

Preparation, Characterization and Corrosion Inhibition of Copper(II) Azo Schiff Base Chelate

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ABSTRACT

The azo Schiff base [Reaction of salicylaldehyde and 2-aminothiophenol] and anthranilic acid have been prepared. One azo Schiff base chelate of copper(II) ion was also prepared. The chemical structures of the azo Schiff base and its chelate were confirmed by various physicochemical analyses such as, CHNS elemental analyses, molar conductance measurements, IR, ¹H NMR, mass and EPR spectroscopy. The CHNS elemental analyses showed the formation of 2:1[M:L] ratio. Based on the IR spectral data, it is found that the azo Schiff base compound acts as neutral tridentate ligand when the metal ion bonded from the Schiff base side and neutral bidentate ligand when the metal ion bonded from the azo side. The entering of hydroxyl, azomethine and thiol groups of the azo Schiff base compound in chelation was confirmed by IR and ¹H NMR spectral results. The electronic spectral data displayed the presence of $\pi \rightarrow \pi^*$ (phenyl ring), $n \rightarrow \pi^*$ (-OH, HC=N and SH) and a square planar geometry was pointed out for the chelate. The mass spectral results confirmed the purity of the azo Schiff base and its chelation. The corrosion inhibition of mild steel in acidic media 0.5M HCl using the azo Schiff base and its Cu(II) chelate as corrosion inhibitor was studied by weight loss method. The obtained results showed that the azo Schiff base chelate efficiently inhibited acidic corrosion.

1. Introduction

Aromatic amines are widely used chemicals. In addition to being intermediates for the synthesis of azo colorants, they may be used to synthesize pesticides, pharmaceuticals, explosives, rubber, epoxy polymers and polyurethane. Aromatic amines may also be used as antioxidants in elastomers. Aromatic amines may be generated through the combustion of organic materials, including in emissions of tobacco smoke. Aromatic amines may be found naturally in plants such as corn grains, beans and tea. Coordination chemistry of the transition metal complexes with azo ligands is an important and fascinating branch of chemistry. The coordination compounds including azo ligands are of significant importance and play a pivotal role in industry, technology and life processes [1]. Colorants which include chromophores of dyes usually consisting of C=C, N=N, C=N, aromatic and heterocyclic rings, containing oxygen, nitrogen or sulfur have been widely used as dyes owing to their versatility in various fields and high technologies, including textiles, paper, leather, plastics, biological staining, lasers, liquid crystalline displays, ink-jet printers and in specialized applications, such as, food, drug, cosmetic and photochemical productions [2,3]. Azo dyes are widely used in the textile industry and are the largest and most versatile group of synthetic organic dyes, with a tremendous number of industrial applications [4]. Schiff base metal complexes have the ability to reversibly bind oxygen in epoxidation reactions [5]. Azo group is characterized by a lone pair of orbital containing two electrons on nitrogen atom, if linked to an aromatic ring carrying an additional donor sites is well suitable for chelation and its complexes contain both azo and azomethine groups. The azo group possesses excellent donor properties and is important in coordination chemistry [6]. A survey of literature revealed that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time. A large number of organic compounds, particularly those containing nitrogen, oxygen or sulphur in a conjugated system are known to be applied as inhibitors to control acid corrosion of iron and steel [7]. The inhibition process has been shown to occur via inhibitor adsorption isotherm and

the efficiency of the inhibitors strongly depends on the structure and chemical characteristics of the adsorbed inhibitor layer formed under particular experimental conditions. Although dyes have been extracted from natural sources for centuries, it was not until 1856 that a synthetic dye was produced commercially [8]. Recently, metal complexes have attained a prominent place as corrosion inhibitors because of their high efficiency even with small dosage. Mild steel is considered as an inexpensive structural material particularly for construction of storage tanks and pipe lines.

Our aim in this investigation is to prepare, characterization of azo Schiff base and its chelate with Cu(II) ion. Also to study their corrosion inhibitions on mild steel in acidic media.

