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Research Article

Preparation, Spectroscopic investigation and Corrosion inhibition of some azo Schiff base chelates

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Abstract

The azo Schiff base (ASB) under investigation was prepared from the reaction of Schiff base and 2-aminophenol, whereas, the used Schiff base was obtained from the condensation of salicylaldehyde and 2-aminothiophenol. The azo Schiff base reacted with Co(II), Ni(II), Cu(II) and Fe(III) ions forming four chelates. The prepared azo Schiff base and its chelates were subjected to several physiochemical tools; in terms, CHNS elemental analyses, molar conductivity Ir, UV-Vis, ^{1}HNMR and Mass spectra.. The used physiochemical tools showed the formation of 2:1 [M:L]chelates and confirm the geometrical structures of the prepared azo Schiff base and its chelates. An octahedral geometry was proposed for Co(II) and Fe(III) chelates and a square planar geometry was proposed for Ni(II) and Cu(II) chelates. Also the corrosion inhibition characteristics of the azo dye on mild steel in hydrochloric acid were studied at 30^{0}C.The results showed a high protection efficiency (greater than 85%) for acid corrosion of steel at its low concentration (3×10^{-5}M).

Keywords: Azo Schiff base, chelates, physiochemical tools. corrosion inhibition.

INTRODUCTION

Schiff bases derived from salicylaldehyde and primary amines and their complexes played an important part in the development of inorganic chemistry as widely studied coordination compounds are increasingly important as biochemical, analytical and antimicrobial reagents.[1,2] Also they have been used as antibacterial, antifungal, anticancer, antitubercular, hypertensive and hypothermic reagents.[3]Complexes of Co(II), Ni(II), Cu(II), Zn(II),Cr(III) and Fe(III) ions with 8-arylazo-6-formyl-7-hydroxy-2-methylchromones have been synthesized and characterized by several physiochemical techniques, a tetrahedral, square and octahedral geometries were proposed for all complexes.[4]Azo Schiff base complexes of VO(II), Mn(II), Co(II), Ni(II) and Cu(II) ions have been synthesized from N'-5-(4-chlorophenyl)diazenyl)-2-hydroxybenzylidene)-2-hydroxybenzohydrazide. The nature of bonding and the structural features of the complexes have been deduced from applying of several physiochemical techniques. The used techniques revealed a square planar geometry for Cu(II) complex, square pyramidal for oxovanadium complex and tetrahedral structure for the other complexes.[5]

This study aims to prepare and investigate azo Schiff base and chelates with Co(II), Ni(II), Zn(II) and Cr(III) ions. Also to study their corrosion inhibition.

EXPERIMENTAL

Chemicals and Methods

All chemicals used in this study are of pure grade (BDH\Aldrich) including salicylaldehyde, 2-aminothiophenol, 2-aminophenol, ethanol, dimethylformamide (DMF), sodium hydroxide, dimethylsulphoxide (DMSO), $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $ZnCl_2$, $CrCl_3.6H_2O$ and double distilled water. The prepared azo Schiff base compound was subjected to CHNS elemental analyses using 2400 elemental analyzer, infrared spectra were obtained by

KBr disc technique by using IFS-25DPUSR\IR spectrometer (Bruker) in the range of 4000-400 cm^{-1}, proton nuclear magnetic resonance spectra were recorded on Varian Gemini 200-200MHz spectrometer using TMS as internal standard and D^6 DMSO as a solvent, ultraviolet spectrum of the azo Schiff base was measured in DOMSO solvent using a Perkin–Elmer-Lambda β–spectrophotometer.The massspectrum of the azo Schiff base was carried out by using Shimadzu QP-2010 Plus. The azo Schiff base chelates were subjected to the same analyses in addition tomolar conductivity measurements. All the mentioned analyses weredone *at Micro analytical center, Cairo University, Giza, Egypt.*

Preparation of Schiff base

The Schiff base was prepared by dissolving 0.01mole;1.22 g of salicylaldehyde and 0.01 mole; 1.25 g of 2-aminothiophenolin 50 ml ethanol. The mixture was refluxed for two hours, then the obtained product was concentrated in vacuum to remove ethanol. The product was filtrated, dried and recrystallized from suitable solvent (yield = 70%).

