Experimental studies of Azo Schiff Base Chelates and their Corrosion Inhibition Behavior

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ABSTRACT: Four new Co(II), Ni(II), Cu(II) and Fe(III) chelates with synthesized azo Schiff base ligand (ASB) derived from Schiff base [salicylaldehyde and 2-aminothiophenol] with aniline were synthesized and characterized on the basis of various physicochemical methods including; CHNS elemental analyses, molar conductivity, magnetic moment measurements, infrared, electronic, mass and proton nuclear magnetic resonance spectra. The used techniques showed the formation of 1:1[M:L] ratio and confirm the geometrical structures of the azo Schiff base and its chelates. A square planar geometry was established for Ni(II) and Cu(II) chelates and octahedral structure for Co(II) and Fe(III) chelates. The corrosion inhibition of mild steel in 0.5M HCl using azo Schiff base as inhibitor has been studied at 30 ^{0}C. High inhibition efficiency (> 90 %) of azo Schiff base for acidic corrosion of steel was determined at its low concentration (3×10^{-4} M) by weight loss measurements.

Keywords: Experimental studies, azo Schiff base, Chelates, Corrosion Inhibition, Spectral techniques.

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INTRODUCTION

The azo compound class accounts for 60 – 70 % of all dyes[1]. Most azo dyes contain only one azo group, but some contain two (diazo), three (triazo) or more. Azo dyes can supply a complete rainbow of colors; they tend to supply yellow, orange, blue and red than other colors[2]. In recent decades, organic color chemistry undergoes very exciting development as a result of the opportunities presented by dye applications in high technology fields: electronic devices[3]. El-ajaily et al.[4] Synthesized and cha racterized a chelate of Co(II) with azo Schiff base by using several physiochemical techniques. The inhibition characteristics of azo Schiff base on steel corrosion in hydrochloric acid media is investigated at 30^{0}C. The results showed high protection efficiency greater than 85% for acid corrosion of steel at its low concentration ($3*10^{-3}$ M). An azo dye ligand derived from 2-hydroxyacetophenone and 2-aminobenzoic acid has been synthesized and characterized by using several tools; such as, elemental analysis, Ir, ^{1}HNMR and mass spectra. The biological activity of compounds was screened on some pathogenic bacteria. The biological activity results showed strong effect for 2-hydroxyacetophenone, no effect for 2-aminobenzoic acid and less inhibitory activity than 2-hydroxyacetophenone[5].

This paper aims to synthesis and characterize some chelates of azo Schiff base with Co(II), Ni(II), Cu(II) and Fe(III) ions and to study the corrosion inhibition behavior of the azo Schiff base compound.

MATERIAL AND METHODS

All chemicals used in this study are salicylaldehyde, 2-aminothiophenol, aniline, ethanol, dimethylformamide (DMF), sodium hydroxide, hydrochloric acid, dimethylsulphoxide (DMSO), $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $FeCl_3.6H_2O$ and double distilled water. The synthesized azo Schiff base and its chelates were subjected to CHNS elemental analyses using Perkin-Elmer 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 of the

azo Schiff base and its Ni(II) chelate were recorded on Varian Gemini 200-200MHz spectrometer using TMS as internal standard and d^6 DMSO as a solvent, The electronic spectra of the azo Schiff base and its chelates were measured in DOMSO solvent using a Perkin–Elmer-Lambda β–spectrophotometer. The mass spectra were carried out by using Shimadzu QP-2010 Plus. The molar conductivity of the chelate was measured in DMF solvent using digital conductivity meter CMD 650, at chemistry department, Sebha University, Sebha, Libya. All the mentioned analyses were done at Micro analytical center, Cairo University, Giza, Egypt.

1. **Synthesis of Schiff base (SB):** The Schiff base was synthesized by dissolving 0.01 mole; 1.22 g of salicylaldehyde and 0.01 mole; 1.25 g of 2-aminothiophenol in 50 mL ethanol. The mixture was refluxed for two hours. The obtained product was concentrated in vacuum to remove the solvent. The product was filtrated, dried and recrystallized from suitable solvent (m.p =142^{0}C, yield = 70.72 %).

2. **Synthesis of azo Schiff base (ASB):** The azo Schiff base under investigation was synthesized by mixing 0.01 mole; 2.29 g of Schiff base with 0.01 mole and 0.93 g of aniline in 50 mL of ethanol in the presence of 10% NaOH solution, $NaNO_2$ 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.

3. **Synthesis of azo Schiff base chelates:** The reaction of azo Schiff base (0.01 mole; 3.33 g) with 0.01 mole of salts [2.38, 2.37, 2.50 and 2.71g] of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $FeCl_3.6H_2O$ 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 desecrator over calcium chloride for a night.

4. **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 and Fe to 100 (by weight). Before the measurements, the samples 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. The samples and solutions were allowed to attain temperature equilibrium for a minimum of 20 min prior to start the corrosion experiments. The reactions were under stagnant conditions at 30 ^{0}C and rates followed for a maximum of 1 hour to avoid drastic changes in surface characteristics.

5. **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 .All tested solutions contain 10 vol. percent of DMF to maintain complete soluble.

RESULTS AND DISCUSSION

The azo Schiff base and its chelates have been investigated on the basis of elemental analysis, molar conductivity, thermogravimetric analysis and spectroscopic techniques. The analytical and spectral data (Table 1) confirm the formation of the azo Schiff base and 1:1[M: L] chelate 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 chelate are 131.60 and >250 ^{0}C, respectively.

1. **CHNS elemental analyses and molar conductance measurements:** The CHNS elemental analyses exhibit that the calculated values are in a good agreement with found data (Table 1). In DMF solvent, the molar conductance values revealed that the synthesized chelates are non-electrolytic nature[6].

Table 1: CHNS elemental analyses and some physical properties of azo Schiff base and its Chelates.

ligand/chelates	Color	M.W	M.P ^{0}C	Calcd.(Found)				Λ
				C%	H%	N%	S%	
ASB;$C_{19}H_{15}N_3OS$	Bright yellowish orange	333	131	68.47 (68.68)	4.50 (4.31)	12.61 (12.62)	9.61 (9.62)	-
[FeL $(OH)_2(H_2O)$]H_2O	Dark clay	458	>250	49.78 (49.91)	4.36 (4.82)	9.17 (9.66)	6.98 (6.99)	7.40
[CoL (OH) $(H_2O)_2$]H_2O	Light Yellowish -Brown	462	>250.	49.35 (49.42)	4.55 (4.82)	9.10 (9.87)	6.93 (6.73)	3.32
[NiL (OH)]H_2O	Dark Yellow	425.7	>250	53.55. (43.55)	3.99 (3.89)	9.87 (9.02)	7.52 (7.55)	8.21
[CuL (OH)]5H_2O	Chocolate	492.5	>250	46.29 (46.91)	5.07 (5.90)	8.53 (8.68)	6.49 (6.91)	1.75

2. **Infrared spectra of azo Schiff base and its chelates:** The infrared spectral data exhibit broad bands in the range of 3265-3440 cm^{-1} corrsponding to presence of water molecules[7]. Meanwhile, the same spectra display a band at 3053 cm^{-1} due to HS group of the thio group in the free ligand. The bands in the range of 1596-1598cm^{-1} assigned the azomethine (HC=N) group, this group is changed on chelation process compared to its position in the free azo Schiff base (1583cm^{-1}) suggesting its participation in coordination with the metal ions [8]. There is no large change in the –N=N band in comparison to free ligand (1482 cm^{-1}), this indicates that no coordination from this group [9]. New bands in the range are 422-458 and 449-747 cm^{-1} assigned to the ν (M-N) and ν (M-O) vibrations [10]. The appearance of these bands supports the involvement of azomethine and thio groups via nitrogen and sulfur atoms in chelation.

