

**SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDY
OF NOVEL AZO-SCHIFF BASE COMPLEXES DERIVED FROM
SULFADIAZINE AND 2-(DIETHYLAMINO)ETHYL -4-
AMINO BENZOATE**

Tarek A. Fahad^{1*}, Kawther A. F. Al Radi¹ and Enas A. Bady²

¹Department of Chemistry, College of Education for Pure Science, Basrah University, Iraq.

²College of Pharmacy University of Basrah.

Article Received on
07 Nov. 2018,

Revised on 27 Nov. 2018,
Accepted on 17 Dec. 2018

DOI: 10.20959/wjpr20191-13920

***Corresponding Author**

Dr. Tarek A. Fahad

Department of Chemistry,
College of Education for
Pure Science, Basrah
University, Iraq.

ABSTRACT

A new series of transition metal complexes of Co (II), Cu (II), Ni (II) and Cr(III). were prepared from the novel azo-schiff base ligand (LH)(L= 3-chloro-N-(2-diethylamino)ethyl)-4-(((Z)-2-hydroxy-5-((Z)-4-(N-(pyrimidin-2-yl)sulfamoyl) phenyl)diazanyl)benzylidene)amino)benzamide) from by coupling reaction of Sulfadiazine, salicylaldehyde and (2-diethylamino)ethyl-4-aminobenzoate). They have been characterized by elemental analysis (C.H.N), molar conductance and spectral techniques such as FT-IR, ¹H-NMR, electronic spectra and mass spectrometry. The analytical and spectral data supported the mononuclear formulation of the complex

with metal to ligand ratio (M:L=1:2) and suggested. The biological activity of the synthesized ligand and its metal complexes were screened for antibacterial activity against some Gram-positive and Gram-negative bacteria.

KEYWORDS: Azo-Schiff base, metal complexes, characterization, antibacterial activity.

INTRODUCTION

Schiff base derivatives attract significant interest and occupy an important role in the development of coordination chemistry. Moreover, Schiff base complexes containing transition metals have been studied in several research areas such as structural chemistry^[1,2], Schiff bases are well-known to have biological activities such as antibacterial^[3], antifungal^[4], antitumor^[5], antiviral^[6], anti-HIV-1^[7] Schiff bases derived from salicylaldehydes are known

polydentate ligands, coordinating to metals in both their deprotonated and neutral forms.^[8] Some cobalt and copper complexes exhibit diverse biological properties viz. anti-inflammatory, antibacterial and anticancer.^[9]

Azo dyes have been widely used in various areas, such as textile dyes, printing systems, photoelectronics, coloring fibres and optical storage technology and in analytical chemistry.^[10-15]

Azo-Schiff base derivatives are known to be important in several classes of medicinal and pharmaceutical fields. Furthermore, some of them show biological activities such as antibacterial, antifungal, anticancer and herbicidal activities.^[17-21] However, the light induced interconversion allows systems incorporating azo group to be used as reversible control over a variety of chemical, electronic and mechanical applications.^{[2],[22,23]}

We report here in the synthesis and spectroscopic studies of a novel Azo-schiff base derivative Ligand (LH) (L= 3-chloro-N-(2-diethylamino)ethyl)-4-(((Z)-2-hydroxy-5-((Z)-4-(N-(pyrimidin-2-yl)sulfamoyl)phenyl)diazenyl)benzylidene)amino)benzamide with some transition metals such as Ni^{II}, Co^{II}, Cu^{II} and Cr(III) complexes. (¹H,) NMR spectra were obtained to determine the structure of the ligand.

EXPERIMENTAL

Materials and measurements

All chemical which are of analar grade are purchased from Aldrich, BDH, Merck and Sigma. All the solvents used of Annular grade. Infrared spectra (as KBr pellets) were recorded on F.T.IR- 8400S shimadzu. NMR spectra were recorded by Bruker ultra shield 300MHz spectrometer DMSO as solvent and TMS as internal reference. Elemental analysis (C.H.N.), were carried out by Perkin element 2400.UV/Vis. absorption spectra of the these compounds in different buffer solutions at room temperature were recorded using Perkin Elmer Lampda EZ 210 UV/ Vis. Spectrophotometer.