Preparation of azo Schiff base (ASB)

The azo Schiff base under investigation was prepared by mixing 0.01 mole; 2.29 g of Schiff base with 0.01 mole; 109 g of 2-aminophenol in 50 mL of ethanolin the presence of 10% NaOH, $NaNO_2$solution and conc. HCl. The obtained azo Schiff base was acidified by dilute hydrochloric acid until pH= 2-4. The isolated compound was filtrated, washed several times with distilled water until the filtrate becomes free from chloride ion by testing it with silver nitrate solution, dried and recrystallized from suitable solvent

Preparation of azo Schiff base chelates

The reaction of azo Schiff base (0.01 mole; 3.49 g) with 0.01 mole of metal salts [2.37, 2.38, 1.71 and 2.71 g] of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $FeCl_3.6H_2O$, respectively, in 50 mL ethanol were refluxed for three hours, then filtered and washed several times with hot ethanol until the filtrates become colorless. The chelates were dried in desecator over calcium chloride for a night.

Corrosion

The corrosion rate of steel sample in 0.5M, HCl was determined by mass loss technique, the specimens used were cut in the form of rods of dimensions 40 mm length and 10 mm diameter. The commercial steel rods that collected from Musrata steel factory was of composition given as: C=0.32, Si=0.21, Mn=0.75, P=0.014, S=0.004, Cr=0.20, Ni=0.001, Cu=0.001,Al=0.002, Fe to 100 (by weight).Before the measurements, the sample were mechanically polished with a series of emery papers with different grades (60,100,120,180,220,320,400 and 1200) starting with coarse one and proceeding to the finer grades. Both sample and solution were allowed to attain temperature equilibrium for a minimum of 20 min prior to starting the corrosion experiments. The reactions were under stagnant conditions at 30^0C and rates followed for a maximum of 1 hour to avoid drastic changes in surface characteristics.

Inhibitors

All the chemicals used are analytical grade. Freshly distilled deionized water was used in all preparations. Azo Schiff base as corrosion inhibitor in 0.5M, HCl medium was prepared in dimethylformamide (DMF). All tested solutions contained 10 vol. percent of DMF to maintain complete soluble.

RESULTS AND DISCUUSION

The azo Schiff base and its chelates have been characterized on the basis of elemental analysis, molar conductivityand spectroscopic techniques. The analytical, IR, electronic, ^{1}HNMR and mass spectral data (Tables I) of the azo Schiff base product suggest that the condensation occurred in 1:1: ratio. The azo Schiff base and its chelates are colored solids and stable in air. They are insoluble in water but soluble in coordinating solvents.The melting points of the azo Schiff base and its chelates are 132.70 and >250 ^{0}C, respectively. The CHNS elemental analyses exhibit that the calculated values are in a good agreement with the found data(Table I). The CHNS elemental analysis results together with the non-electrolytic nature, [6] in DMF solvent suggest 2:1 [M:L]ratio of the chelates.

Infrared spectra of azo Schiff base and its chelates

The infrared spectral data of the azo Schiff base and its chelates were listed in table II. The infrared spectra of the synthesized azo Schiff base chelates exhibited bands in the range of 3157-3426 cm^{-1} corresponding to the existence of water molecule as hydrated and coordinated. [7] Meanwhile, the same spectra showed bands in the range of 1597-1602 cm^{-1} attributed to υ (–C=N) vibration, the changing of these bands comparing to the free ligand (1585 cm^{-1}) confirmed the participation of this group in chelation through nitrogen atom.[8] The spectra of the chelates exhibited a change in the position of the thio group (SH) indicating the involvement of this group in complexation through sulfur atom. [9]Also the same spectra exhibited bands in the range of 1476-1482 cm^{-1} due to the presence of azo (-N=N-) group, this group is changed to lower frequency suggesting its participation in bonding with the metal ions.[10]New bands in the range of 514-616 and 433-564cm^{-1}which are not present in the azo Schiff base are assigned to υ(M-O) and υ(M-N) vibrations,[11] and the appearance of these vibrations supported the involvement of oxygen and nitrogen atoms of the azomethine, azo and OH groups of the free ligand in chelation process.