Table 2: Infrared and electronic spectral data of the azo Schiff base and its chelates

Ligand/ chelate	ν-OH(H_2O)	ν-HC=N	ν-M-N	ν-M-O -	ν-SH	UV-Vis spectral data nm (cm^{-1})
ASB; $C_{19}H_{15}N_3OS$	3431	1583	-	-	3053	329 (**30395**) 274 (**36496**)
[FeL $(OH)_2(H_2O)$]H_2O	3265	1596	452	620	-	329 (**30395**) 273(**36630**)
[CoL (OH) $(H_2O)_2$]H_2O	3440	1597	422	626	3052	330 (**30303**) 290 (**34483**)
[NiL (OH)]H_2O	3439	1598	558	832	3054	329 (**30395**) 284(**35211**)
[CuL (OH)]5H_2O	3417	1598	428	545	3057	329 (**30395**) 284 (**35211**)

3. **Proton nuclear magnetic resonance spectra of azo Schiff base and Ni(II) chelate:** The ^{1}HNMR spectra have useful data to establish the nature and structure of azo Schiff base and chelates. The ^{1}HNMR spectrum of the azo Schiff base was measured in d^6-DMSO solvent. The azo Schiff base spectral results show signals at 8.17 and 11.57 ppm which are assigned to the presence of azomethine and hydroxyl groups, respectively. Also, the same spectrum displays signals in the range of 7.023-7.547 ppm attributed to protons of phenyl rings. The signals at 2.50 and 3.30 ppm due to the existence of methyl and DMSO solvent groups. Meanwhile, the signal which appeared at 3.31 ppm in the spectrum of the azo Schiff base is attributed to the presence of thio (SH) group [11]. In the case of the diamagnetic Ni(II) chelate, the spectrum shows the absence of OH and SH groups which observed at

11.57 and 3.30 ppm in the azo Schiff base indicating their participation in chelation [12]. Whereas, the position of HC=N group which appeared at 8.17 ppm is shifted to lower field (9.16 ppm) suggesting its involvement in complexation[13].