2. Experimental Methods

2.1 Chemicals and Methods

All chemicals used in this study are pure of BDH/Aldrich, including; salicylaldehyde, 2-aminothiophenol, anthranilic acid, ethanol, DMF, sodium hydroxide, hydrochloric acid, sodium nitrite, DMSO, CuCl₂·2H₂O and double distilled water. The prepared azo Schiff base and its chelate were subjected to CHNS elemental analyses using Perkin-Elmer 2400 elemental analyzer. The molar conductivity of the chelate was measured in DMF solvent using digital conductivity meter CMD 650 at Chemistry Department, Sebha University, Sebha, Libya, infrared spectra were obtained by KBr disc technique by using IFS-25DPUSR/IR spectrometer (Bruker) in the range of 4000–400 cm⁻¹. The proton nuclear magnetic resonance spectrum of the azo Schiff base compound was recorded on Varian Gemini200-200 MHz spectrometer using TMS as internal standard and D₆-DMSO as a solvent. The electronic spectra of the azo Schiff base and its chelate were measured in DMSO solvent using a Perkin-Elmer-Lambda β-spectrophotometer. The mass spectra were carried out by using Shimadzu QP-2010 Plus. The EPR spectrum of Cu(II) azo Schiff base chelate was carried out by using EMX EPR spectrometer (Bruker). All the CHNS and spectroscopic analyses were done at Micro analytical center, Cairo University and Tanta University, Egypt.

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2.2 Preparation of Schiff base

The Schiff base was prepared 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, and the obtained product was concentrated in vacuum to remove the solvent. The product was filtrated, dried and recrystallized from suitable solvent (m.p. = 142 °C, yield=70.72%).

2.3 Preparation of Azo Schiff Base

The azo Schiff base under investigation was prepared by mixing 0.01 mole of 2.29 g of Schiff base with 0.01 mole of 1.37 g of anthranilic acid in 50 mL of ethanol in presence of 10% NaOH solution, NaNO₂ 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 few drops of silver nitrate solution, dried and recrystallized from suitable solvent (m.p.= 132.10 °C, yield = 64.94%).

2.4 Preparation of Azo Schiff Base Chelate

The reaction of the azo Schiff base (0.01mole; 3.77g) with 0.01mole of the salt (1.71g) of CuCl₂.2H₂O in 50 mL ethanol was refluxed for three hours, then filtered and washed several times with hot ethanol until the filtrates become colorless. The resulted chelate was dried in desecrator over calcium chloride for a night.

2.5. Corrosion

The corrosion rate of mild steel in 0.5M HCl was determined by weight 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 = 98.498 (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 °C and rates followed for a maximum of 1 hour to avoid drastic changes in surface characteristics.

2.6. Inhibitors

All the used chemicals are analytical grade. Freshly distilled deionized water was used in all preparations. Azo Schiff base chelate as corrosion inhibitor in 0.5M HCl medium was prepared in DMF solvent. All tested solutions contain 10 volume percent of DMF to maintain complete soluble.

3. Results and Discussion

3.1. Physical Properties, Microanalysis and Molar Conductivity

The chelate is air-stable, non-hygroscopic, colored solid, insoluble in water, ethanol and methanol, but partially soluble in chloroform, DMSO and DMF solvents. The obtained elemental analysis values of the azo Schiff base and its Cu(II) chelate (Table 1) are consistent with the calculated values. The result of molar conductivity measurement (Table 1) reveals that the chelate is non-electrolytes in nature [9].

Table 1 CHNS elemental analyses and some physical properties of the azo Schiff base and itsCu(II) chelate

Ligand/Chelates	L; C ₁₉ H ₁₅ N ₃ O ₃ S	[Cu ₂ (L) (OH) ₂ (H ₂ O)] H ₂ O
Color	Bright, light-golden	Light brown
M.W	377	573
M.P °C	132.1	>250
Calcd. (Found)	C%	63.66 (63.68)
	H%	3.98 (3.00)
	N%	11.14 (11.73)
	S%	8.49 (8.25)
Λ _m	-	2.83
g _{eff} - values	-	2.0103
purity	64.94	87.94