Proton nuclear magnetic resonance spectrum of azo Schiff base compound

The ^{1}HNMR spectrum of the azo Schiff base compound(Fig. 1) was measured in d^6-DMSOsolvent. The azo Schiff base spectral results showed signals at 8.18 and 11.59 ppm which are assigned to the presence of azomethine and hydroxyl groups, respectively. Also, the same spectrum displayed signals between 7.00-7.55 ppm attributed to phenyl rings (Fig.1). The signals at 2.51 and 3.50 ppm due to the existence of methyl and solvent groups in the compound. [13]

Mass spectra of the azo Schiff base and its Ni(II) and Fe(III) chelates

The mass spectral fragmentations of the azo Schiff base and theirNi(II) and Fe(III) chelates are shown in schemes 1-3, table 2 and figures2-4. The base peak ofazo Schiff base at m\e+ = 349. is attributed to the original molecular weight. Meanwhile, the peak at m\e+ =331 is analogous to the loss of oxygen and two hydrogen atoms from the compound. The loss of two nitrogen and two hydrogen atoms give a peak at m\e+ = 301. The peak at m\e+ = 256 due to loss of azomethine group, oxygen and three hydrogen atoms. The same spectrum showed a peak at m\e+= 110 corresponding to loss of twelve carbon and two hydrogen atoms. A peak at m\e+=55 is analogous to C_4H_7 ion. For Ni(II) chelate, the spectrum exhibited a peak at m\e+ =448 due to loss of four hydrogen and oxygen atoms. The peak at m\e+ = 421 corresponding to the loss of azomethine group and the peak at m\e+ = 404 due to the loss of hydroxyl group. The loss of the azo group(N=N) and Ni(II) atom give a peak of 318. The same spectrum showed a peak at m\e+ = 227 suggesting the loss of another Ni(II) atom and thio group (SH). The final peak at m\e+ = 52 is analogous to the appearance of C_4H_4 ion. The mass spectrum of iron chelate exhibited peaks at m\e+ = 444, 344, 237 and 55, these peaks attributed to loss of different atoms (see table 2). The above fragmentations illustrated the formation of the azo Schiff base and the formation of the chelates in 2:1 [M:L] ratio.

Electronic spectra of azo Schiff base chelates

The electronic spectral results of the azo Schiff base showed several bands (Table 3) due to $\pi\rightarrow\pi^*$ (Phenyl rings) and $n\rightarrow\pi^*$(H-C=N and azo group) transitions.[14] The electronic spectral studies of Ni(II), Cu(II)and Fe(III) chelates with the azo Schiff base were carried out in DMSO solvent. The square planar chelates that contain ametal ion of d^8 electronic configuration are diamagnetic, which is the case for the Ni metal chelate. The spectrum of Ni(II) chelate showed two bands at 328nm (20487cm^{-1}) and 383nm (26110cm^{-1}) ascribed to the two component excitation$^1A_1g\rightarrow{}^1B_3u$, B_2u transitions. [15]The electronic spectrum of copper(II) chelate exhibited three bands at 289, 328 and 411 nm (34602, 30489 and 24331 cm^{-1}) due to d-d and $^2B_1g\rightarrow$ ^2Eg transitions which is consistent with square planar geometry. [16] The electronic spectral data of Fe(III) chelate showed two bands (see table 3) attributed to $^3A_2g\rightarrow{}^3T_1g$ transition. The nature of the bands of the chelate confirmed the existence of an octahedral geometry.[17]

Corrosion Inhibitions

Rates of dissolution were determined chemically by WL at 30^{0}C. Table (2) gives the corrosion rate and inhibitor efficiency for mild steel in 0.5M HCl, 10% DMF in absence and presence of different concentrations of azo Schiff base at 30^{0}C. This shows that the corrosion rate decreases and inhibitor efficiencies increase with increasing concentration of each inhibitor at given temperature.

Figure (4) shows the variation of the corrosion rate as a function of the concentration of Azo Schiff base at 30^{0}C. As show in this figureon increasing the concentration of Azo Schiff base (A.S.B) inhibitor, the corrosion rate decreases.