Preparation of novel azo-schiffbase ligand (L)^[24-25]

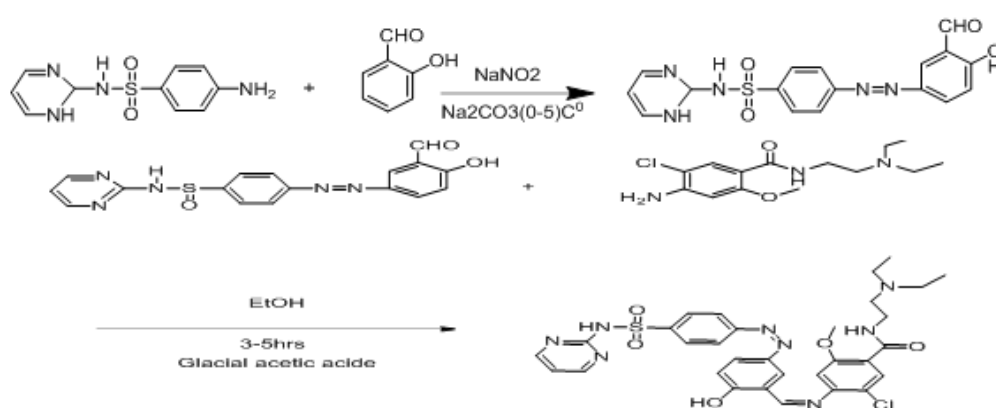
Synthesis of the azo dye compound (Z)

The azo dye compound Z been synthesized by the diazotization coupling reaction by flowing methods proposed (schem-1) Sulphadiazene, (0.01mol) was dissolved in mixture a solution from 3ml HCl(37%) and 30 ml distilled water. An aqueous solution 20 ml of NaNO₂ (0-

0.1mol, dissolved in 20ml distilled water) was added in drops while maintaining the temperature between 0-5°C to the mixture with continuous stirring. After that the diazonium chloride was added drop wise respectively with constant stirring to cold aqueous solution of Salicylaldehyde (1.2gm, 0.01mol) and then solution of 2ml acetic acid was added to the dark red colored mixture. The mixture was stirred for 1 hour at 0-5°C. The precipitate was filtered and washed with distilled water and 5ml ethanol solution to remove the excess of unreacted substances and recrystallized from ethanol and dried in oven at 50°C for several hours. The purity was confirmed by the elemental analysis (C.H.N) and TLC techniques. The yield was 82% of dark red crystals and m.p=218°C. The structure of azo compound (Z) is convert by, IR and UV-vis. spectra.

Synthesis of novel azo-Schiff base ligand (L)

The novel azo-schiff base ligand (L), (scheme 1) was synthesized by condensation of Metoclopramide (2-(diethyl amino)ethyl 4-aminobenzoate) (0.01 mole) with azo dye compound Z (0.01 mole) in 70 ml ethanol in the presences 4 drops of glacial acetic acid as a catalyst. The mixture refluxed for three hours, then the obtained product was concentrated in vacuum to remove ethanol. A Brown color precipitate were obtained, Which were filtered and washed with distilled water and twice recrystallized from hot ethanol, then dried in oven at 70°C for several hours. The yield 78% of reddish orange crystals and m.p=259°C. The purity was confirmed by the elemental analysis and TLC techniques. The structure of azo - Schiff base ligand (L) is convert by ¹H-NMR, mass spectrum, IR and UV-visb. spectra.



Schem 1: Synthesis of the novel azo-schiffbase ligand(L).

Preparation of metal complexes^[26]

To an ethanolic solution of azo-schiffbaes ligand (L) an ethanolic solution of the Cobalt (II), Copper (II), Nickel (II) and Cr(III). metal chloride and was added in a molar ratio[1:2]. The

mixture was refluxed for about 40 minutes. The mixture was cooled in ice bath. The obtained solid precipitate was collected by filtration washed with distilled water and washed with 10 ml hot ethanol to remove any traces of the unreacted materials and dried in vacuum. Table-1 shows the collected physical properties and analytical data for the prepared azo-schiff base ligand and their complexes.

