of corrosion inhibition has been obtained with a computer-controlled potentiostat (PCI4/750, GAMRY Instruments, Inc., Warminster, PA) and Nikon ME - 600 optical microscope provided with a NIKON camera, DXM-1200F which used to show the images of the surfaces of the electrodes, at Technology / University Baghdad-Iraq.

3. Preparation of the ligands (L\(^1\)and L\(^2\))
A (2.53g, 16.63mmol) and (1.99g, 13.08mmol) from vanillin dissolved in (15ml) ethanol was mixed with (0.50g, 8.33mmol) and (0.50g, 6.57mmol) from urea or thiourea, respectively, dissolved in (15ml) ethanol and then added few drops of (10% NaOH) to adjust pH of the obtained reaction mixture, then heated with stirring for two hours. The products were filtered off, washed and recrystallized from absolute ethanol[13], Scheme (1) represents synthesis rout of two ligands.

![Scheme 1: Synthesis Rout of the L1 and L2](image_url)

4. Preparation of [Cu\(_2\)L\(^1\)Cl\(_6\)]
To a (15 ml) ethanolic solution (1.02g, 3.11mmol) of L\(^1\) and (1.10g, 3.19mmol) of L\(^2\), respectively, (10 ml) ethanolic solution (1.06g, 6.22mmol) and (1.09g, 6.39mmol), of cupper(II) chloride have been
added with heating and stirring for 2h. The products were filtered off, washed and recrystallized from absolute ethanol.

5. Preparation of [HgL\textsuperscript{n}Cl]\textsubscript{2}Cl
A similar procedure described to that mentioned in preparation of Cu\textsuperscript{II} complexes was used to prepare the complexes of L\textsubscript{1} and L\textsubscript{2} with [HgL\textsuperscript{n}] ion, but in 1:1 mole ratio.

6. Study of Corrosion inhibition
Electrochemical studies of the Cu\textsuperscript{II} corrosion were obtained with potentiostat polarization. All experiments were carried out with a potentiostat (PC14/750, GAMRY Instruments). Six different solutions from the prepared compounds were tested for corrosion inhibition study in (0.1M) HCl, two blank solution were used (HCl solution) blank 1 and (HCl + DMSO solution) blank 2. The test solutions include L\textsubscript{1}, L\textsubscript{2}, [Cu\textsubscript{2}L\textsubscript{1}Cl\textsubscript{4}] and [Cu\textsubscript{2}L\textsubscript{2}Cl\textsubscript{4}] solutions in one liter of distilled water at room temperature. Platinum electrodes and Ag/AgCl were used as auxiliary and reference electrode, respectively. Working electrodes were immersed into the solution until a steady open circuit potential (OCP) obtained. The exposed area of the tested specimens was (10 mm\textsuperscript{2}), the data have been adjusted according to the surface area. The sweep was taken from (-200 to + 200) mV relative to (OCP), scan rate (10mV/sec). A linear data fitting of the standard model gives an estimate of the polarization resistance, which is used to calculate (Icorr) and (Ecorr).

7. Metallographic Studies
Preparation of samples included many steps, sampling, grinding, polishing and etching. First, the samples were filed and ground. Grinding was done on a roll grinder using silicon carbide abrasive papers of 220, 320, 400, and 600 grits. Polishing process was done to the samples by using diamond paste of size (1μm) with special polishing cloth and lubricant followed by cleaning with water and alcohol and drying with hot air. Then the samples were scanned using Nikon ME-600 optical microscope provided with a NIKON camera, DXM-1200F.

8. Results and Discussion
shows some physical properties, and microelemental analysis (C.H.N.S) and chloride content and molar conductivity(solvent in DMSO) of the prepared compounds.