Figure (5) represents the variation of percentage inhibitor as a function of the logarithmic concentration of Azo Schiff base (A.S.B) at 30^{0}C. As shown in this figure that the efficiency of inhibition of acid corrosion of steel by Azo Schiff base is increased as concentration of inhibitor increase at 30^{0}C.

In figure (6), the results have characteristics of S-shaped adsorption isotherm indicative of adsorption mechanisms for the inhibition process.

It is evident that the presence of different windrowing groups have clear influence on inhibitor efficiency created by adsorption centers (HC=N-,N=N-, -SH,-OH,-OH).The inhibition effect could be attributed to physisorption process between clean charged steel surface in acidic medium followed by chemisorption forming coordinate-covalent bond due to its free electron pair atoms. The inhibition effect also could be increased by forming breaking H-bond that allowed coordination bond between –SH and OH groups with clear charged steel surface. The results shown that at 30^{0}C and low concentration range (4×10^{-3}- 3×10^{-5} M) gives (85-97%) protection efficiency. The gradual increase in these protection efficiency percentages can be discussed on the basis that presence of double bonds and electron pair atoms resulting of interaction between this molecule and the metal surface.

Table1: Elemental analyses and some physical properties of azo Schiff base and its chelates

Compound	M.Wt	Color	M.P 0C	Yield	%Found	(Calcd.),%	C HN S
A.S.B ($C_{19}H_{15}N_3O_2S$)	349.00	Bright brown	132.70	66 65.33 (66.68)	4.29 (3.00)	12.03 (11.73)	9.17 (9.25)
[Co_2(ASB)$(OH)_2(H_2O)$]H_2O	535.00	Green	>250.00	6242.62 (42.33)	3.55 (3.00)	7.85 (6.25)	5.98 (6.16)
[Ni_2(A.S.B)(OH)2(H2O)]H_2O	534.40	Olive green	>250.00	5442.66 (42.68)	3.56 (3.90)	7.86 (7. 55)	5..99(5.27)
[Cu_2(A.S.B)$(OH)_2(H_2O)$]H_2O	544.00	Dark brown	>250.00	41.91 (41.87)	3.49 (4.10)	7.72 (6.92)	5.88 (5.41)
[Fe_2(A.S.B)$(OH)_4(H_2O)$3]H_2O	599.00	Dark clay	>250.00	7738..06 (37.56)	4.17 (4.65)	7.01 (6.41)	5.34 (5.80)

Table2. Infrared spectral data and mass spectral data of azo Schiff base and Ni(II), Cu(II) and Fe(III) chelates

Compound	υ(OH)	υ(HCN)	υ(N=N)	υ(C-OH)	υ(SH)	υ(M-O)	υ(M-N)	m\e+
A.S.B ($C_{19}H_{15}$N3O$_2$S); L	3421	1585	1482	1314	3054	-	-	349,331,301,256,110,55
[Ni_2(A.S.B)$(OH)_2(H_2O)$]H_2O	3426	1597	1476	1272	3051	517	433	448,421,404,318,227,52
[Cu_2(A.S.B)$(OH)_2(H_2O)$]H_2O	3382	1602	1478	1276	3057	514	462	451,285,256,227,127,55
[Fe_2(A.S.B)$(OH)_4(H_2O)$3]H_2O	3157	1598	1479	1290	-	616	564	444,344,237,55

