Preparation , Spectral Characterization and anti Corrosion Property of new azo- azomethine ligand and its Chelate complexes for Carbon Steel in Acid Solution

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Abstract :

Anew azo–Schiff base ligand(4-((E)-(3-iodophenyl)diazenyl)-2-((3-(triflurommethyl) phenyl imino)methyl) phenol (IFPMP) was prepaered by condensation of ((E)2-hydroxy-5-((3-iodophenyl) diazenyl) benzaldehyde with 3- (triflurommethyl)aniline .This azo-azomethine ligand was reacted with some transition metal ions such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) forming seven chelate complexes . The structural features have been arrived from their C.H.N elemental analysis ,FT-IR , UV-Vis , ^{1}HNMR , Mass spectra, magnetic moment measurement and molar conductance. The data show that complexes have the composition of $[M(L)_2(H_2O)_2]$ for all chelate complexes except of Cr(III) and Fe(III) which were found that the composition as $[M(L)_2Cl(H_2O)]$ .Based on this data we propose octahedral geometry for all metal complexes. The influence of the prepared new ligand and its chelate complex on the corrosion inhibition of carbon steel in (0.5M) HCl solution was studied by weight loss. Results show that maximum inhibition efficiency of 47.8% is afforded by the studied concentration of the ligand (4ppm) at 298K , while the maximum inhibition efficiency of its ligand complex is 29.5% by (20ppm) at 298K from weight loss method measurements.

Key words: Corrosion protection, Azo-Schiff base ligand, Metal chelate complexes,Acid corrosion , Carbon steel

1.Introduction :

Azo dyes are an interesting class of organic compounds that have found wide application, such as food colorant, pharmaceutical precursor , paints and polymers[1,2].About 50% of the dyes produced in the world are derived from azo compounds. The main characteristic of there dyes is the presence of the azo group (−N=N−), which allows larger extension of π-electronic conjugation and, therefore, intense absorption of light in the visible region of the electromagnetic spectrum. Schiff base ligands are able to coordinate with many different metals and large number of there complexes have been used in catalytic reactions [3] and as models for biological systems[4]. The protection of C-steel in aqueous solutions is universal request, economic, environmental, and aesthetical important[5]. The organic assembled was commonly utilized as corrosion inhibitors as it contains heteroatom such as O, N, P, S, and heavy metals. But the organic compounds are hazards and unfriendly environment inhibitors [6-8].

2. Experimental

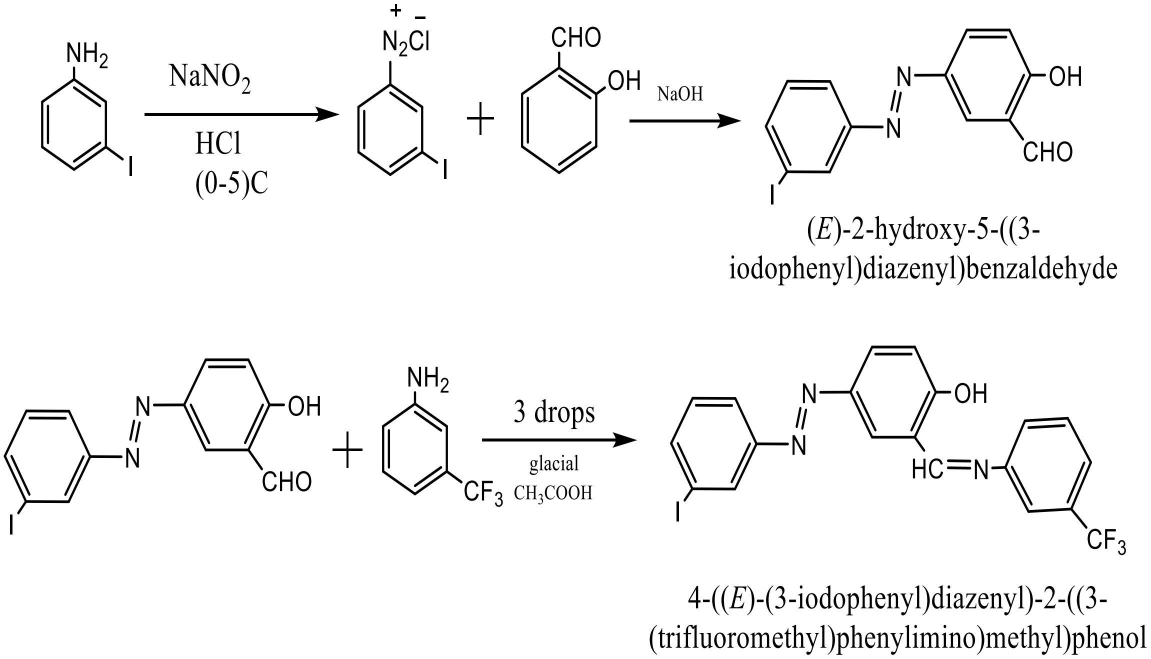
2.1. Materials and measurements

All chemicals are of highest purity and used as supplied by the manufactures . Melting points was determined by open capillary tube method and are uncorrected by using a Stuart melting point SMP10. Elemental analyses (C.H.N) were carried out using Euro vector, EA 2000 A elemental analyzer. The metal contents of chelate complexes were measured using atomic absorption technique by Shimadzu AA-6300. Mass spectrum of organic ligand was obtained using Gc-Mass Qp 2010 (Shimadzu Instruments), but mass spectrum of Ni(II) complex was obtained by using, Agilent technologies (5975 C) Mass spectrophoto-meter at (70eV). The ^{1}HNMR spectrum of azo ligand was recorded on Bruker 500 MHz spectrophotometer in DMSO-d6 using (TMS) as internal reference. IR spectra were recorded on a Shimadzu 8000S FT-IR spectrophotometer in the (4000-400) cm^{-1} range using KBr discs. Electronic spectra were obtained on a Shimadzu 1700 UV spectrometer using ethanol as solvent in the (1100-200) nm range. Magnetic susceptibilities were determined by faraday method at room temperature using Sherwood scientific Balance apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constant[17].Molar conductance of the metal chelate complexes were determined in DMSO using conductivity meter Alpha-800 at 25°C

2.2. Synthesis of azo-Schiff dye(IFPMP)

Organic ligand was prepared according to the following general procedure (Scheme 1). 3- iodo aniline (2.19g, 10 mmol) was dissolved in 30 mL of water and 3.0 mL of concentrated hydrochloric acid. This solution was diazotized below 5°C with 10 ml of aqueous (0.7g, 0.01 mol) sodium nitrite which added dropewise and the reaction mixture is tested from time to time with starch-iodide paper until nitrous acid persists in the solution during a 10 min interval. The resulting diazonium chloride, solution was mixed with salcyaldehyde (1.22g, 10 mmol) dissolved in 150 mL alkaline ethanol cooled below 5°C. After leaving in the refrigerator for 10hrs, the mixture was acidified with (0.1 molL^{-1}) hydrochloric acid until (pH ~ 7). The precipitate was filtered off, air dried and twice recrystallized from hot ethanol, then dried in the oven at 50°C for several hrs.