**Table (1):** some physical properties, microelemental analysis (C.H.N.S) ,chloride content and molar conductivity of the prepared compounds.

| Empirical formula | M. wt g.mol\textsuperscript{-1} | Yield % | Color | m.p. \degree C | C% | H% | N% | S% | (Calc.), Found % | Am S.cm\textsuperscript{2} molar\textsuperscript{-1} |
|-------------------|-----------------|---------|-------|--------|------|-----|-----|-----|-----------------|---------------------|
| L\textsubscript{1}  | 328.32          | 54      | Light white | 200    | (62.19) | 62.12 | (4.91) | 4.82 | (8.53) | 8.51     | -                  | -                   |
| [CuL/Cl]          | 597.22          | 51      | Light Orange | 270    | -     | -   | -   | -   | (21.28) | 21.23 | (23.75) | 23.70 | 11.5     |
| [HgL2Cl]Cl | 599.82 | 53 | Light White | 250 | - | - | - | - | (33.44) | 33.43 | (11.82) | 11.79 | 35.7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| L2 | 344.38 | 64 | Light White | 230 | (59.29) | 59.23 | (4.68) | 4.60 | (8.13) | 8.10 | (9.31) | 9.29 | - | - | - |
| [CuL2Cl]2 | 613.29 | 51 | Light Orange | 290 | - | - | - | - | (20.72) | 20.70 | (23.12) | 23.10 | 14.1 |
| [HgL2Cl]Cl | 615.88 | 53 | Light White | 280 | - | - | - | - | (32.57) | 32.50 | (11.51) | 11.48 | 38.5 |

9. FTIR-Spectra of Precursors, Ligands and Complexes

The spectrum of the urea show bands at (3448) cm\(^{-1}\) and (3350) cm\(^{-1}\) may be attributed to the v(N-H) asym. and (N-H) sym. of (NH\(_2\)) group[14]. The spectrum shows band at (1685) cm\(^{-1}\) may attributed to v(C=O) group[15]. The spectrum of starting material thiourea, shows the bands at (3373) cm\(^{-1}\) and (3271) cm\(^{-1}\) may be attributed to the v(N-H) asym. and (N-H) sym. bands of (NH\(_2\)) group[14]. The band at (1248) cm\(^{-1}\) attributed to v(C=S) group[15]. The spectrum of vanillin, shows sharp band at (3180) cm\(^{-1}\) belong to v(OH) may referred to the phenolic group and the band at (2983) cm\(^{-1}\) may be referred to the v(OCH\(_3\)) group. The bands at (2947) cm\(^{-1}\) and (2848) cm\(^{-1}\) may be attributed to stretching vibration of the aldehydic proton. The spectrum shows band at (1678) cm\(^{-1}\) attributed to v(C=O) group and the bands at (1205) cm\(^{-1}\) and (1014) cm\(^{-1}\) may be belong to the u(C-O) vibration [15].