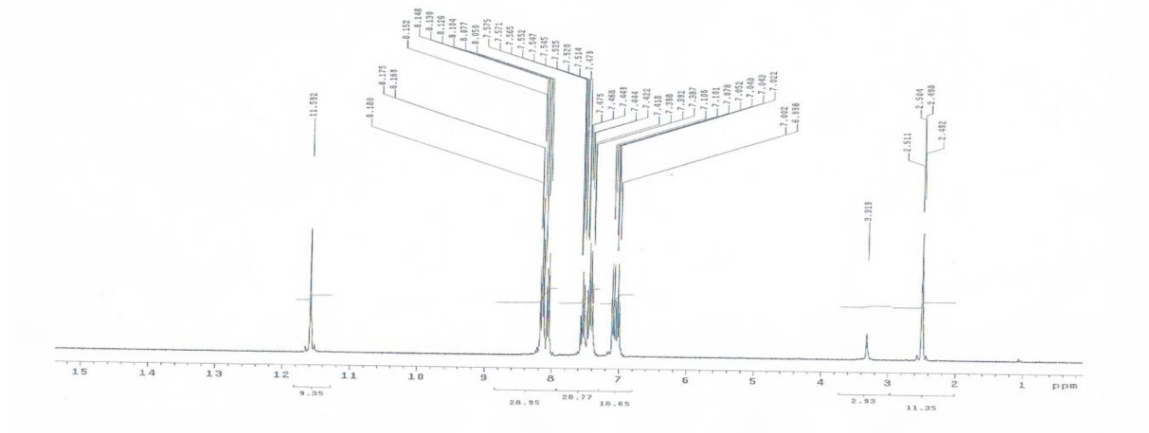
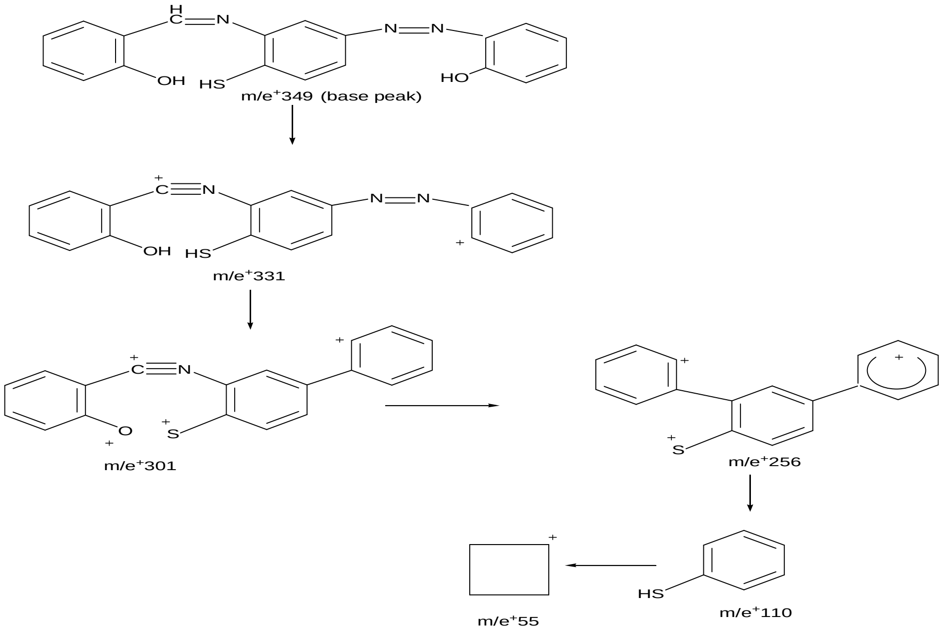


Figure1.^{1}HNMR spectrum of the azo Schiff base compound.



Scheme (1): Mass spectral fragmentation of the azo Schiff base.