The pure solid azo compound (E)- 2-hydroxy-5-((3-iodophenyl)diazenyl)benzaldehyde (3.52g,0.01mol)dissolved in 50 mL absolute ethanol was mixed with 30 mL solution of (1.61g,0.01mol) from 3-(trifluromethyl)aniline .The mixture was reflexed 10 hrs after added few drops of glacial acetic acid .Solid precipitate was filtered, air dried and was recrystallized from hot ethanol and dried in electronic oven at 50°C for 1hr.



Scheme .1. preparation of azo Schiff base ligand (IFPMP)

2.3. Synthesis of complexes

The chelate complexes have been obtained by adding (0.495 g, 0.001mol) of ligand dissolved in ethanol 30 mL to 20mL of ethanolic solution of ($CrCl_3.H_2O$, $MnCl_2.4H_2O$, $FeCl_3$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ metal salts (1:2) (metal:ligand) mole ratio. The reaction mixture was refluxed for one hour, then concentrated until the solid compounds precipitated. They were filtered off, washed with ethanol 5 mL to remove the remaining un reacted substances, and dried in the electric oven at 100 °C for 6hrs.

2.4. Corrosion

The corrosion rate of steel sample in 0.5 M HCl was determined by weight loss technique, the mild steel was of composition given as :C= 0.17, Si= 0.3, Mn= 1.4, S=0.045, P= 0.045, N=0.009 ,Fe to 100 (by weight). Before the measurement the samples were mechanicaly polished with a series of emery papers with different grades(600,800,1000) to obtain a smooth surface, then washing with distilled water and dried .Weight loss measurements were carried out by weighing the mild steel specimens before and after immersion in 500 mL acid solution for different time intervals in the presence and absence of various concentrations of ligand (IFPMP) and Cu(II) complex. Experiments were also performed at room temperature in HCl solutions.

The rate corrosion (C.R), the inhibition efficiency (IE%) and the surface coverage(θ) , that represents the weight of metal surface covered by inhibitor molecules ,was calculated using the following equations[9]:

$$\Delta W = W_o - W_{corr.} \ldots\ldots\ldots\ldots (1)$$

$$CR(mpy) = (K\ \Delta W) / (D\ A\ T) \ \ldots\ldots\ldots (2)$$

$$(IE\%) = (W_o - W_{corr.} / W_o) \times 100 \ \ldots\ldots\ldots (3)$$

$$\theta = W_o - W_{corr.} / W_o \ \ldots\ldots\ldots (4)$$

2.5. Inhibitors

All the chemical used are analytical grade. Distilled water was used in all preparation. Organic ligand (IFPMP) and its complex of Cu(II) as corrosion inhibitors in 0.5M HCl medium was prepared in ethanol. All tested solutions containing 15mL present of ethanol to maintain complete soluble.

3. Results and Discussion

3.1. Characterization of ligand and its complexes

The azo-azomethine ligand (IFPMP) was deep red crystal, but the prepared complexes of this ligand vary in color from red to brown. The solid complexes are stable at room temperature and soluble in acetone, DMF and DMSO, but insoluble in water. The elemental analyses and metal contents data were surmised in Table.1, for the ligand and complexes are in a good agreement with the suggested formula.

The elemental analyses of the metal complexes indicate that the (M : L) ratios were (1:2) and the chemical formula was $[M(IFPMP)_2(H_2O)_2]$,when[M=Mn(II), Co(II), Ni(II) and Zn(II)] or $[M(IFPMP)_2(H_2O)Cl]$ when [M=Cr(III) and Fe(III)],chelate complexes, while Cu(II) complex unique $[CuL_2].2H_2O$. All prepared compounds were quiet air stable, insoluble in distilled water but soluble in common organic solvents such as methanol, ethanol, acetone, chloroform, and pyridine giving stable solutions at room temperature.

Table .1: Some physical and analytical data of azo Schiff ligand and its complexes

No.	*Formula*	*M:L*	*Color*	*M.P°C*	*Yield %*	*C % (cal.)*	*H % (cal.)*	*N % (cal.)*	*M % (cal.)*
1	$C_{20}H_{13}N_3OF_3I$	----	Deep red	127-129	69	48.37 (48.48)	2.56 (2.62)	8.50 (8.48)	--------
2	$[Cr(C_{20}H_{12}N_3OF_3I)_2\ Cl(H_2O)]$	1:2	Brown	220-223	77	43.55 (43.89)	2.12 (2.21)	7.63 (7.75)	5.33 (5.41)
3	$[Mn(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	1:2	Brown	114-116	79	44.37 (44.48)	2.14 (2.22)	7.59 (7.78)	4.99 (5.08)
4	$[Fe(C_{20}H_{12}N_3OF_3I)_2\ Cl(H_2O)]$	1:2	Deep brown	153-155	80	43.55 (43.74)	2.10 (2.18)	7.40 (7.65)	4.98 (5.08)
5	$[Co(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	1:2	Brown	130-132	71	44.21 (44.34)	2.09 (2.21)	7.57 (7.76)	5.21 (5.40)
6	$[Ni(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	1:2	red	132-35	64	44.17 (44.32)	2.09 (2.21)	7.52 (7.75)	5.24 (5.4)
7	$[Cu(C_{20}H_{12}N_3OF_3I)_2].2H_2O$	1:2	Red brown	247-248	82	43.99 (44.13)	2.11 (2.20)	7.59 (7.72)	5.59 (5.83)
8	$[Zn(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	1:2	Light red	113-115	73	43.93 (44.06)	2.12 (2.20)	7.56 (7.71)	5.88 (6.00)

3.2. Mass spectrum of azo -Schiff ligand (IFPMP)

Mass spectrometer data support the proposed structure. The ligand was analyzed as the direct inlet probe. The peak M^+ at (m/z=495) that is corresponding to a molecular formula of $[C_{20}H_{12}N_3OF_3I]$, the calculated formula weight is (495). This is the ligand formula. The fragments at (m/z=476 and 450) corresponding to ($C_{20}H_{13}N_3OF_2I$ and $(C_{19}H_{13}N_2OF_2I)^+$respectively. This two fragments due to losing of florid and azomethine group respectively. Another fragments at (m/z = 390,264,203,76and 65), which due to $(C_{18}H_{12}OFI)^+$,$(C_{18}H_{13}OF)^+$, $(C_{16}H_{12})^+$, $(C_6H_4)^+$ and $(C_5H_5)^+$ respectively .Figure.1 and scheme .2, showed the mass spectrum and fragmentation pattern of azo-Schiff base ligand.

Mass Spectrum of Ni(II) complex

The mass Fragment and fragmentation pattern of the metal chelate complex are shown in figure .2 and scheme.3. The spectrum would not have originated a molecular ion peak M^+ at (m/z 1082) that is equivalent to molecular weight of [Ni(IFPMP)$_2$(H_2O)$_2$]. The molecular ion loss of ligand molecule gate ion peak at (m/z= 552) due to the fragment [Ni(IFPMP)(H_2O)$_2$]$^+$. Another ion peaks at (m/z= 497-2H, 478, 450, 256, 167 and 93) were appeared in this spectrum which due to the fragments $(C_{20}H_{13}N_3OF_3I)^+$,$(C_{20}H_{12}N_3F_3I)^+$,$(C_{20}H_{13}NF_3I)^+$,$(C_{20}H_{15}N)^+$,$(C_{13}H_{11})^+$ and $(C_7H_8)^+$ respectively.