4. **Mass spectra of the azo Schiff base and its chelates:** The mass spectral fragmentations of the azo Schiff base and its Co(II) chelate is shown in schemes 1-3 and figures 1-3. The mass spectrum of the azo Schiff base ' displays a base peak at m/e+ =333 which corresponds to the exact molecular weight of the synthesized azo Schiff base. The peak at m\e+ = 316 due to loss of hydroxyl group, while a peak at m\e+ = 255 leads to the loss of two nitrogen atoms and thio group from the azo Schiff. The loss of CN group gives a peak at m\e+ = 228. Meanwhile, the peak at m\e+ = 152 is corresponding to loss six carbon and four hydrogen atoms. The same spectrum shows a peak at m\e+ =77 analogous to $C_6H_6^+$ ion. A peak at m\e+ = 51 is attributed to the appearance of C_4H_3 ion. The mass spectrum of the cobalt(II) azo Schiff base ligand chelate shows a base peak at m/e+ = 461, which is corresponding to $[Co(ASB)(OH)(H_2O)_2]^+$. Whereas, the peak at m/e+ = 391 analogues to the loss of two hydroxyl groups and two water molecules. The peak at m/e+ =342 due to loss of thio group and oxygen atom. The peak appeared at m/e+ = 283 attributed to loss of cobalt ion'. The last peak at m\e+= 132 is corresponding to $C_{10}H_4N_2^+$. The m\e+ at 80, 64 and 55 are attributed to $C_5H_7N^+$, $C_5H_5^+$ and $C_4H_8^+$. The mass spectrum of the copper (II) azo Schiff base chelate displays a base peak at m/e+ = 503, which is analogous to the original molecular formula of the chelate. The same spectrum shows a peak at m/e+ = 420 represents the loss of three water molecules andazo group. The peak at m/e+ =384 attributed to loss of two hydrated water molecules from the chelate. The peak appeared at m/e+ = 352 due to loss of sulfur atom. The spectrum exhibits a peak at m\e+ = 228 is corresponding to loss of HCN, Cu, O and OH groups. The peak at m\e+ = 77 is attributed to $C_6H_6^+$ ion and the peak at m\e+ = 64 is analogous to $C_5H_5^+$ ion. The mass spectrum of the nickel(II) azo Schiff base chelate exhibits a base peak at m/e+ = 425, which is analogous to the original molecular formula of the chelate. Meanwhile, another peak at m/e+ = 351 analogous to the loss of nickel and oxygen atoms. The peak at m/e+ = 316 attributed to loss of hydrated water molecule and –OH group. The peak appeared at m/e+ = 283due to loss of thio group. The same spectrum reveals a peak at m\e+ = 228 are corresponding to loss of HCN and azo groups. The peak at m\e+ =165 is attributed to $C_{13}H_{10}^+$ ion and the peaks at m\e+ = 71, 57 and 52 are analogous to $C_5H_{12}^+$, C_4H_8- and C_4H_4 ion. The mass spectrum of the iron (III) azo Schiff base ligand chelate shows a base peak at m/e+ = 476, which is analogous to the original molecular formula of the chelate. Whereas, the peak at m/e+ = 388 represents the loss of three water molecules, oxygen atom and hydroxyl group. The peak at m/e+ =371 due to loss of oxygen atom from the ligand. The peak appeared at m/e+ = 316 attributed to loss of iron ion. The spectrum exhibits a peak at m\e+ = 227 is corresponding to loss of HCN, N_2 and SH groups. The m\e+ at 55 is attributed to $C_4H_8^+$.
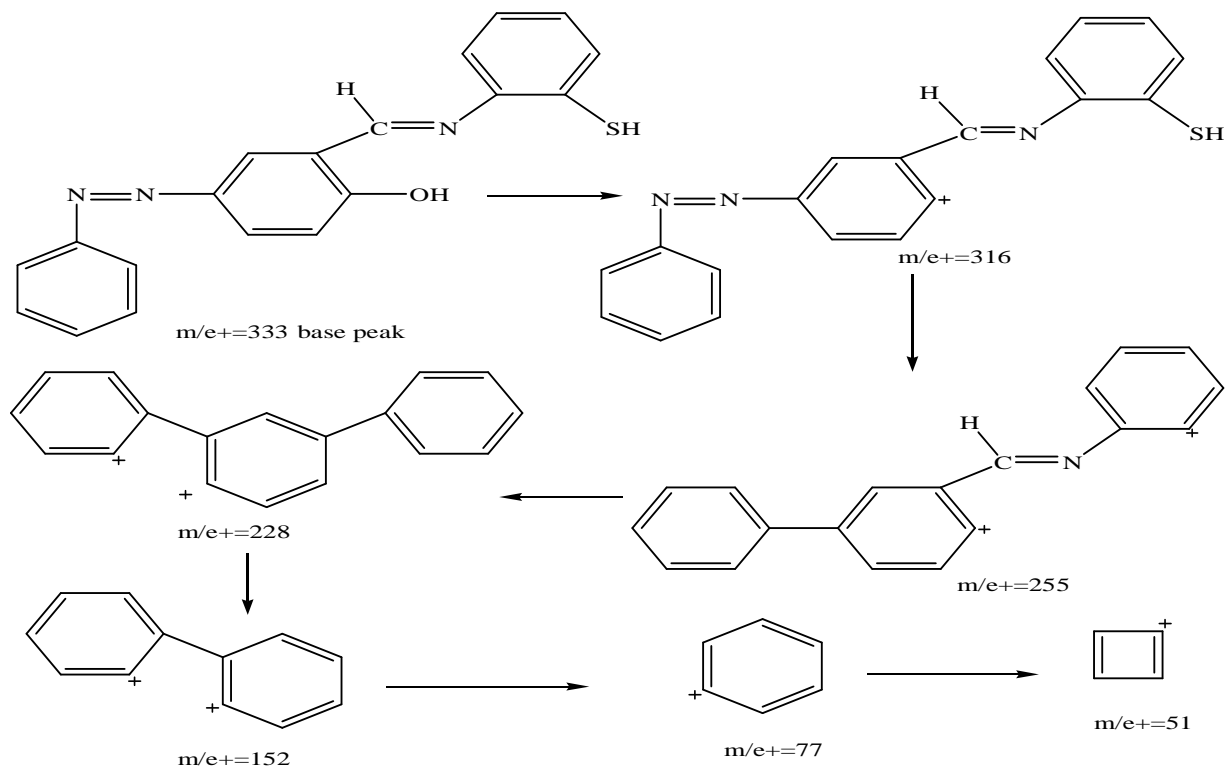
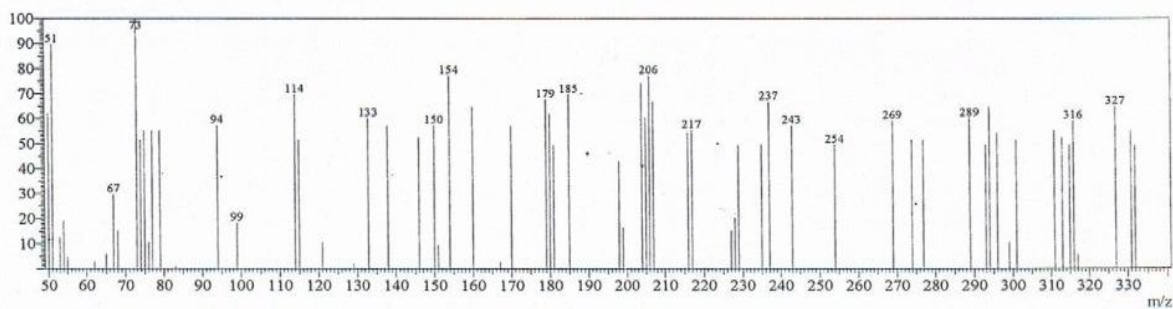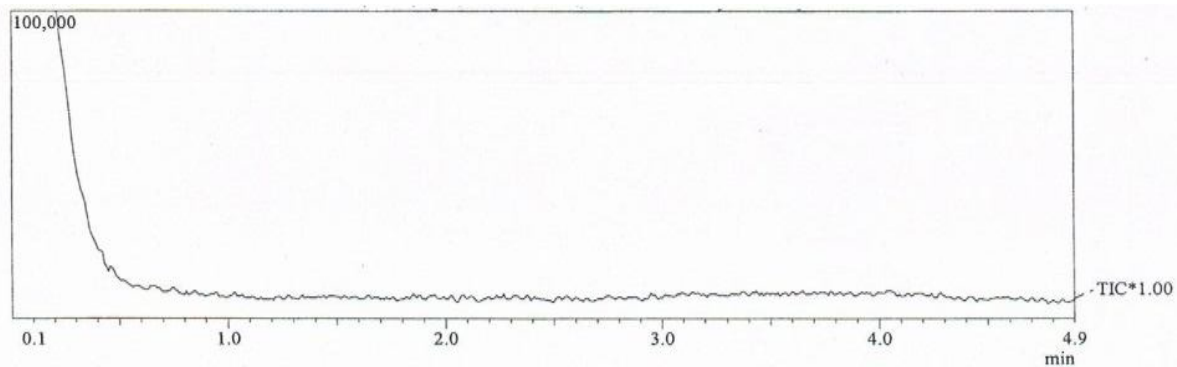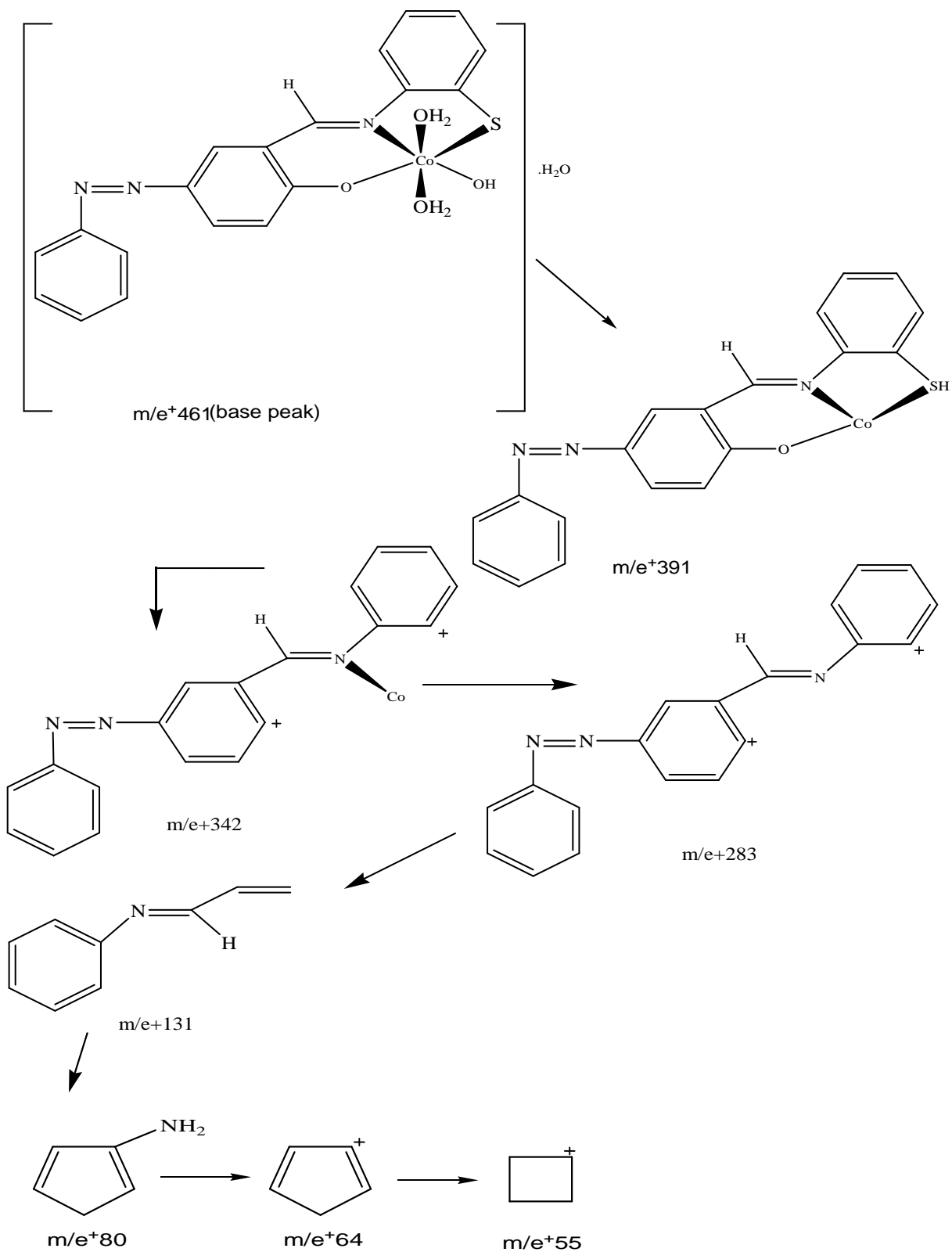**Scheme 1: Mass spectral fragmentation of the azo Schiff base.**

Figure 1: Mass spectrum of the azo Schiff base.

m/e$^+$461(base peak)