Λ_m= molar conductivity, g_{eff} = EPR, () = Calculated value

3.2. Infrared Spectra

The infrared spectral data of the azo Schiff base and its Cu(II) chelate were examined in detail. The significant vibrational bands and their assignments are given in Table 2. IR spectrum of the azo Schiff base exhibits band at 1482 cm⁻¹ due to azo group (N=N) vibration which is shifted to lower wave numbers in the chelate (Table 2) indicating its participation in chelation through nitrogen atom [10]. A band at 3436 cm⁻¹ corresponds to the presence of water molecules in the chelate [11], the band at 1583 cm⁻¹ is characteristic of the azomethine group (HC=N) in the azo Schiff base. The change of this group in the spectrum of the chelate (1597 cm⁻¹) indicating the involvement of azo Schiff base compound in complexation with the metal ion through azomethine nitrogen atom and this also shows the reduction of electron density in the azomethine ligand [12]. A band at 2762 cm⁻¹ which is assigned to the ν(COOH) vibration in the azo Schiff base compound disappeared in the chelate formation showing its participation in chelation [13]. The spectrum of the Cu(II) chelate shows a change in the position of the thio group (-SH) suggesting its participation in chelation with the metal ion through sulfur atom [14]. The new band found in the spectrum of the chelate at 453 cm⁻¹ is assigned to ν(M-N) mode. The involvement of the oxygen atom of the hydroxyl group of the azo Schiff base is confirmed by the appearance of new band at 619 cm⁻¹ which is not present in the azo Schiff base indicating the existence of the νM-O vibrations [15].

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

Ligand/chelate	L;C ₂₀ H ₁₅ N ₃ O ₃ S	[Cu ₂ (L)(OH) ₂ (H ₂ O)].H ₂ O
IR Bands (cm ⁻¹)	νOH (H ₂ O)	3436
	νN=N	1482
	ν C=N	1583
	νSH	3054
	νC-OOH	2762
	νM-O	-
	ν M-N	-
nm (cm ⁻¹)		287 (34843)
		329 (30395)

3.3. Proton Nuclear Magnetic Resonance Spectrum of Azo Schiff Base

The ¹H NMR spectrum of the azo Schiff base compound was measured using in d₆-DMSO solvent. The azo Schiff base spectral results show singles at 8.19 and 11.58 ppm which are attributed to the presence of protons of the azomethine and hydroxyl groups, respectively. The same spectrum displays singles between 7.00-7.56 ppm attributed to phenyl rings. The single which appeared at 3.31 ppm in the spectrum of the azo Schiff base compound is due to the presence of thio group (SH). Meanwhile, the singles at 2.51 and 3.51 ppm assigned to the existence of methyl and DMSO solvent groups in the compound [16].

3.4. Electronic Spectra

The electronic spectrum of the azo Schiff base compound was measured in DMF solvent. The most important bands in this spectrum are 287 nm (34843 cm⁻¹) and 329 nm (30395 cm⁻¹). The first band is assigned to π→π* (aromatic system) and the second one is due to n→π* (N=N, -OH, SH and C=N) [17]. The electronic spectral data of the Cu(II) chelate exhibit two bands at 290 nm (34483 cm⁻¹) and 329 nm (30395cm⁻¹) due to charge transfer and ²B_{1g} → ²E_{1g} transitions. The paramagnetic phenomena and the nature of the bands support the existence of a square planar geometry [18].

3.5. Mass Spectra

The mass spectral fragmentations of the azo Schiff base chelate are shown in Scheme 1. For Cu(II) chelate (Fig. 1), the spectrum exhibits a peak at m/e⁺ = 555 due to loss to water molecule. The peak at m/e⁺ = 528 corresponding to the loss of HC=N group. The peak at m/e⁺ = 433 assigned to loss of COO, OH groups oxygen atom and water molecular from Cu(II) chelate. The same spectrum shows a peak at m/e⁺ = 255 due to loss of SH, OH groups and two of copper atoms. The loss of N=N group and C₆H₄ gives a peak at m/e⁺ = 151. The peak at m/e⁺ = 90 corresponding to the loss of five carbon and hydrogen atoms. The appearance of a peak at m/e⁺ = 71 attributed to C₅H₁₀⁺ ion. A peak at m/e⁺ = 58 is due to the appearance C₄H₈⁺ ion.