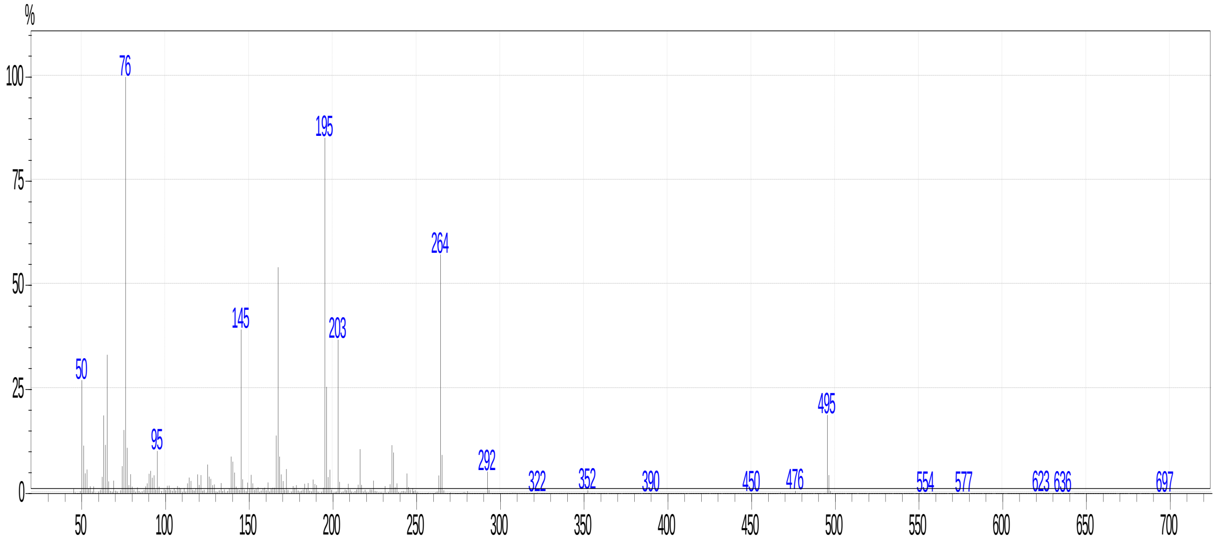


Fig.1 **Mass spectrum of (IFPMP) ligand**

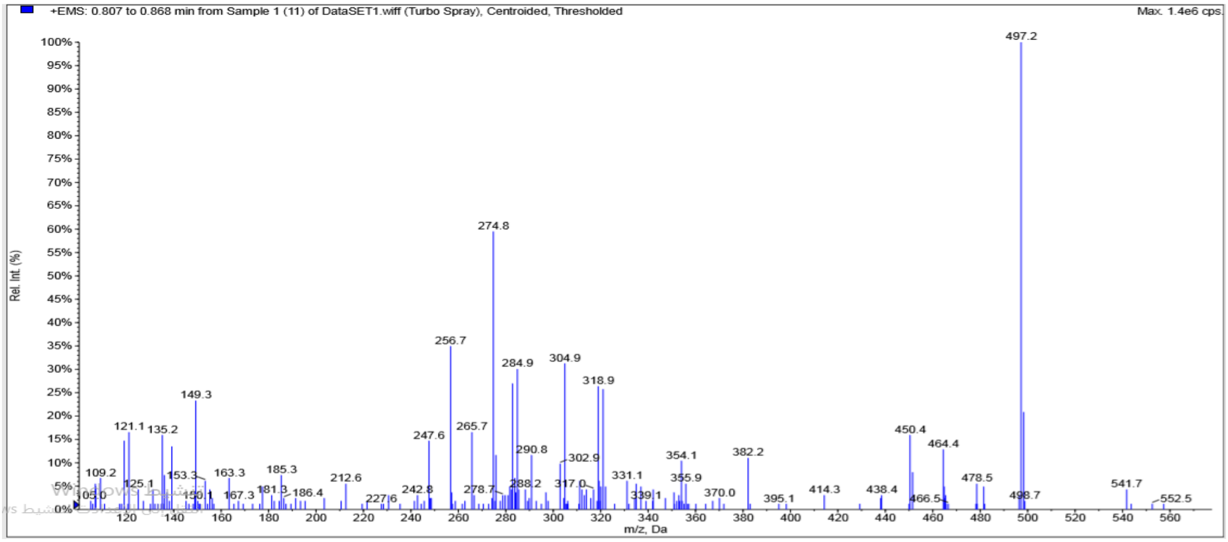
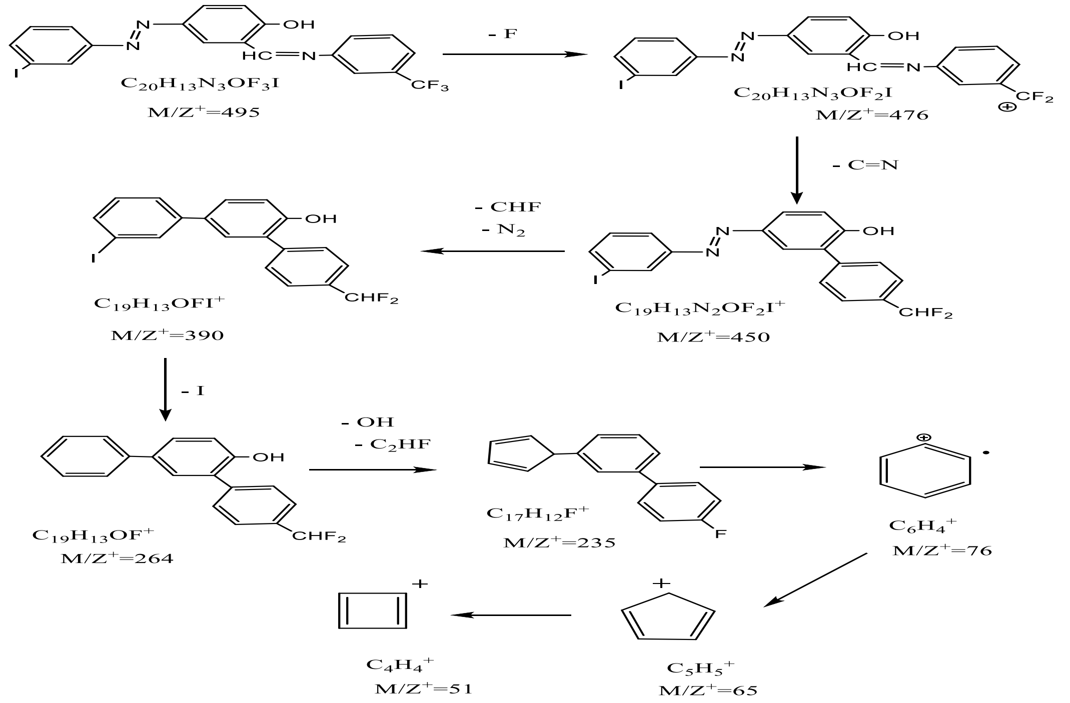
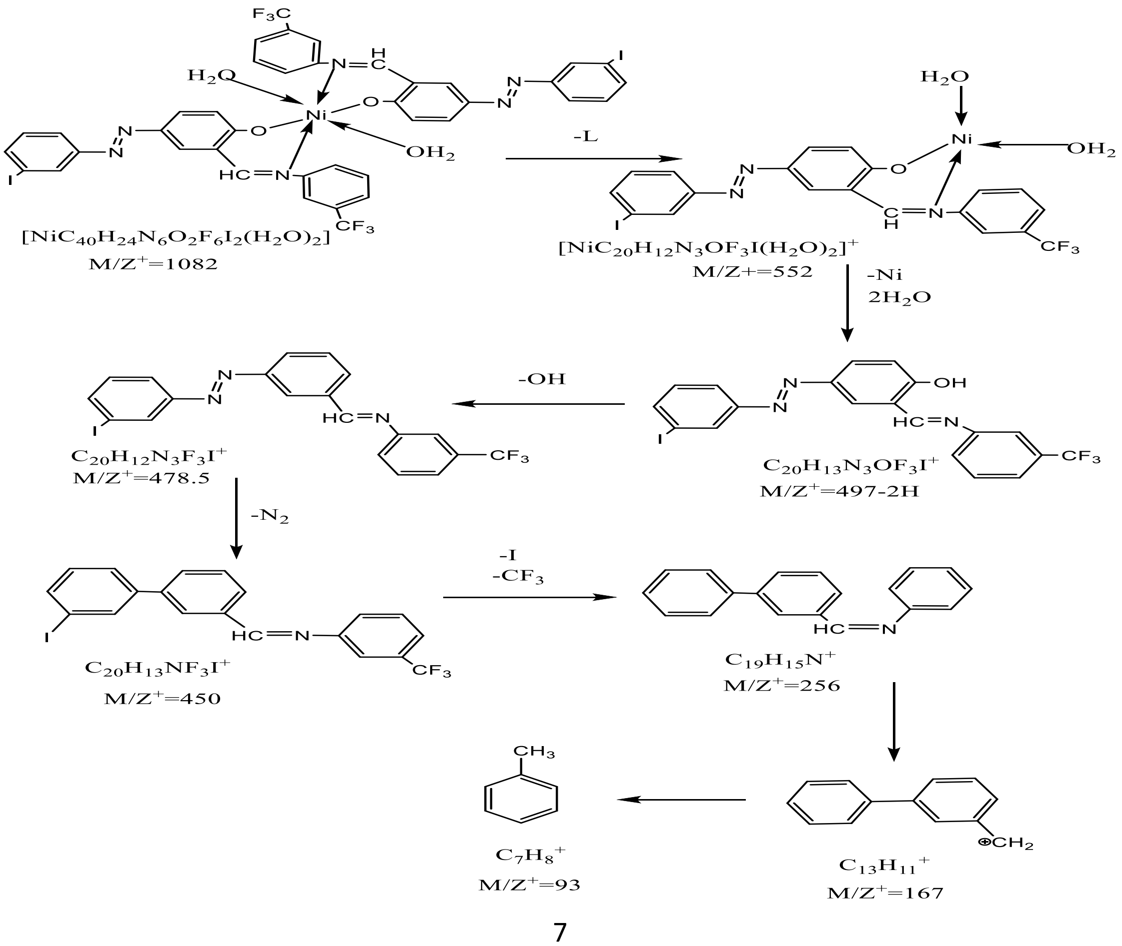