.H$_2$O

m/e$^+$391

m/e+342

m/e+283

m/e+131

m/e$^+$80

m/e$^+$64

m/e$^+$55

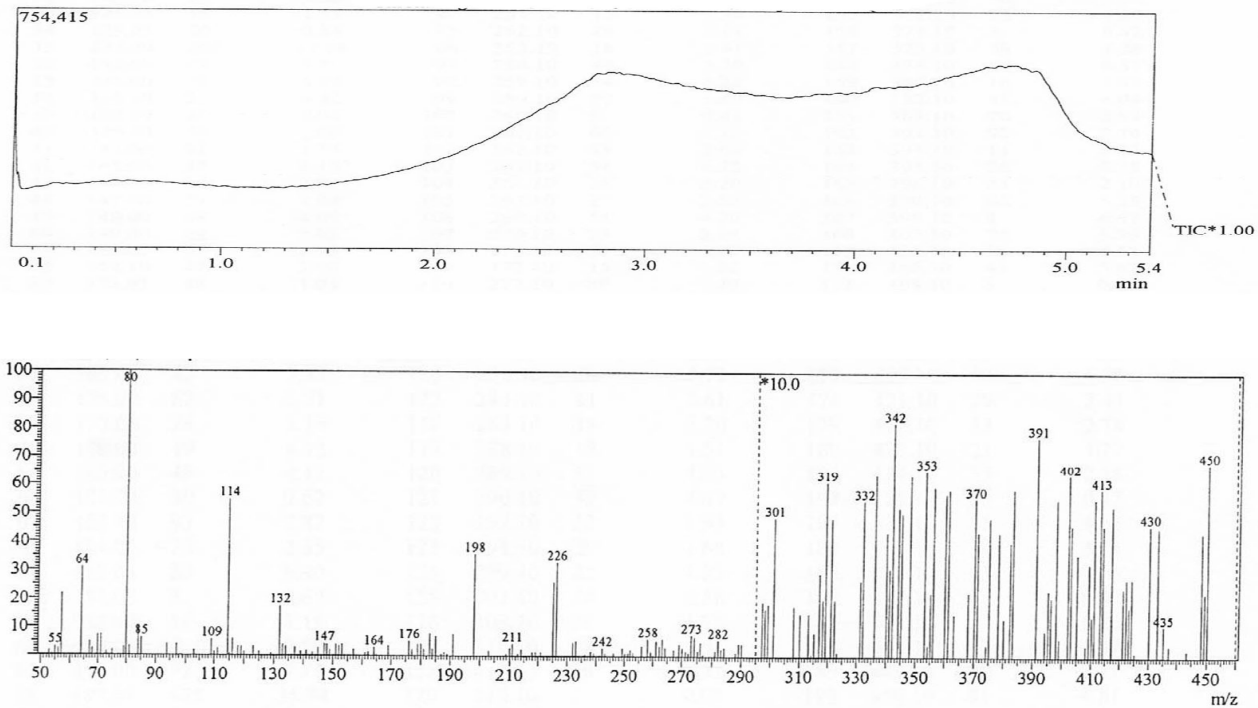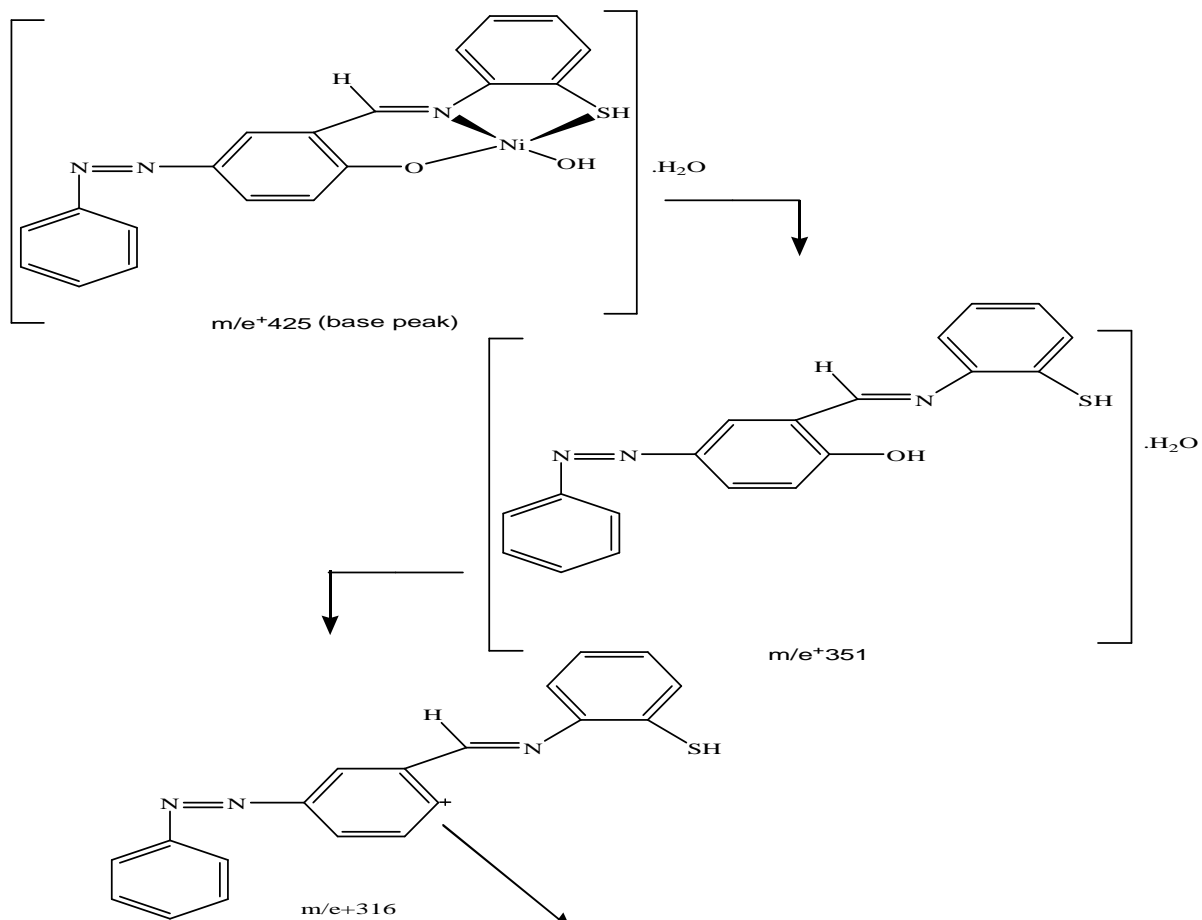**Scheme 2: Mass spectral fragmentation of Co(II) azo Schiff base chelate**

Figure2: Mass spectrum of Co(II) azo Schiff base chelate.