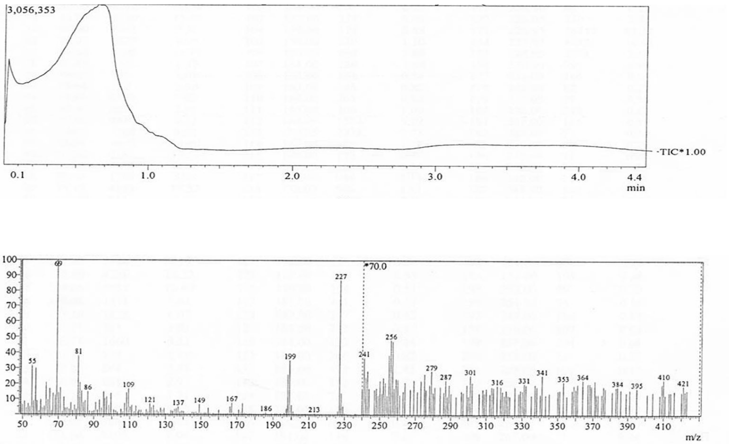
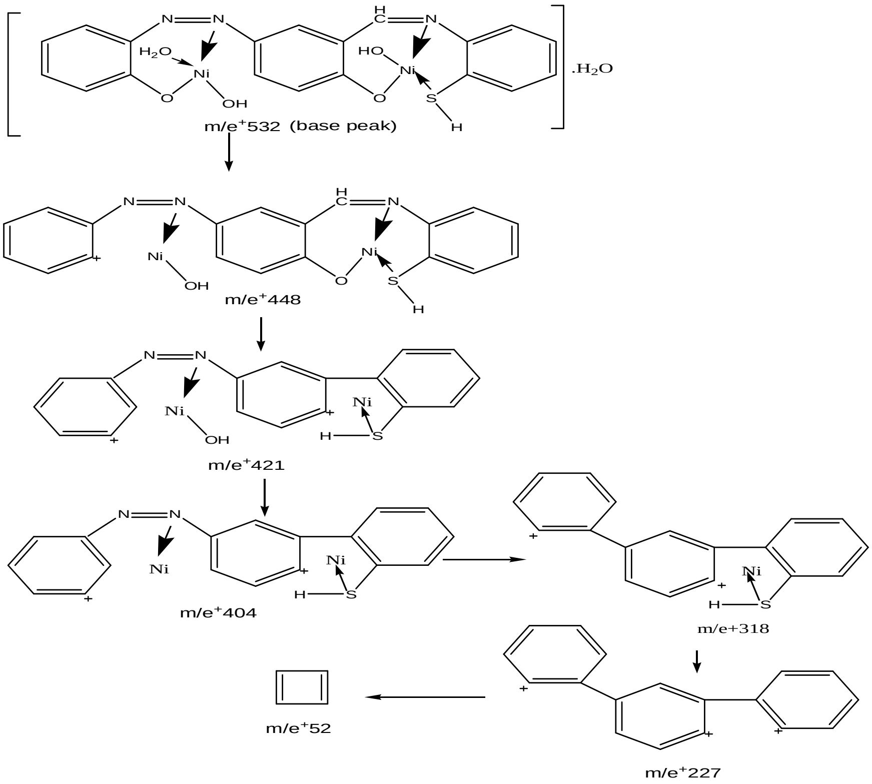


Figure (2):Mass spectrum of the azo Schiff base



Scheme (2): Mass spectral fragmentation of Ni_2-chelate

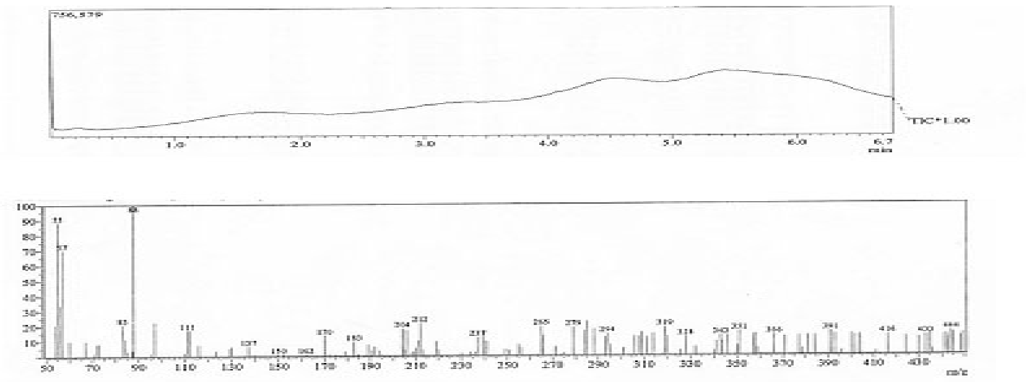
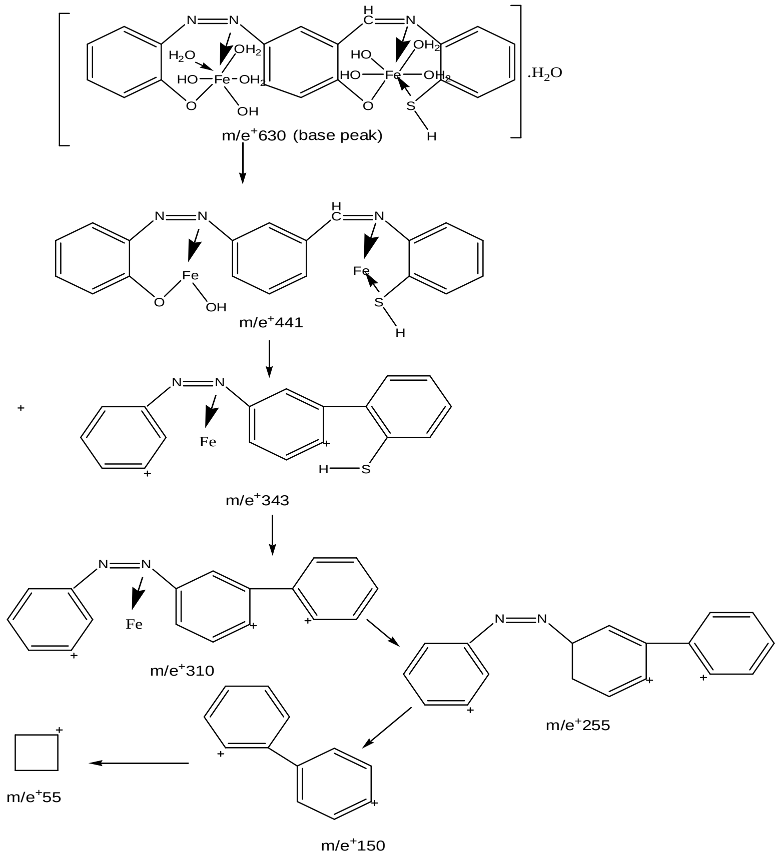