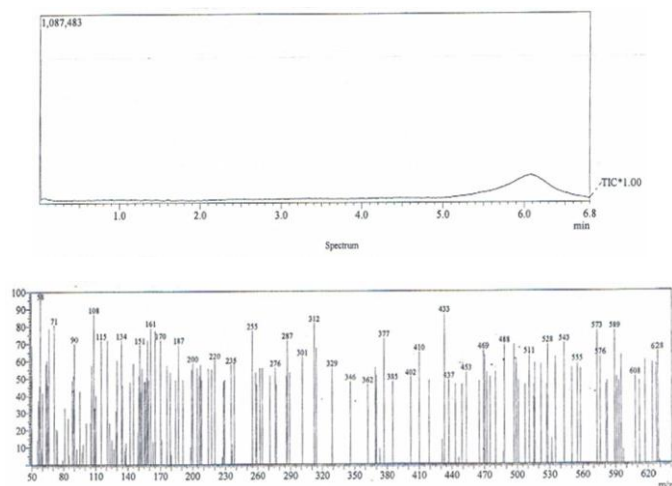
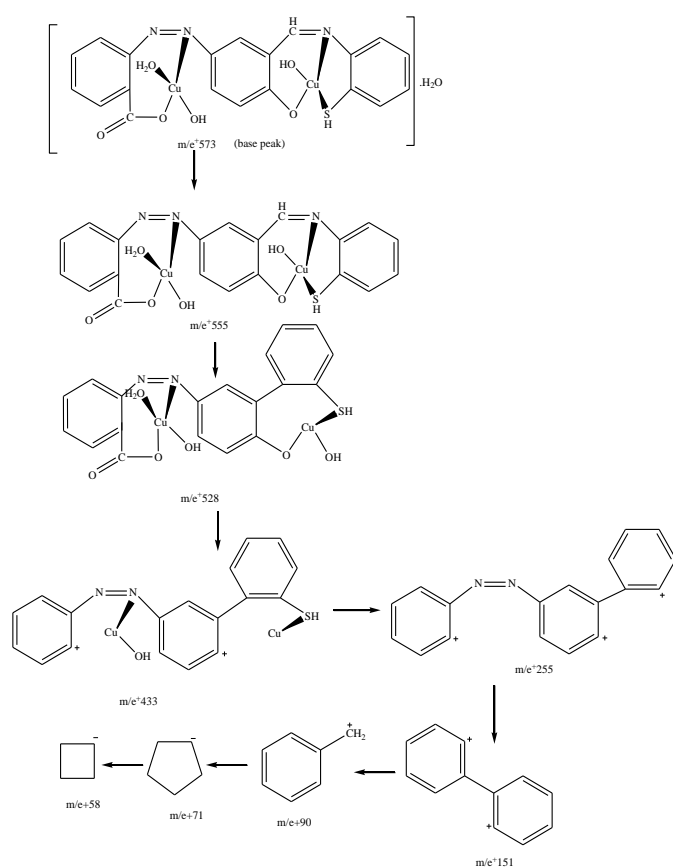


Fig. 1 Mass spectrum of the $[\text{Cu}_2(\text{L})(\text{OH})_2(\text{H}_2\text{O})]\text{H}_2\text{O}$ chelate



Scheme 1 Mass spectral fragmentations of $[\text{Cu}_2(\text{L})(\text{OH})_2(\text{H}_2\text{O})]\text{H}_2\text{O}$ chelate

3.6. Electron Paramagnetic Resonance Spectrum of Azo Schiff Base Chelate

The electron paramagnetic resonance spectrum of $\text{Cu}(\text{II})$ chelate shows g_{eff} value of 2.0103, and this value is deviated from the ideal value (2.0023) indicating the presence of partial ionic character of the covalent bond between $\text{Cu}(\text{II})$ ion and azo Schiff base compound. This value supports the existence of square planer geometry around the chelate [19], and confirms the data which obtained from the electronic spectral study and CHNS elemental analyses.

3.7 Corrosion Study

Fig. 2 shows the variation of the corrosion rate and concentration of azo Schiff base chelate at 30°C . As it can be seen from this figure, the corrosion rate decreases with increasing concentration of azo Schiff base chelate as inhibitor. Meanwhile, Fig. 3 gives the variation percentage inhibition with logarithm of the concentration of azo Schiff base chelate. The curve has characteristics of S-shaped adsorption isotherm indicative of adsorption

mechanisms for the inhibition process. The obtained results also indicate high inhibition efficiency (90%) can be achieved by azo Schiff base chelate concentration as low as 0.003 M. The inhibition process can be attributed to adsorption of inhibition by electron-donor specie on charged mild steel surface in acidic media. The inhibition efficiency can be also discussed on the basis of the large azo Schiff base chelate molecular size and electron donating nature leading to chemisorption process with large surface coverage. This happens because the adsorption of chelate molecules is a chemical adsorption process which involves the donation of a pair of electrons present on the nitrogen atom to iron metal. The N-N and C-N bonds in chelate molecule are of p- π conjugation property which remarkably strengthen the chemical adsorption of the nitrogen atom on the metal surface [20]. The corrosion inhibition in $\text{Cu}_2\text{-L}$ chelate may be due to the breaking of the bonds between N, O, S and Cu atoms. Therefore, because of highly active $\text{Fe}(\text{II})$ ion on steel surface comparing with copper ion, the electron pair N,O,S atoms may be linked with $\text{Fe}(\text{II})$ ion instead of copper(II) ion, and the copper (II) ion precipitated on mild steel with reddish-orange color as protective layer. The coverage of the surface increases by copper(II) ion with increasing concentration of $\text{Cu}_2\text{-L}$ chelate as shown in Fig. 4.