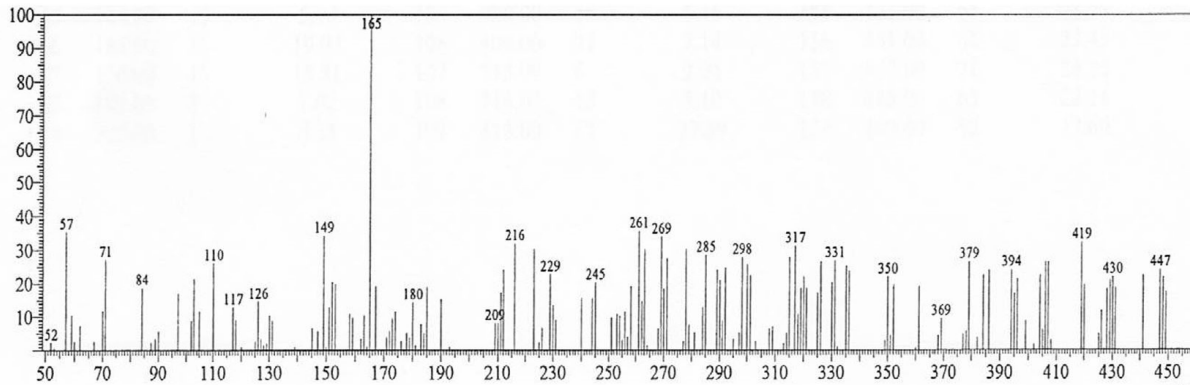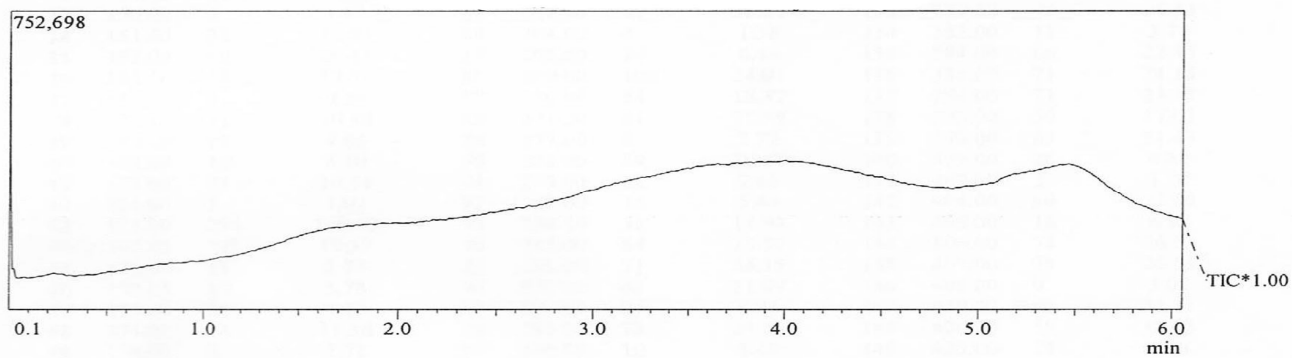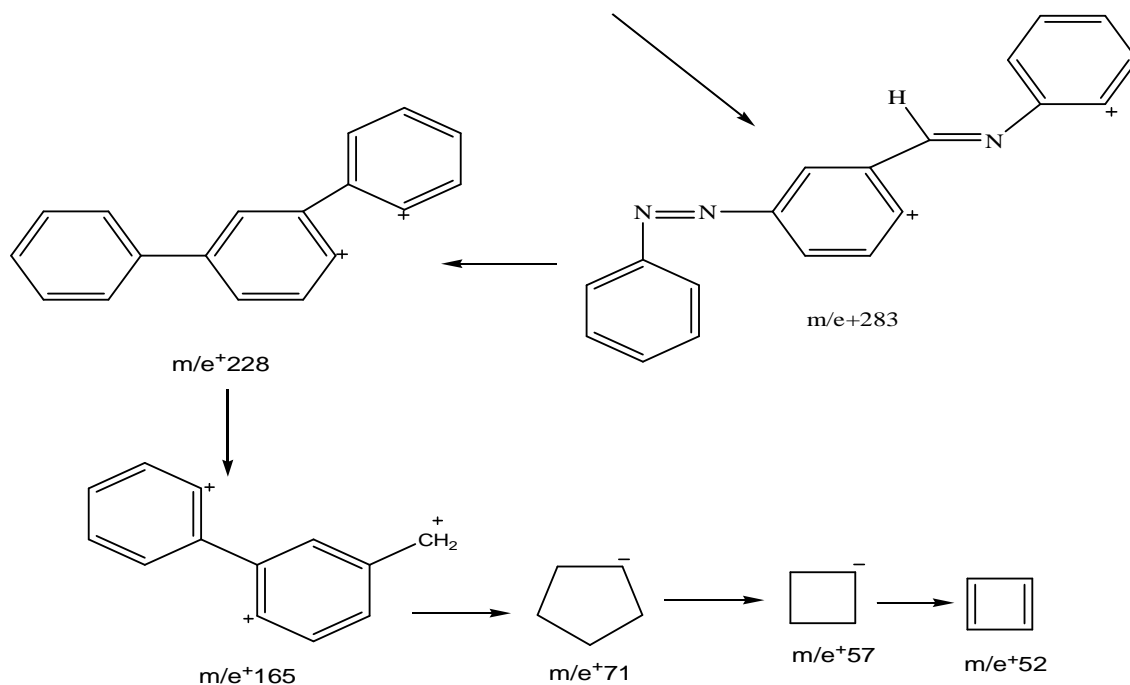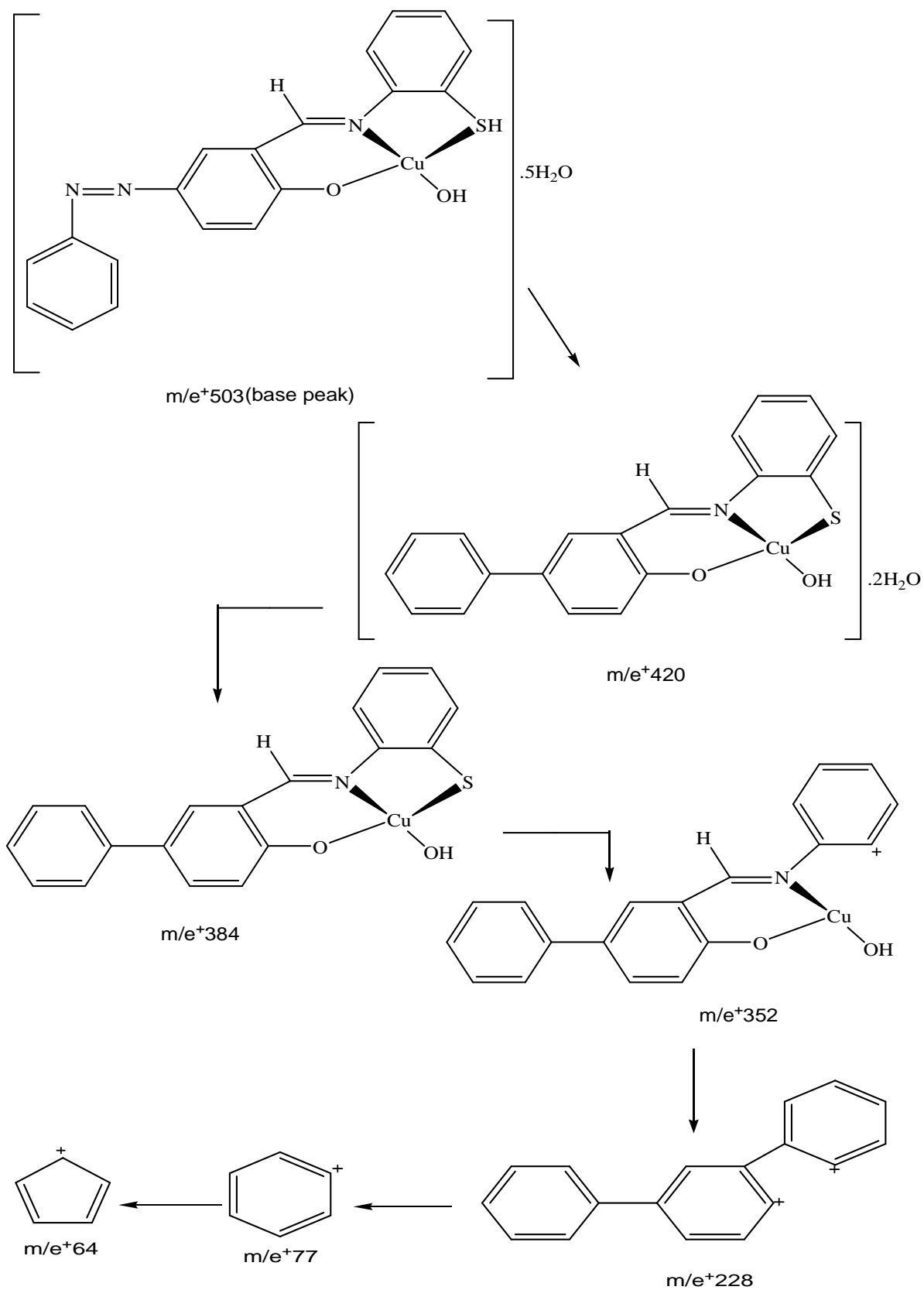m/e$^+$425 (base peak)

.H$_2$O

m/e$^+$351

.H$_2$O

m/e+316

m/e$^+$283

m/e$^+$228

m/e$^+$165

m/e$^+$71

m/e$^+$57

m/e$^+$52

Scheme 3: Mass spectral fragmentation of Ni(II) azo Schiff base chelate.