FT-IR spectra of L\(^1\) and L\(^2\), Figures (1) and (2), showed broad bands at (3440) cm\(^{-1}\) and (3444) cm\(^{-1}\), respectively which assigned to u(OH) of phenolic groups[16]. The bands at (3013) cm\(^{-1}\) and (3063) cm\(^{-1}\) may be referred to aromatic v(C-H)[15] of L\(^1\) and L\(^2\), respectively. The spectra showed two bands at (2833) cm\(^{-1}\) and (2841) cm\(^{-1}\) referred to stretching vibration of (-OCH\(_3\)) group[15,17] for L\(^1\) and L\(^2\) respectively. The spectra have been also showed bands at (2715) cm\(^{-1}\) and (2719) cm\(^{-1}\) attributed to iminic v(C-H) vibrations [18] of L\(^1\) and L\(^2\) respectively. The strong bands have been noticed in spectra of L\(^1\) and L\(^2\) at (1591) cm\(^{-1}\) and (1658) cm\(^{-1}\) may be assigned to u(C=O) vibrations of imine groups[19,20], the appearance of these bands and disappearance of amine (NH\(_2\)) and aldehyde (CHO) bands in the spectra confirms the formation of Schiff base ligands[21]. The bands appeared at (1666) cm\(^{-1}\) and (1223) cm\(^{-1}\) in the spectrum due to u(C=O) group for L\(^1\) and u(C=S) for L\(^2\) [15]. The assignment of characteristic bands are summarized in Table (2).The band at (1591) cm\(^{-1}\) in L\(^1\) spectrum may assigned to u(C=N) stretching, shifted to the lower frequencies in the complexes of Cu\(^{II}\) and Hg\(^{II}\) and appears at (1587) cm\(^{-1}\) and (1579) cm\(^{-1}\) respectively, the shift in u(C=N) suggests weak co-ordination of L\(^1\) to metal ion [19]. While the band at (1658) cm\(^{-1}\) for L\(^2\) belong to u(C=S) shifted to the higher frequencies in the Cu\(^{II}\) and Hg\(^{II}\) complexes and appears at (1666)cm\(^{-1}\) and (1685) cm\(^{-1}\) respectively compared with L\(^2\), indicating that azomethine nitrogen is involved in the coordination with the metal ions [20]. The band at (1666) cm\(^{-1}\) in the spectrum due to u(C-O) vibrations in L\(^1\) shifted towards higher values in the complexes Cu\(^{II}\) and Hg\(^{II}\) respectively and appeared at (1671) cm\(^{-1}\) and (1682) cm\(^{-1}\) as a result suggests the coordination of ligand to metal ion via the C=O group [22,23].The band at (1223) cm\(^{-1}\) in the spectrum due to u(C=S) stretching vibration in L\(^2\) shifted towards lower values in the complex Cu\(^{II}\) and Hg\(^{II}\) respectively and appears at (1130) cm\(^{-1}\) and (1192) cm\(^{-1}\), this shift indicating the coordination of the sulphur atom of the ligand, referred to the charge transfer from the ligand to the metal [24,25]. The emergence of two new bands in the regions (588) cm\(^{-1}\), (482) cm\(^{-1}\) and (503) cm\(^{-1}\), (420) cm\(^{-1}\) in the spectra of the L\(^1\) complexes Cu\(^{II}\) and Hg\(^{II}\) respectively may refer to u(M-N) and u(M-O). The appearance of two new bands in the regions (590) cm\(^{-1}\), (480) cm\(^{-1}\) and (511) cm\(^{-1}\), (463) cm\(^{-1}\) in the spectra of the L\(^2\) complexes Cu\(^{II}\) and Hg\(^{II}\) respectively may refer to u(M-N) and u(M-S). The new bands confirmed the formation of metal...
complexes through coordination from the iminic nitrogen, carbonyl and thiocarbonyl groups[12]. The characteristic FT-IR data are presented in Table (2). The spectra of the ligands and complexes were shown in 'Figures (3-6)'.

Figure 1: FT-IR spectrum of the L₁

Figure 2: FT-IR spectrum of the L₂

Figure 3: FT-IR spectrum of the [Cu₂L¹Cl₄]
Figure 4: FT-IR spectrum of the $[\text{HgL}^1\text{Cl}]\text{Cl}$

Figure 5: FT-IR spectrum of the $[\text{Cu}_2\text{L}^2\text{Cl}_4]$.

Figure 6: FT-IR spectrum of the $[\text{HgL}^2\text{Cl}]\text{Cl}$

Table 2: Infrared data of ligands (cm$^{-1}$) and starting materials and complexes

| Compound | $\tilde{v}$(OH) | $\tilde{v}$(NH$_2$) | $\tilde{v}$(C=O) | $\tilde{v}$(C=S) | $\tilde{v}$(C=N) | $\tilde{v}$(M-N) | $\tilde{v}$(M-S) | $\tilde{v}$(M-O) | Additional bands |
|----------|----------------|------------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|
| $\text{L}^1$ | 3440 | 1666 | 1591 | - | - | - | - | $\tilde{v}$(C-H)aro. 3013 | $\tilde{v}$(OCH$_3$) 2833 | $\tilde{v}$(C=O) 1504 |
| $\text{L}^2$ | 3444 | 1223 | 1658 | - | - | - | $\tilde{v}$(C-H)aro. 3063 | $\tilde{v}$(OCH$_3$) 2841 | $\tilde{v}$(C=O) 1595 – 1512 |
Electronic Spectra: Ligands and magnetic susceptibility for the complexes
Table (3) summarized the electronic data of two ligands and their complexes. The electronic spectra of two ligands (L₁ and L₂) at (10⁻³ M) in ethanol showed one π-π* transition at (267 nm) and (267 nm) and the three peaks at (300 nm), (335 nm) and (383 nm) for L₁ and (305 nm), (345 nm) and (372 nm) for L₂ represented n-π* transition resulted from the presence of the lone pairs of the groups (C-OH, C=O and HC=N groups) of L₁ and (C-OH, C=S and HC=N groups) for L₂[26,19], Figures (7) and (8).