Figure 3: Mass spectrum of the $[Ni_2(ASB)(OH)_2(H_2O)]H_2O$



Scheme (3): Mass spectral fragmentation of Fe_2-chelat

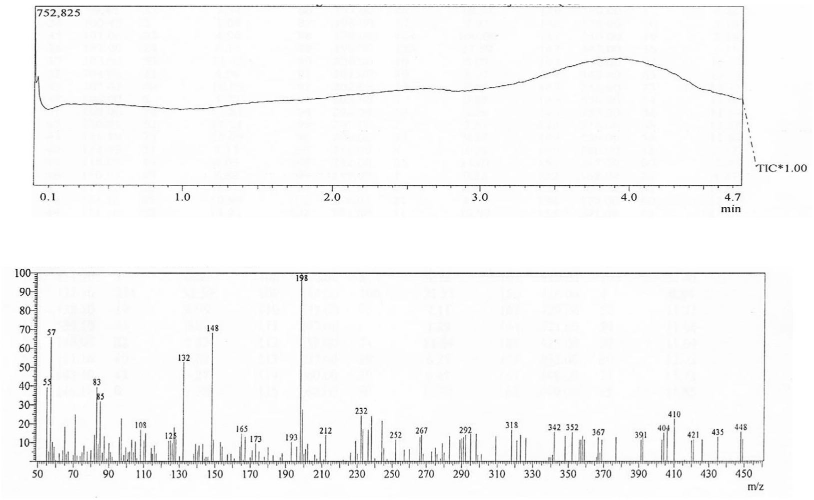


Figure 4: Mass spectrum of the $[Fe_2 (ASB)(OH)_4(H_2O)_3]H_2O$

Table 3: Electronic spectral data of the azo Schiff base and its chelates

Ligands\chelates	**UV-Vis nm** (cm-1)
AzoSchiff base	**294**(34013), **311**(32154), **320** (31290), **332** (30120), **348** (28736)
Ni$_2$ chelate	**328**(30487), **383**(26110)
Cu$_2$ chelate	**289**(34602), **328**(30489), **411**(24331)
Fe$_2$ chelate	**329**(30395), **274**(36630)

Table 4: Corrosion parameters obtained from WL data for mild steel in 0.5 M, HCl, 10% DMF in absence and presence of different concentrations of azo Schiff base at 30^{0}C