Figure3: Mass spectrum of Ni(II) azo Schiff base chelate

m/e⁺503(base peak)

.5H₂O

.2H₂O

m/e⁺420

m/e⁺384

m/e⁺352

m/e⁺228

m/e⁺77

m/e⁺64

Scheme 4: Mass spectral fragmentation of Cu(II) azo Schiff base chelate
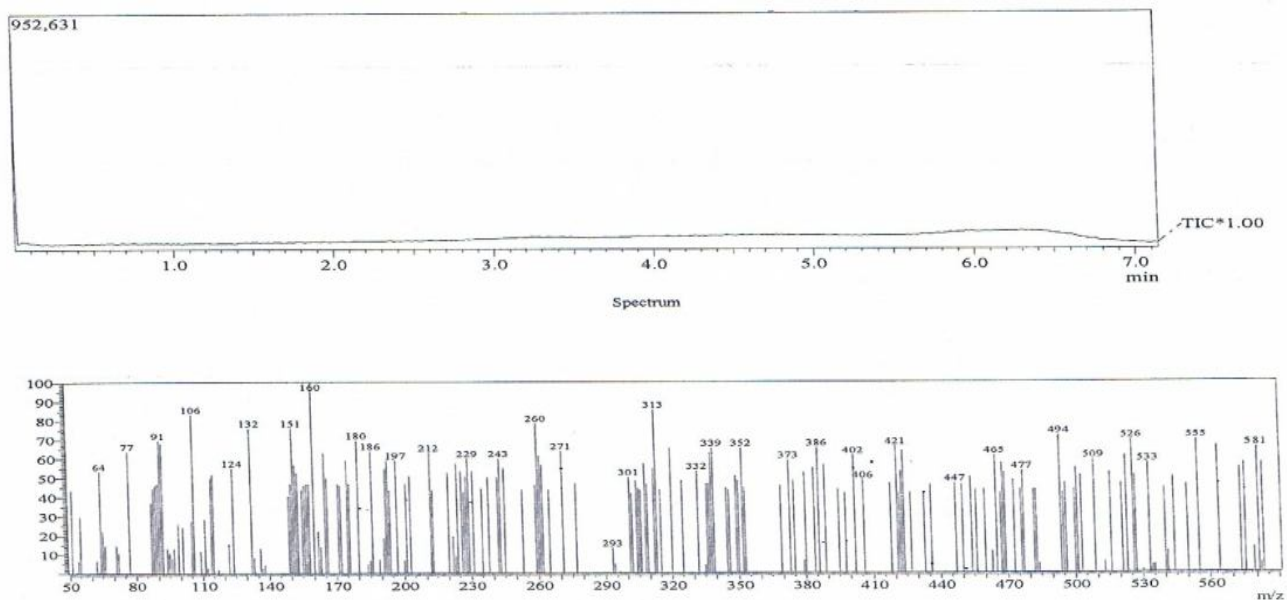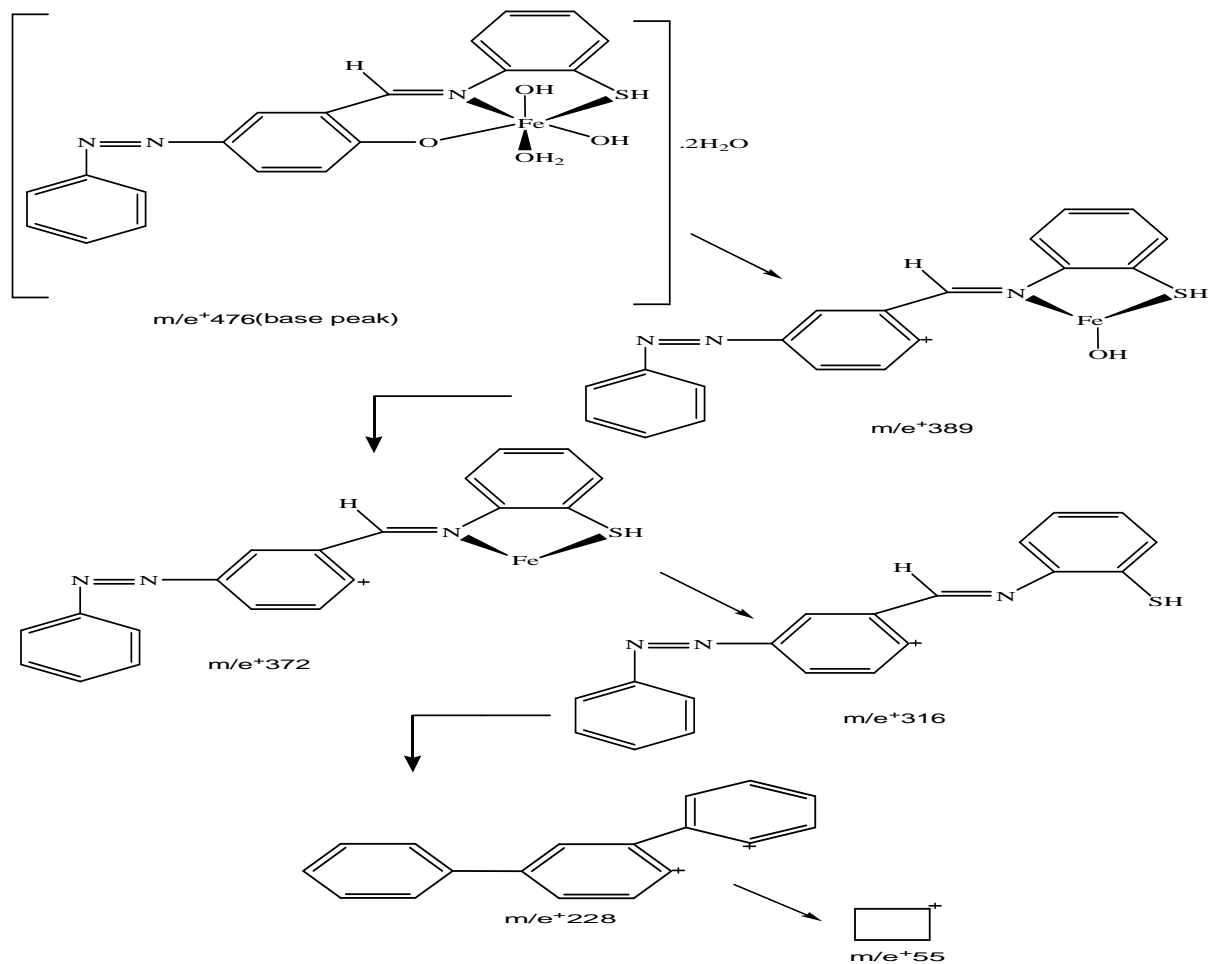
Figure 4: Mass spectrum of Cu(II) azo Schiff base chelate.