The U.V - Visible spectra of [Cu₂L₁Cl₄], showed in Figure (9) and [Cu₂L₂Cl₄], Figure (10), in (10⁻³M) ethanol solutions. In each case it was noticed a shift in π-π* and n-π* transitions and intensity change in the complexes compared with those of ligands, indicating the coordination to metal. Two peaks for [Cu₂L₁Cl₄] and [Cu₂L₂Cl₄] complexes at (358 nm) and (358 nm) with high intensities are most probably due to charge transfer transition [27]. The peaks in the visible region can be associated with d-d transitions. The [Cu₂L₁Cl₄] shows peak at (788 nm) assigned to ²B₁g→²A₁g while [Cu₂L₂Cl₄] shows two peaks at (716 nm) and (814 nm) assigned to ²B₁g→²B₂g and ²B₁g→²A₁g suggesting square planar geometry around the Cu²⁺ ion[5,27,28]. The magnetic moment values(1.56 and 1.64 BM) for complexes [Cu₂L₁Cl₄] and [Cu₂L₂Cl₄] are indicative of square-planar geometry[28,29].

The U.V / Visible spectra of [HgL₁Cl]Cl, Figure (11) and [HgL₂Cl]Cl, Figure (12) exhibited peaks at (375 nm) and (375 nm) assigned to charge transfer transitions. Finally Hg²⁺ ions belong to d⁰ configuration and they don’t have d-d transition. On considering the position of the bands, the tetrahedral structure may be proposed for these complexes [5, 30,31].

|        | 1671 | 1587 | 588 | - | 482 |
|--------|------|------|-----|---|-----|
| [Cu₂L₁Cl₄] | 3437 | -    | 1587| 588| -   |
| [HgL₁Cl]Cl | 3475 | 1682 | 1579| 503| -   |
| [Cu₂L₂Cl₄] | 3431 | -    | 1666| 590| 480 |
| [HgL₂Cl]Cl | 3433 | -    | 1192| 511| 463 |

|        | 1671 | 1587 | 588 | - | 482 |
|--------|------|------|-----|---|-----|
| [Cu₂L₁Cl₄] | 3437 | -    | 1587| 588| -   |
| [HgL₁Cl]Cl | 3475 | 1682 | 1579| 503| -   |
| [Cu₂L₂Cl₄] | 3431 | -    | 1666| 590| 480 |
| [HgL₂Cl]Cl | 3433 | -    | 1192| 511| 463 |

**Figure 7:** UV spectrum of the L₁
Figure 8: UV spectrum of the $L^2$

Figure 9: UV spectrum of the $[\text{Cu}_3L^1\text{Cl}_4]$  

Figure 10: UV spectrum of the $[\text{Cu}_3L^2\text{Cl}_4]$  

Figure 11: UV spectrum of the $[\text{HgL}^1\text{Cl}]\text{Cl}$
Table 3: Electronic spectral data of ligands and metal complexes