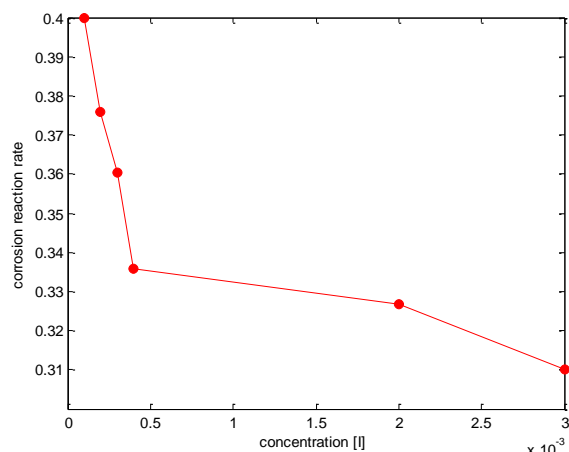


Fig. 2 Variation of the corrosion rate with the concentration of azo Schiff base $\text{Cu}(\text{II})$ chelate at 30°C

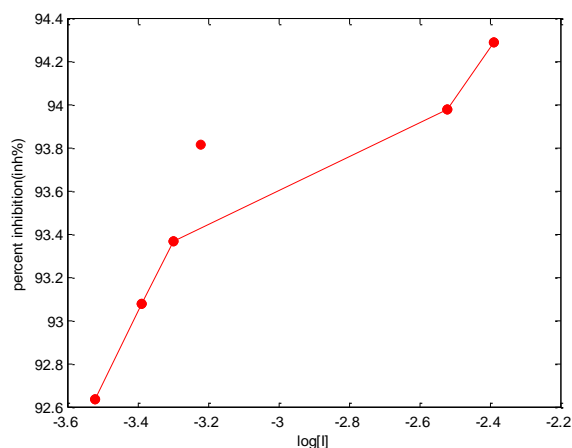


Fig. 3 Variation of percentage inhibition with the logarithmic concentration of azo Schiff base $\text{Cu}(\text{II})$ chelate

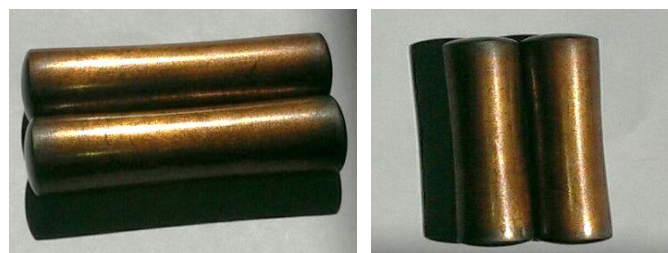
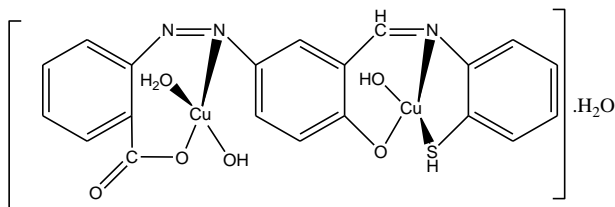


Fig. 4 The mild steel specimens in 0.5M HCl at 3×10^{-3} M from $\text{Cu}_2\text{-L}$ inhibitor

4. Conclusion

From the physicochemical analysis data, the following structure was established for the chelate under investigation. To compare the performance of the azo Schiff base chelate, the obtained percentage inhibition efficiency was plotted against the concentrations of inhibitor solution used. It has been found that all these azo Schiff base chelate inhibits the corrosion of mild steel in HCl solution at all concentrations used in this study except in the case of few lower concentrations of Cu₂-L chelate. It also noticed that the inhibition efficiency for the chelate increases with increasing in the inhibitor concentration. Among the azo Schiff base (Ligand) and its Cu(II) chelate, the azo Schiff base shows greater inhibition efficiency than its chelate.



Geometrical structure of the Cu₂-L chelate

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