Fig .2: Mass spectrum of Zn(II) complex



Scheme (2):The Proposed Fragmentation Pattern of (IFPMP)



Scheme (3): The Proposed Fragmentation Pattern of $[Ni(IFPMP)_2(H_2O)_2]$

3.3. ^{1}HNMR spectra

^{1}HNMR spectrum of organic ligand Fig.3 showed clear signals involved singlet at =2.5ppm belong to (DMSO) solvent proton. The multiplet signals at (6.9-7.9) ppm which were assigned to aromatic protons[10] . Another Singlet signal at= (9.1 and 10.3 ppm) due to proton of azomethine (CH=N) and hydroxyl (O-H) groups respectively[11,12]. This peak noted in spectrum of the complex, disappear the signal at 10.3 ppm indicates to contribute hydroxyl group in complexity. Another group there is no appreciable change signals in this complex. as shown in Fig.3.

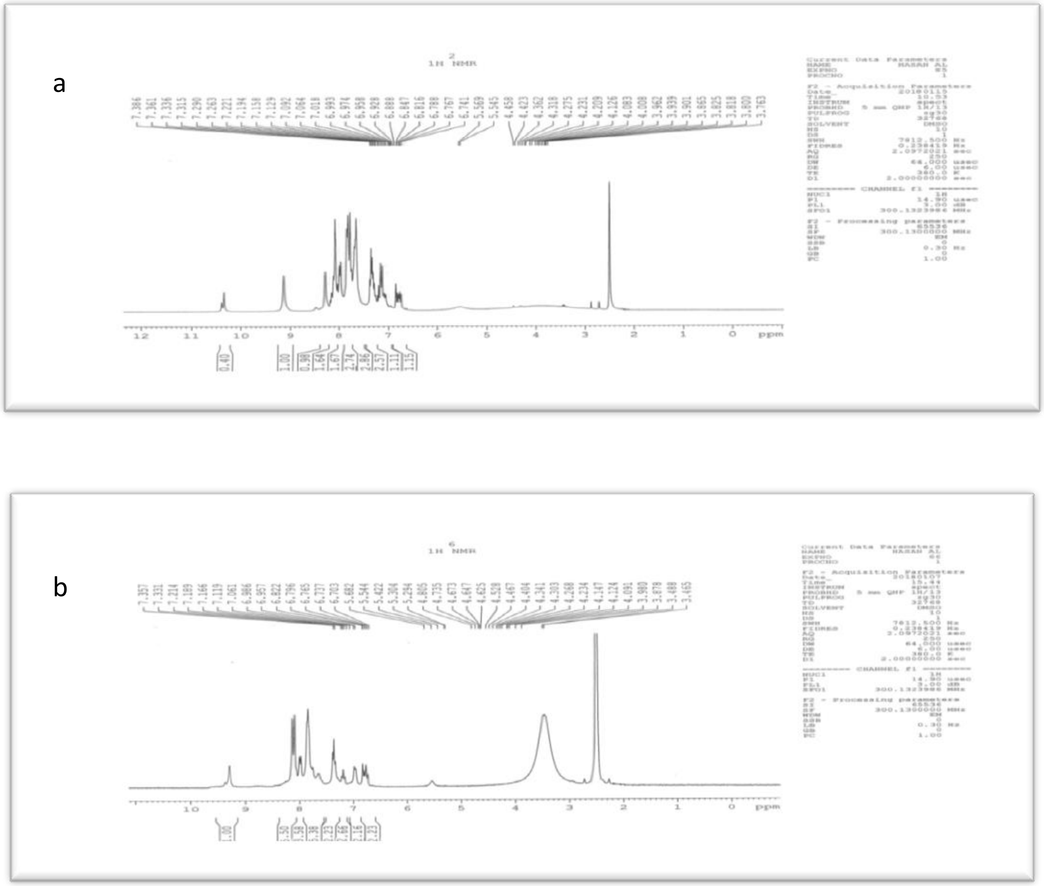


Fig .3: ^{1}H-NMR spectrum of : (a) the azo- schiff base ligand & (b) Zn (II)complex

3.4. IR spectra

The IR spectra of (IFPMP) ligand and its metal complexes were recorded between 4000-400 cm^{-1} and the obtained data were summarized in Table.2 with some assignments of the important characteristic bands.