| Compound | Transition | $\varepsilon_{\text{max}}$ molar$^{-1}$ cm$^{-1}$ | Assignment | $\mu_{\text{eff.}}$ (B.M.) | Suggested structure |
|----------|------------|----------------------------------|------------|-----------------|-------------------|
| $L^1$    | 267        | 3745                             | $\pi-\pi^*$| -               | -                 |
|          | 300        | 3333                             | n-$\pi^*$  |                 |                   |
|          | 335        | 2985                             | n-$\pi^*$  |                 |                   |
|          | 383        | 2610                             | n-$\pi^*$  |                 |                   |
| $[\text{Cu}_2L^1\text{Cl}]$ | 283        | 3533                             | $\pi-\pi^*$| 1.56            | Square planar     |
|          | 298        | 3355                             | n-$\pi^*$  |                 |                   |
|          | 345        | 2898                             | n-$\pi^*$  |                 |                   |
|          | 350        | 2857                             | n-$\pi^*$  |                 |                   |
|          | 358        | 2793                             | CT         |                 |                   |
|          | 788        | 1269                             | $2^3\text{B}_{1g}\rightarrow2^3\text{A}_{1g}$ |     |                   |
| $[\text{HgL}^1\text{Cl}]\text{Cl}$ | 275        | 3636                             | $\pi-\pi^*$|                 | Diamagnetic       |
|          | 299        | 3344                             | n-$\pi^*$  |                 | Tetrahedral       |
|          | 342        | 2923                             | n-$\pi^*$  |                 |                   |
|          | 368        | 2717                             | n-$\pi^*$  |                 |                   |
|          | 375        | 2666                             | CT         |                 |                   |
| $L^2$    | 267        | 3745                             | $\pi-\pi^*$| -               | -                 |
|          | 305        | 3278                             | n-$\pi^*$  |                 |                   |
|          | 345        | 2898                             | n-$\pi^*$  |                 |                   |
|          | 372        | 2688                             | n-$\pi^*$  |                 |                   |
|          | 275        | 3636                             | $\pi-\pi^*$|                 |                   |
|          | 301        | 3322                             | $\pi-\pi^*$|                 |                   |
10. ¹HNMR Spectra of Ligands and Their Hg⁺ Complexes

The ¹H-NMR spectrum of L¹, Figure (13), exhibits the following signals: (3.75), (6.15), (6.93-7.07) and (9.23) ppm which are assigned to the (-OCH₃), (-OH), aromatic and (-CH=N-) protons, respectively. The two signals at (2.49 and 3.5) ppm assigned to protons of solvent (DMSO) and water, respectively.

The ¹H-NMR spectrum of [HgL¹Cl] complex, Figure (14), exhibits the following signals: (3.7), (7.22-7.49) and 9.63 ppm which are assigned to the (-OCH₃), aromatic and (-CH=N) protons, respectively. The signal of (-CH=N-) proton shifted to the downfield region (9.63) ppm due to coordination to Hg⁺ ion. The signal of (-OH) proton disappeared because of exchange with solvent[15,32].

The ¹H-NMR spectrum of L², Figure (15), exhibits the following signals: (3.66), (6.11), (6.91-7.04) and (9.21) ppm which are assigned to the (-OCH₃), (-OH), aromatic and (-HC=N) protons, respectively.

The ¹H-NMR spectrum of the [HgL²Cl] complex, Figure (16) exhibits the following signals: (3.78), (6.9), (7.17-7.45) and (9.57) ppm which are assigned to the, (-OCH₃), (-OH), (aromatic) and (-HC=N) protons, respectively. The (-CH=N-) shifted to the downfield region (9.57) ppm compared to that of free ligand indicating that the azomethine nitrogen involving in coordination with Hg⁺ ion[15,32].

The characteristic ¹H-NMR spectral data are presented in Table (4).
Figure 14: $^1$H-NMR spectrum of the [HgL$^1$Cl]Cl

Figure 15: $^1$H-NMR spectrum for the L$^2$

Figure 16: $^1$H-NMR spectrum of the [HgL$^2$Cl]Cl

Table 4: $^1$H-NMR Spectral data of two ligands and two HgII Complexes in DMSO-d6