Scheme 5: Mass spectral fragmentation of Fe(III) azo Schiff base chelate.
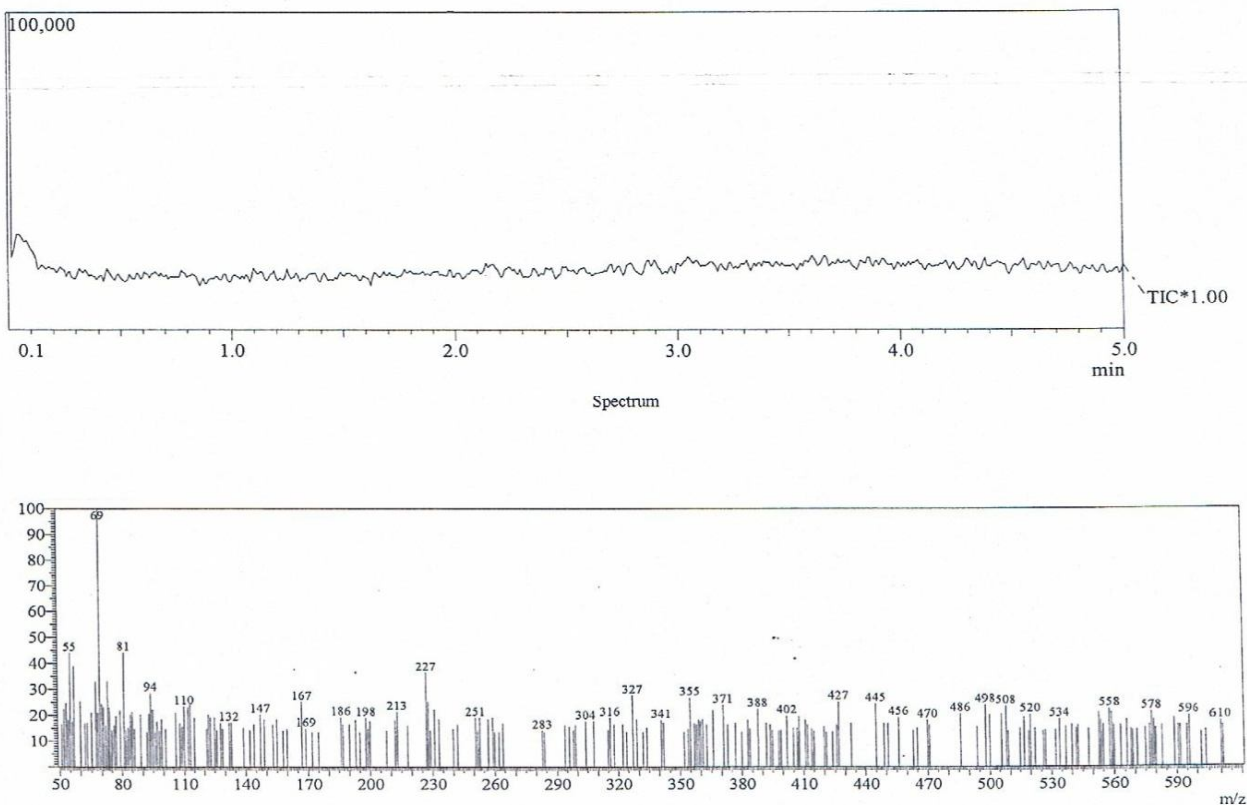
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Figure 5: Mass spectrum of Fe(III) azo Schiff base chelate.

5. **Electronic spectra of azo Schiff base chelates:** The electronic spectral results of the azo Schiff base and its chelates are shown in Table 2. The electronic spectral studies of the chelates of Co(II), Ni(II), Cu(II) and Fe(III) ions were carried out in DMF solvent. The electronic spectra of the azo Schiff base exhibits $\pi \rightarrow \pi^*$ (phenyl rings) and $n \rightarrow \pi^*$ (HCN and –N=N-) transitions (Table 2)[14]. For Co(II) chelate, the electronic spectral results display two bands at 290nm (34483 cm^{-1}) and 330 nm (30303 cm^{-1}) assigned to $^4T_1g(F) \rightarrow ^4T_2g(F)$ and $^4T_1g(F) \rightarrow ^4T_1g(P)$ transitions, respectively, in octahedral field. The intensity of the obtained bands supports the structure[15]. The spectrum of Ni(II) chelate shows two bands at 284 nm (35211 cm^{-1}) and 329 nm (30395 cm^{-1}) corresponding to charge transfer and $^1A_1g \rightarrow ^1B_2g$ transition. Based on the nature of the bands and the diamagnetic character which confirmed by ^{1}HNMR spectrum, a square planar geometry was proposed[16 & 17]. The spectrum of Cu(II) chelate reveals two bands at 284 nm (35211 cm^{-1}) and 329 nm (30395 cm^{-1}) due to charge transfer and $^2B_1g \rightarrow ^2Eg$ transitions, which is consistent with square planar structure [18]. The spectrum of Fe(III) chelate exhibits two bands at 273 nm (36630 cm^{-1}) and 329 nm (30395 cm^{-1}) analogous to charge transfer and $^2Eg \rightarrow ^2T_2g$ transitions. The strength of the bands supports the existence of an octahedral structure around the Fe(III) chelate[19].

6. **Corrosion Inhibition:** Rates of dissolution were determined chemically by WL at 30 ^{0}C. Table (3) gives the corrosion rate and inhibitor efficiency for mild steel in 0.5M HCl, 10% DMF solvent 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.

Table 3: Corrosion parameters obtained from WL data for mild steel in 0.5 M, HCl, 10% DMF solvent in absence and presence of different concentrations of azo Schiff base at 30 ^{0}C.

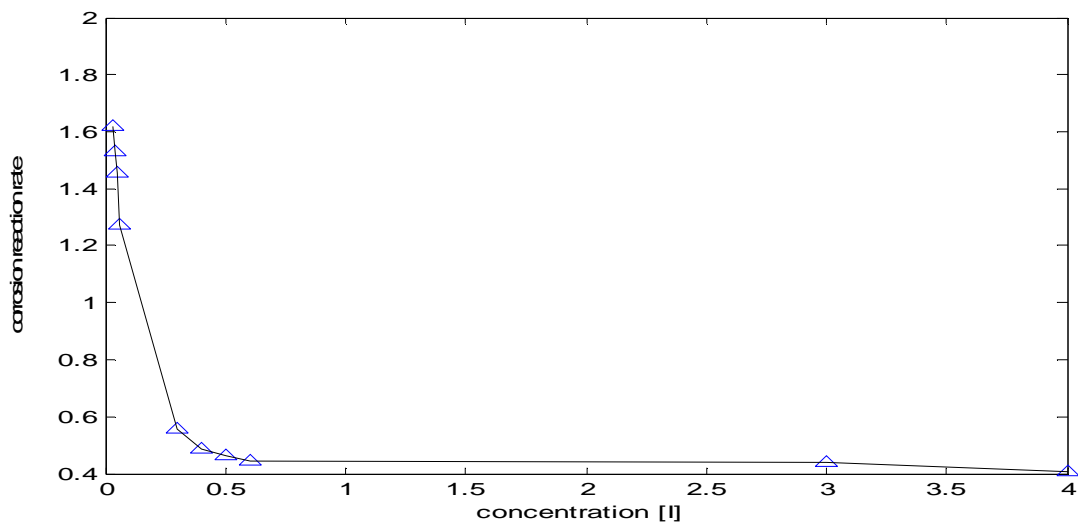| Inhibitor concentration ×10^{-3}M/litter	log[I]	C.R×10^{-5} mg/cm^2 min	Inh. %
4	-2.39794	0.4049	92.55
3	-2.52287845	0.4396	0.9191
0.6	-3.2218487	0.4456	0.8091
0.5	-3.30102999	0.4627	0.4891
0.4	-3.39794000	0.486	0.0591
0.3	-3.522878745	0.5553	0.7889
0.06	-4.22184875	1.2729	0.5876
0.05	-4.301029996	1.4528	0.2773
0.04	-4.397940009	1.5276	0.8971
0.03	-4.522878745	1.6203	0.1970