The spectrum of free ligand show broad and medium band in the region 3446 cm^{-1} assignable to (OH) group. Abroad band is observed in all the complexes in the range 3398-3425 cm^{-1} due to υ(OH) of the coordinated water molecule[13] , this is supported by the appearance of an additional band in the rang 829-898 cm^{-1} for (O-H) vibration deformation. These bands were not observed in the spectrum of the azo-shiff ligand. The band observed at 1618 cm^{-1} is characteristic of the azomethine group in free ligand[14]. In the complexes spectra, this band is shifted to lower frequency 1600-1612 cm^{-1}, indicating the coordination of nitrogen atom of azomethine group[15]. The presence of bands at 503-530 cm^{-1} in the IR spectra of complexes are due to M-O stretching vibrations[16]. In the spectra of these complexes, the new bands which appear in the 420-460 cm^{-1} region are assigned to the υ(M-N)[17]. While a band at 1487 cm^{-1} which observed in the spectrum of the free ligand due to υ(N=N) stretching vibration negligible change is observed for this band in the spectra of chelate complexes this indicate that no coordination from this group[18]. Representative example for there is given in Fig .4.

Table.2: Some IR frequencies in (cm^{-1}) of the ligand and its chelate complexes

Ligand/complexes	*υ(OH) water*	*υ(C=N)*	*υ(N=N)*	*υ(H_2O)*	*υ(M-O)*	*υ(M-N)*
$C_{20}H_{13}N_3OF_3I$	**3446**	**1618**	**1487**	**---**	**---**	**---**
$[Cr(C_{20}H_{12}N_3OF_3I)_2\ Cl(H_2O)]$	**3410**	**1612**	**1450**	**898**	**524**	**420**
$[Mn(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	**3425**	**1600**	**1452**	**835**	**526**	**441**
$[Fe(C_{20}H_{12}N_3OF_3I)_2\ Cl(H_2O)]$	**3398**	**1604**	**1485**	**885**	**524**	**439**
$[Co(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	**3421**	**1612**	**1462**	**829**	**509**	**440**
$[Ni(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	**3412**	**1612**	**1463**	**835**	**503**	**437**
$[Cu(C_{20}H_{12}N_3OF_3I)_2].2H_2O$	**3419**	**1604**	**1462**	**---**	**530**	**433**
$[Zn(C_{20}H_{12}N_3OF_3I)_2(H_2O)_2]$	**3415**	**1608**	**1450**	**831**	**507**	**460**

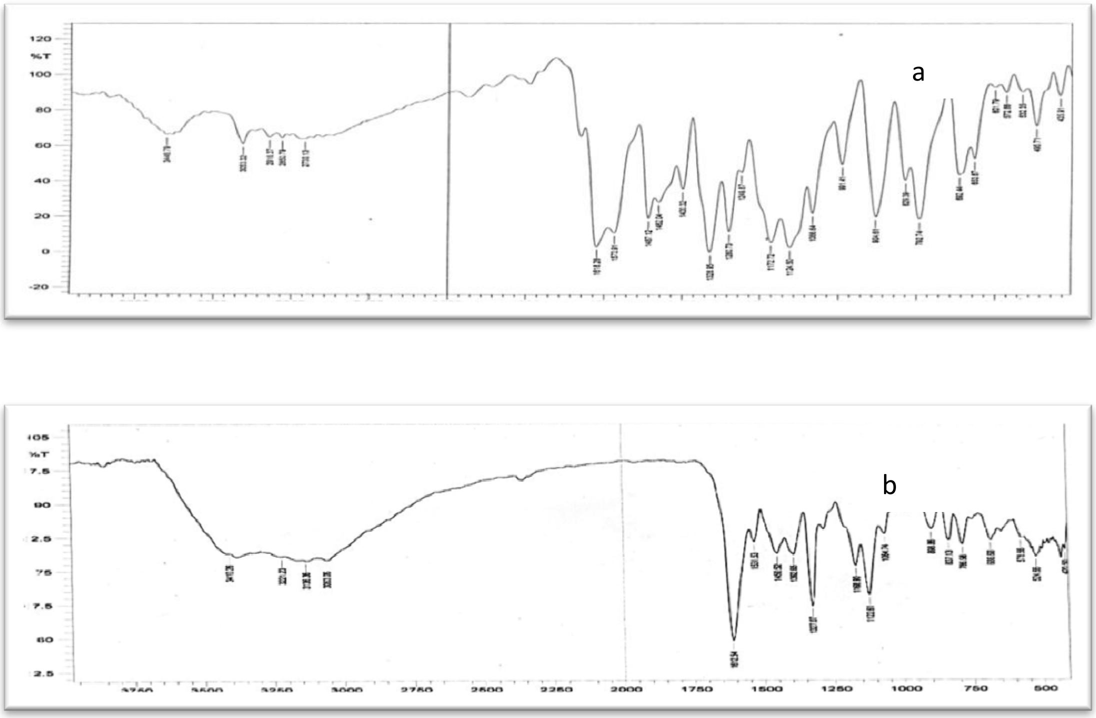


Fig .4:IR spectra of :(a) the azo- schiff base ligand & (b) Cr(III) complex

3.5. Magnetic Preparation and Electronic Spectra

The spectral data and the magnetic moment of prepared complexes are listed in Table.3. Fig.5. shows the spectra of ligand and its $[Co(L)_2(H_2O)_2]$ complex.

The electronic absorption spectrum of the ligand shows two bands at (273nm) 36630 cm^{-1} and (350nm) 28571 cm^{-1} which assigned to π-$\pi^*$and n-π^* respectively.

1- Chromium (II) complex

The Uv-vis spectrum of Cr(III) complex display three peaks at (984nm) 10162 cm^{-1} , (636nm) 15723 cm^{-1} and (376 nm) 26595 cm^{-1} which attributed to $^4A_2g \rightarrow {}^4T_2g_{(F)}$, $^4A_2g \rightarrow {}^4T_1g_{(F)}$ and $^4A_2g \rightarrow {}^4T_1g_{(P)}$ electronic transition respectively[19]. The magnetic moment value of these complex was found to be (3.8 BM) suggested the octahedral geometry for this complex[20].

2-Manganese(II) complex

The spectrum of this complex showed three peaks at (409nm) 24449 cm^{-1} , (396nm) 25252 cm^{-1} and (380nm) 26315cm^{-1} which assigned to charge transfer transition [21,22]. The magnetic moment value of solid complex (5.4 B.M) which is well within the range of high spin octahedral complex (t_2g^3 eg^2)[23].

3-Iron(III) complex

The spectrum of this complex showed three peaks at (993nm) 10070 cm^{-1}, (404nm) 24752 $cm^{-1}$and(347nm) 28818cm^{-1} there peaks assignable to $^6A_1g_{(S)}\rightarrow^4T_1g_{(G)}$,$^6A_1g_{(S)}\rightarrow^4T_2g_{(G)}$ and $^6A_1g_{(S)}\rightarrow^4Eg,^4A_1g_{(G)}$ transitions respectively [24]. The Fe(III) complex showed magnetic value at μeff (5.42B.M) which is consistent with a high spin octahedral geometry[25].