|       | L$^1$ [HgL$^1$Cl] | L$^2$ [HgL$^2$Cl] | (δ ppm) | Assignment | (δ ppm) | Assignment | (δ ppm) | Assignment | (δ ppm) | Assignment |
|-------|-------------------|-------------------|---------|------------|---------|------------|---------|------------|---------|------------|
|       |                   |                   |         |            |         |            |         |            |         |            |
| (3.75)| (-OCH$_3$)       | (3.7)             | (3.66)  | (-OCH$_3$) | (3.66)  | (-OCH$_3$) | (3.78)  | (-OCH$_3$) | (3.78)  | (-OCH$_3$) |
| (6.15)| (-OH)            | ---               | (6.11)  | (-OH)      | (6.11)  | (-OH)      | (6.9)   | (-OH)      | (6.9)   | (-OH)      |
| (6.93-7.07)| (Ar-H)      | (7.22-7.49)       | (6.91-7.04)| (Ar-H)  | (6.91-7.04)| (7.17-7.45)| (Ar-H)  | (7.17-7.45)| (Ar-H)  | (7.17-7.45)|
| (9.23)| (-CH=N)          | (9.63)            | (9.21)  | (-CH=N)    | (9.21)  | (-CH=N)    | (9.57)  | (-CH=N)    | (9.57)  | (-CH=N)    |
11. The proposed structure

According to the results obtained from (IR, UV/visible, 'H-NMR, microelemental analysis (C.H.N.S), magnetic susceptibility measurements, atomic absorption, chloride content along with conductivity and melting point measurements for the prepared complexes, the proposed molecular structure of the complexes has an square planar Cu^{II} and tetrahedral Hg^{II} structure as shown in Fig.(17) and (18).

![Diagram of proposed structures](image)

**Figure (17): Proposed Structures of Prepared Complexes**

![Chemical structures](image)

**Figure (18): The proposed molecular structure of the complexes**

Conclusions

Corrosion inhibition efficiency of two ligands with two copper complexes electrodes in 10% HCl solution have been studied using potentiometric method. All synthesized inhibitors showed inhibition characteristics for copper corrosion in 10% HCl solution. The chelates displaying high surface activity and low solubility in solution. The synthesized inhibitors due to containing one or more functional groups, containing one or more hetero atoms, N, O, S, this may increases the ability of the inhibitor molecule to cover a large surface area of the metal surface[33]. The inhibition efficiency of synthesized inhibitors increased in the following order: L^2-> blank 1->L^1-> [Cu_{2}L^2Cl_4 ] > blank 2->[Cu_{2}L^1Cl_4 ], see Figures (19) and (20) and metallographic Figures (21), (22), (23), (24), (25), (26) and (27) show the corrosion inhibition ability of the prepared ligands and two cupper complexes, the results are summarized in Table (5).
Figure 19: Tafel polarization curves for corrosion in (1 M) HCl in the absence and presence of different concentrations of inhibitors for [1(blank 1), 3(L₁), 2(blank 2), 5(Cu₂L₁Cl₄)]

Figure 20: Tafel polarization curves for corrosion in (1 M) HCl in the absence and presence of different concentrations of inhibitors for [1(blank 1), 4(L₂), 2(blank 2), 6(Cu₂L₂Cl₄)]

Figure 21: Micrograph of the electrode before corrosion

Figure 22: Micrograph of the electrode in blank 1
Figure 23: Micrograph of the electrode in blank 2
Figure 24: Micrograph of the electrode with L^1
Figure 25: Micrograph of the electrode with L^2
Figure 26: Micrograph of the electrode with [Cu_2L^1Cl_4]
Figure 27: Micrograph of the electrode with [Cu_2L^2Cl_4]

Table 5: Results of Corrosion inhibition

| Sample No. | Sample Solution | $E_{corr}$ | $I_{corr}$ |
|------------|-----------------|------------|------------|
| 1          | Blank 1         | -68.1 [mv] | 768.92 A/cm^2 |
| 2          | Blank 2         | 40.5 [mv] | 7.71 A/cm^2 |
| 3          | L^1             | -27.0 [mv] | 444.97 A/cm^2 |
| 4          | L^2             | 25.9 [mv] | 992.84 A/cm^2 |
| 5          | [Cu_2L^1Cl_4]   | 36.0 [mv] | 4.34 A/cm^2 |
| 6          | [Cu_2L^2Cl_4]   | 61.8 [mv] | 81.08 A/cm^2 |
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