Figure 6: Variation of the corrosion rate with the concentration of azo Schiff base at 30^{0}C.
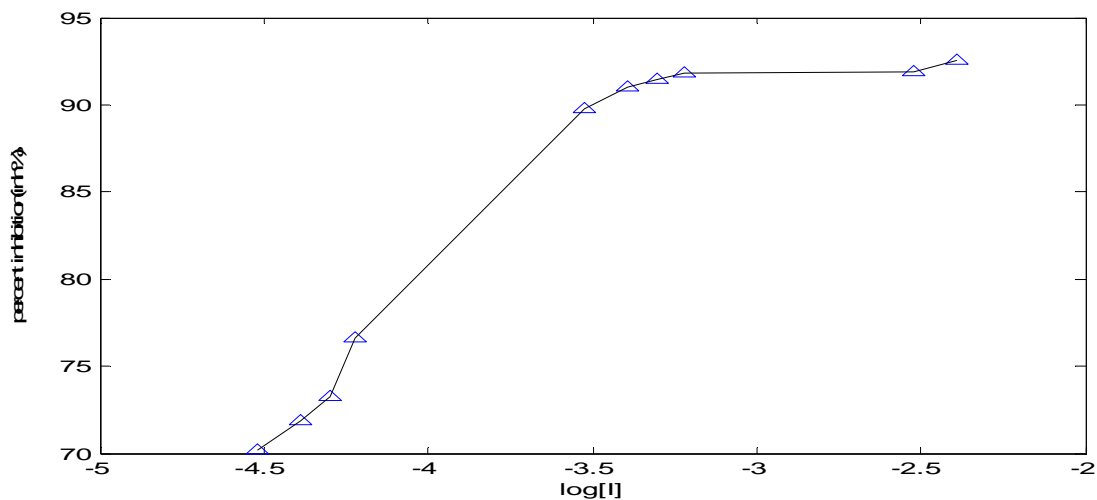

Figure 7: Variation of percentage inhibition with the logarithmic concentration of azo Schiff base.

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 Figure 6 shows the variation of the corrosion rate as a function of the concentration of azo Schiff base at 30 ^{0}C, the corrosion rate decreases with increasing the azo Schiff base inhibitor concentration. This indicates that azo Schiff base retards the dissolution rate of steel in acidic media. Figure 7 gives the variation of percentage inhibitor efficiency with the logarithmic concentration of azo Schiff base. The obtained results have characteristics of S-shaped adsorption isotherm and are indicative of adsorption mechanisms for the inhibition process.

Inspection of results showed in Table 3 indicates clear evidence that the application of the used azo dye has clear inhibiting effect on steel acidic corrosion. The inhibition efficiency of this compound can be attributed to physisorption followed by chemisorptions between clear charged steel surface in acidic media and adsorption active centers (-SH,-OH, N=N and C=N). The results show that at 30 ^{0}C and low concentration range (3×10^{-5}- 4×10^{-3}M) gives (70-92%) protection efficiency. The gradual increase in these protection efficiency percentages can be discussed on the basis that presence of polar groups of electron pair atoms resulting of interaction between this molecule and the metal surface. Moreover, the size of azo Schiff base inhibitor molecule with π-delocalized system can create rigidity and increase its attachment to metallic surface.

CONCLUSION

The obtained Co(II), Ni(II), Cu(II) and Fe(III) azo Schiff base chelates were synthesized and characterized by using several physical techniques, elemental analysis, molar conductivity, infrared, proton nuclear magnetic resonance, electronic and mass spectroscopes. All the experimental data confirm the existence of an octahedral geometry for Co(II) and Fe(III) chelates and square planar for Ni(II) and Cu(II) chelates as shown below. Also the corrosion inhabitation results illustrated that the azo Schiff base compound has 70-92% protection efficiency.
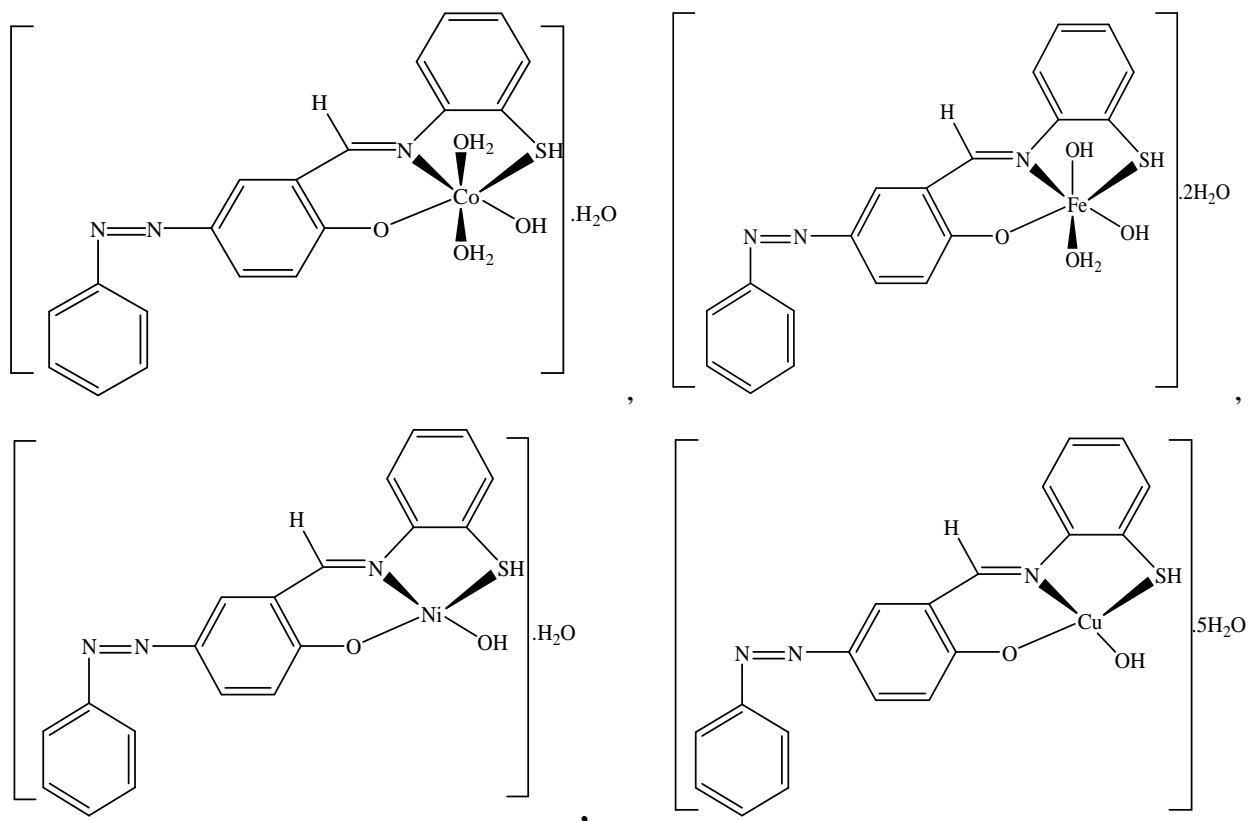
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