4- Cobalt (II) Complex

The magnetic moment value of the Co(II) (d^7) complex is (4.76B.M). The electronic spectrum of this complex show bands at (886nm) 11286 cm^{-1}, (657nm) 15220 cm^{-1} and (377nm) 26525cm^{-1} which can be assigned to $^4T_1g\rightarrow^4T_2g(F)$, $^4T_1g\rightarrow^4A_2g(F)$,and $^4T_1g\rightarrow^4T_1g(P)$, respectively. The spectrum resemble those reported for octahedral complexes[26].

5- Nickel (II) Complex

The magnetic moment for the complex of Ni(II) (d^8) was found to be (3.85 B.M), which is with the range of octahedral Ni(II) complexes[27]. The electronic spectrum of this complex show bands at (771nm) 12970 cm^{-1}, (405nm) 24691 $cm^{-1}$and (295nm) 33898 cm^{-1} which can be assigned to $^3A_2g\rightarrow^3T_1g(F)$, $^3A_2g\rightarrow^3T_1g(F)$ and charge transfer, respectively[28].

6- Copper (II) Complex

The magnetic moment value of the Cu(II) complex is (1.84B.M), which may suggest an tetrahedral structure[29]. It's electronic spectrum show bands at (901nm) 11098 cm^{-1} which may assigned to$^2T_2\rightarrow^2E$ transition an approximately tetrahedral environment.

7- Zinc(II) complex

This metal complex is diamagnetic consistent with the ($3d^{10}$) configuration and the electronic spectrum of this complex exhibit high intense charge transfer transition to (INCT)[30].

Table.3 : Electronic spectra, conductivity and magnetic moment of complexes

Compound	Assigument	Absorption band(nm)	Wave number cm^{-1}	Λ_M ($S.cm^2.mol^{-1}$) In (DMSO)	μ eff. B.M
HL_2	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	350nm 273nm	28571 36630	--------	
$[CrL_2Cl(H_2O)]$	${}^4A_2g\rightarrow{}^4T_2g_{(F)}$ ${}^4A_2g\rightarrow{}^4T_1g_{(F)}$ ${}^4A_2g\rightarrow{}^4T_1g_{(P)}$	984nm 636nm 376nm	10162 15723 26595	12.65	3.8
$[MnL_2(H_2O)_2]$	${}^6A_1g\rightarrow{}^4Eg$ C. T C. T	409nm 396nm 380nm	24449 25252 26315	11.98	5.4
$[FeL_2Cl(H_2O)]$	${}^6A_1g\rightarrow{}^4T_1g(G)$ ${}^6A_1g\rightarrow{}^4T_2g(G)$ ${}^6A_1g(S)\rightarrow{}^4Eg,{}^4A_1g(G)$	993nm 404nm 347nm	10070 24752 28818	10.70	5.42
$[CoL_2(H_2O)_2]$	${}^4T_1g\rightarrow{}^4T_2g(F)$ ${}^4T_1g\rightarrow{}^4A_2g(F)$ ${}^4T_1g\rightarrow{}^4T_1g(P)$	886nm 657nm 377nm	11286 15220 26525	11.77	4.76
$[NiL_2(H_2O)_2]$	${}^3A_2g\rightarrow{}^3T_2g(F)$ ${}^3A_2g\rightarrow{}^3T_1g(F)$ ${}^3A_2g\rightarrow{}^3T_1g(P)$	771nm 405nm 295nm	12970 24691 33898	12.56	3.85
$[CuL_2].2H_2O$	${}^2T_2\rightarrow{}^2E$ C.T C.T	901nm	11098	10.84	1.84
$[ZnL_2(H_2O)_2]$	C.T	375nm	26666	13.34	Dia

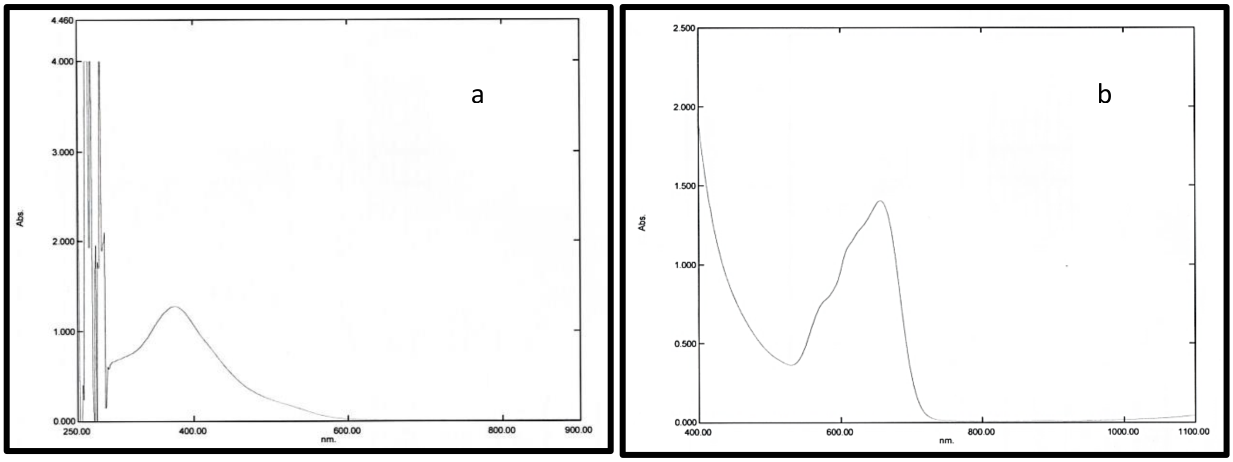
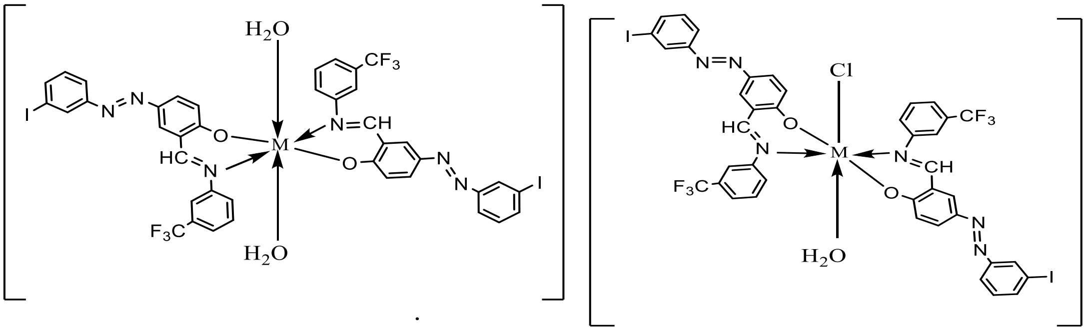


Fig.5: Uv-Vis of (a) (IFPMP) ligand & (b) $[Co(L)_2(H_2O)_2]$ complex

3.6. Conductivity measurement

The values obtained from the measurements of molar conductance of each metal complexes included in Table(3). Molar conductance measurements (10.70 -13.34 S. cm^2. Mol^{-1}) in DMSO (10^{-3} M) at room temperature exhibit non electrolytic behavior of the complexes. According to these results the following structural formula of these complexes may be proposed in figure.6 .