Inhibitor concentration 10^{-3}M/litter×	**log[I]**	**C.R×10^{-5} mg/cm^2 min**	**Inh%**
4	-2.39794	0.1156	97.87
3	-2.52287845	0.2893	94.67
0.6	-3.2218487	0.5167	90.49
0.5	-3.30102999	0.5651	89.60
0.4	-3.39794000	0.6114	88.75
0.3	-3.522878745	0.6735	87.60
0.06	-4.22184875	0.6619	87.82
0.05	-4.301029996	0.80303	85.22
0.04	-4.397940009	0.7288	86.59
0.03	-4.522878745	0.8099	85.10

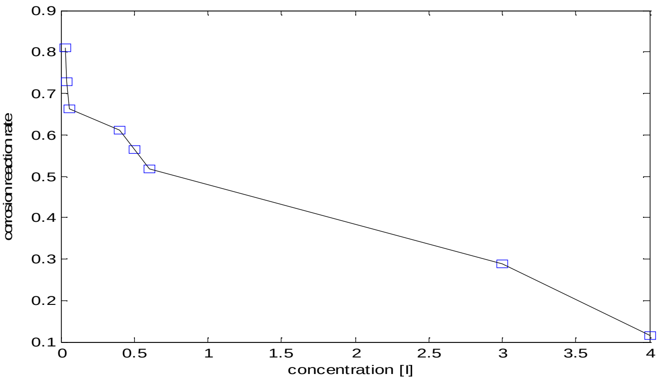


Fig (5):Variation of the corrosion rate with the concentration of azo Schiff base at 30^{0}C.

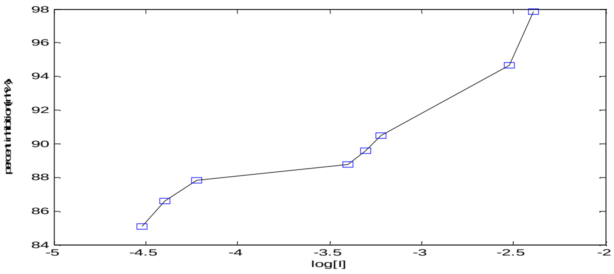
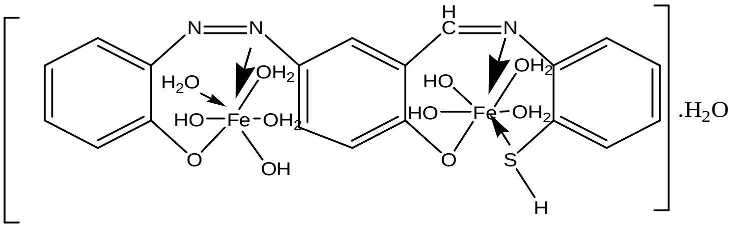


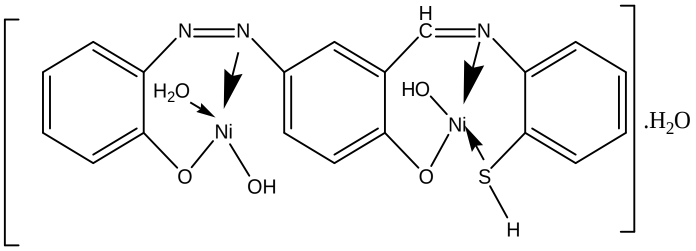
Fig (6):Variation of percentage inhibitor with the logarithmic concentration of azo Schiff base

Conclusion

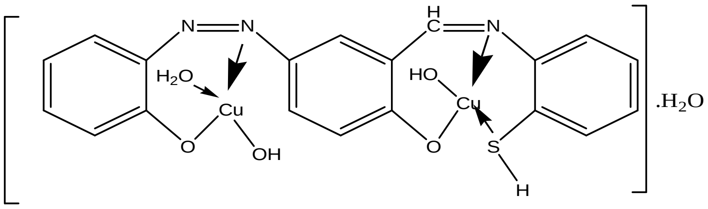
From the obtained results, we can suggest the following structures for all synthesized chelates.



$[Fe_2(ASB)(OH)_4(H_2O)_3]H_2O$



$[Ni_2(ASB)(OH)_2(H_2O)]H_2O$



$[Cu_2(ASB)(OH)_2(H_2O)]H_2O$

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