M= Mn(II), Co(II) ,Ni(II) and Zn(II) **M= Cr(III) and Fe(III)**

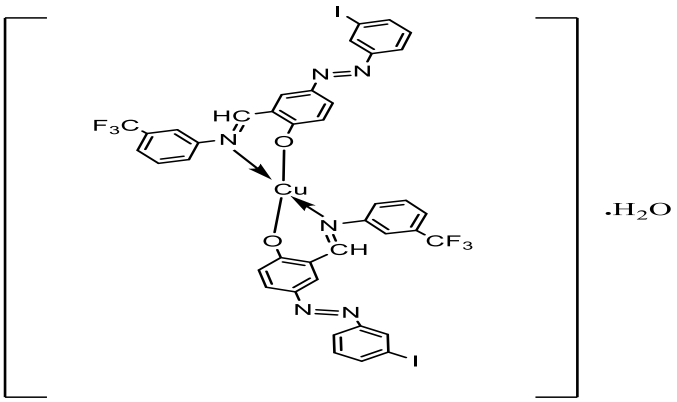
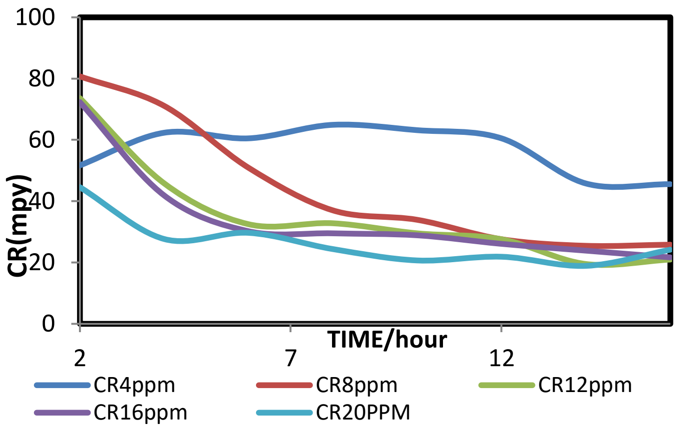


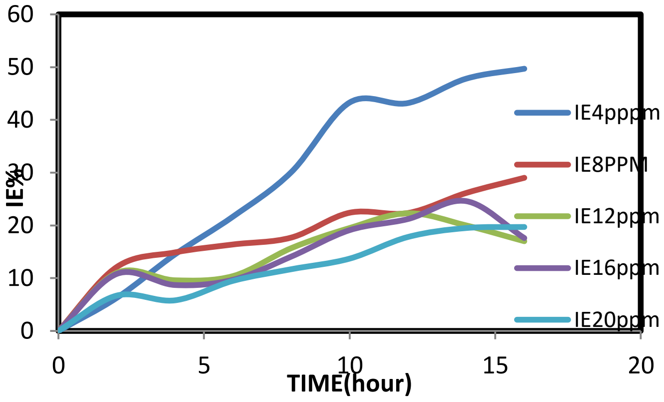
Fig.6: The proposed structural formula of the metal chelate complexes.

3.7. Weight loss measurements

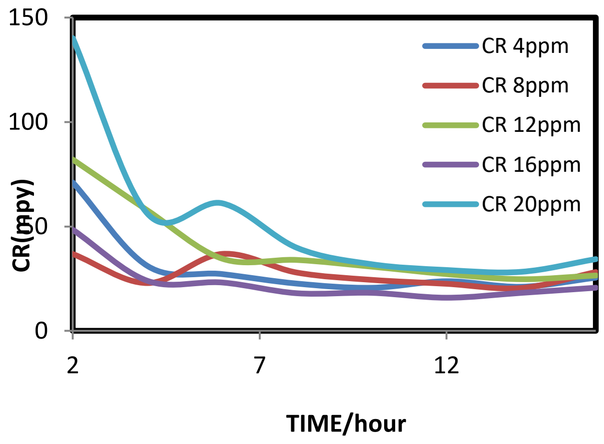
Weight loss of mild steel electrode was determined at various time intervals in absence and present of different concentrations of azo dye and Cu(II) complex at 298K .Table 4 gives the corrosion rate and inhibition efficiency for carbon steel in 0.5M HCl. This shows that the corrosion rate decreases and inhibitor efficiencies decrease with increasing concentration of ligand and increase with increasing concentration of its complex at given temperature.



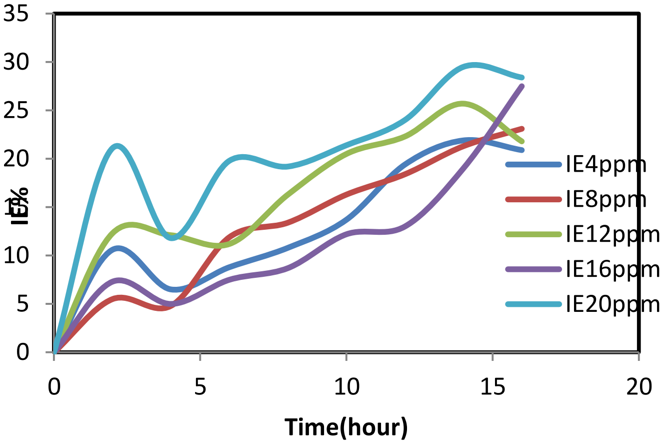
Relation between C.R and time in 0.5M HCl of ligand



Relation between I.E% and time in 0.5M HCl of ligand



Relation between C.R and time in 0.5M HCl Cu(II)complex



Relation between I.E% and time in 0.5M HCl of of Cu(II) complex

Table :4 The value of (CR)and (%IE) in (0.5M) of HCl at 298K of ligand and its complex

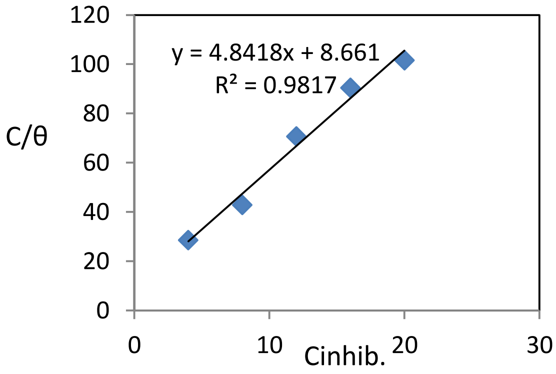
	Immersion time															
Conc.of ihib. ppm	**2h**		**4h**		**6h**		**8h**		**10h**		**12h**		**14h**		**16h**	
	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE	CR mpy	%IE
Blank	103	-	68.98	-	49.32	-	39.89	-	32.75	-	28.87	-	34.60	-	31.07	-
HL_2																
4	51.66	6.26	62.32	14.5	60.49	21.69	64.9	30.11	63.16	43.2	60.49	43.18	45.76	47.8	45.53	14.0
8	80.73	12.1	71.09	14.8	50.9	16.39	36.99	17.7	33.91	22.4	27.56	22.34	25.42	26.14	25.8	29.02
12	73.62	11	45.81	9.6	32.47	10.4	32.78	15.7	29.49	19.5	27.56	22.3	19.48	20	20.93	17
16	72.336	10.8	41.86	8.7	30.19	9.7	29.49	14.1	28.85	19.1	26.06	21.2	23.84	24.6	21.65	17.7
20	44.56	6.7	27.64	5.8	29.66	9.5	24.35	11.7	20.64	13.7	21.85	17.8	18.88	19.5	24.15	19.7
HL_2+Cu																
4	71.04	10.6	31.07	6.5	27.20	8.8	22.64	10.8	20.64	13.7	23.78	19.4	21.14	21.9	25.47	20.9
8	36.81	5.5	22.90	4.8	36.86	11.9	27.91	13.4	24.43	16.3	22.55	18.4	20.53	21.3	28.17	23.1
12	82.02	12.3	57.66	12.1	34.58	11.2	33.96	16.3	30.75	20.5	27.20	22.3	24.75	25.7	26.52	21.8
16	48.43	7.3	23.96	5	23.17	7.5	18.03	8.7	18.22	12.2	15.88	13	18.20	19	20.67	27.5
20	140.15	21.1	56.08	18	61.08	19.8	39.76	19.2	31.91	21.4	29.14	24	28.28	29.5	34.36	28.4

3.8. Adsorption Isotherm

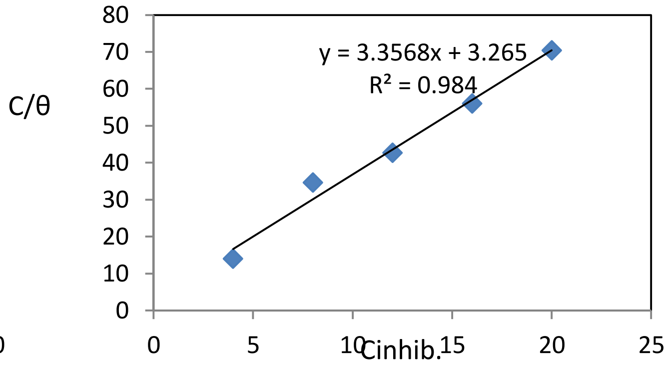
In order to confirm the adsorption of the investigated inhibitor on metal surface, the adsorption isothermwas studied. The adsorption isotherm can provide basic information on the interaction of inhibitor with metal surface. The use of Langmuir equation for adsorption was found to be suitable for adsorption of ligands (HL_2) and its complex of Cu(II) in medium of hydrochloric acid (0.5M) .

Table 5: The value of Cinhi./θ and Kads. of ligand and its complex in (0.5M) HCl at 298K

Immersion time **(16h)**				
Conc. Of inhib.ppm	**θ**	**$C_{inhib.}/\theta$**	**$K_{ads.}$**	**$-\Delta G_{ads.}$ KJ mol^{-1} K^{-1}**
HL_2				
4	**0.140**	**28.50**	**0.2065**	**6.041**
8	**0.290**	**42.79**		
12	**0.170**	**70.59**		
16	**0.177**	**90.40**		
20	**0.197**	**101.53**		
		16h		
HL_2+Cu				
4	**0.209**	**13.97**	**0.2980**	**6.949**
8	**0.231**	**34.63**		
12	**0.218**	**42.71**		
16	**0.275**	**56.0**		
20	**0.284**	**70.42**		



Adsorption Isotherm of ligand at 16 h



Adsorption Isotherm of Cu(II)complex at 16 h

3.9. Study of SEM

The SEM obtained of carbon steel samples after immersion in 0.5M HCl in absence and presence of 20ppm inhibitor for 16 hours. It is clear that carbon steel surface in the absence of the inhibitor are strongly damaged. While the morphology of carbon steel surface in presence of inhibitor is quite different from the previous one, the specimen surface was smoother.

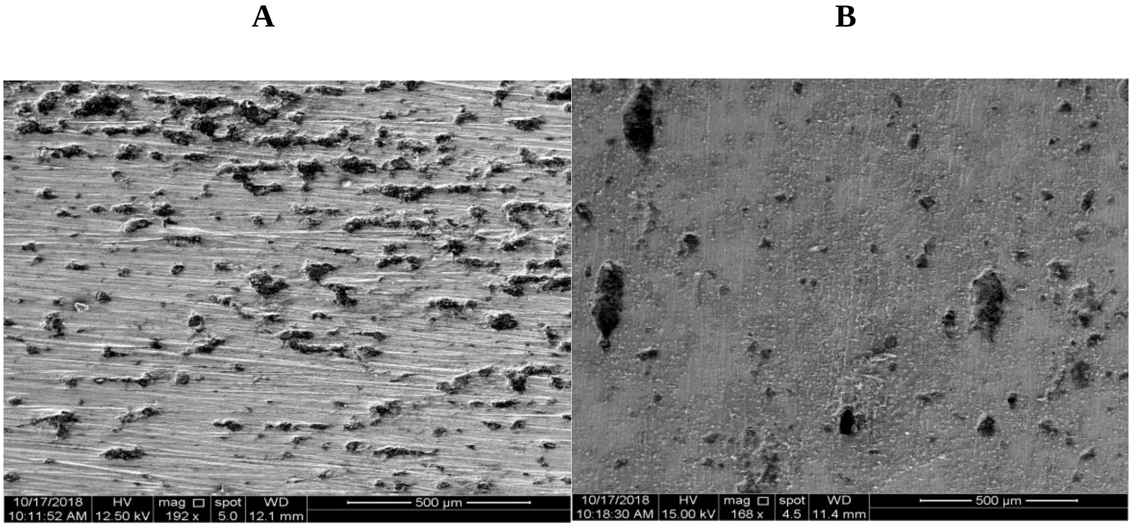


Fig.7: SEM micrographs for C-steel in (0.5M) HCl (A) and presence of inhibitor HL_2 (B).

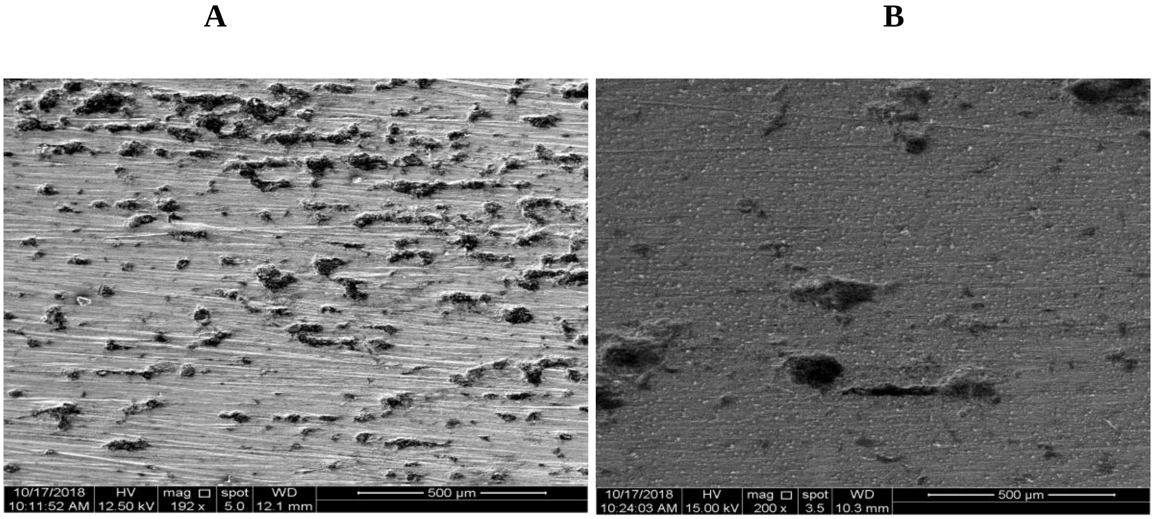


Fig.8:SEM micrographs for C-steel in (0.5M) HCl (A)and presence of inhibitor Cu(II) complex(B).

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