Table (1): Physical properties and elemental analysis for novel azo-schiff base ligand (L) and their metal complexes.

| Compound | Molecular formula | m.p °C | Yield (%) | COLOR | Found (Calc.) % | | |
|----------|---|-----------|--------------|--------|------------------|--------------|----------------|
| | | | | | C | H | N |
| Z | C ₁₇ H ₁₃ N ₅ O ₄ S | 218 | 69 | Yellow | 52.89 (53.26) | 3.65 3.42 | 18.09 18.27 |
| L | C ₃₁ H ₃₃ ClN ₈ O ₅ S | 259 | 60 | Orange | 56.69 (56.73) | 5.50 5.32 | 14.89 14.31 |
| M1 | [Cu(C ₃₁ H ₃₃ ClN ₈ O ₅ S) ₂] | 265 | 62 | Brown | 52.71 53.52 | 4.46 4.55 | 26.02 26.47 |
| M2 | [Ni(C ₃₁ H ₃₃ ClN ₈ O ₅ S) ₂] | >300 | 61 | Orange | 52.32 53.70 | 4.34 4.47 | 26.50 26.56 |
| M3 | [Co(C ₃₁ H ₃₃ ClN ₈ O ₅ S) ₂] | 246 | 64 | Green | 53.71 54.60 | 4.22 4.47 | 26.56 27.01 |
| M4 | [Cr(C ₃₁ H ₃₃ ClN ₈ O ₅ S) ₂ (H ₂ O) ₂]Cl | >300 | 86 | Green | 52.60 53.07 | 5.21 4.94 | 26.01 26.40 |

RESULTS AND DISCUSSION

The ligand and their complexes are stable in air at room temperature and soluble in DMF, DMSO, methanol, ethanol and acetone but insoluble in water on the basis of analytical data the metal complexes are found [1:2] metal:ligand.

The new azo-schiff base ligand (L) is yellow crystals but the prepared complexes of this ligand were crystalline and different colour depending on the metal ion. The ligand and their complexes are stable in air at room temperature. The analytical data and spectroscopic data for the newly prepared metal complexes are in good agreement with proposed molecular formula that ligand is behaving as Bidentate in all prepared complexes.

All the prepared complexes in this paper were insoluble in water but soluble in DMSO. The range of conductance values in DMSO which are listed in table 1 indicates that all the metal complexes have a non-electrolyte nature except Cr complex.

Infrared spectra of novel azo-schiff base and their metal complexes

The most important IR absorption bands corresponding to the ligand and the complexes (fig.1&2) are presented in table 2. The observed band in the range 1450 cm^{-1} is due to $\nu(\text{N}=\text{N})$ group of the ligand. These bands are shifted to higher region during the complex formation indicating its participation in coordination with the metal ions. The sharp band in the range $1521\text{--}1587\text{ cm}^{-1}$ are due to $\nu(\text{C}=\text{C})$ respectively (fig -1). The intense band was observed in the range 1622 cm^{-1} . The appearance of these bands medium support the involvement of $-\text{OH}$, and $\text{N}=\text{N}$ groups in the formation of new azo ligand complexes. Some bands in the range of $470\text{--}480$ and $530\text{--}567\text{ cm}^{-1}$ which are not present in the free ligand assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations.^[28] appearance In all complexes).

Table 2: Selected infrared and uv.visible data of Z, L and complexes.

| Comp. | $\nu(\text{OH})$ cm^{-1} | $\nu(\text{N}=\text{N})$ cm^{-1} | $\nu(\text{C}=\text{C})$ cm^{-1} | $\nu(\text{C}=\text{N})$ cm^{-1} | $\nu(\text{M}-\text{O})$ cm^{-1} | $\nu(\text{M}-\text{N})$ cm^{-1} |
|-------|--------------------------------------|--|--|--|--|--|
| Z | 3425 | 1442 | 1581 | - | - | - |
| L | 3456 | 1442 | 1581 1521 | 1622 | - | - |
| M1 | 3425 | 1417 | 1585 1544 | 1620 | 586 | 470 |
| M2 | 3427 | 1494 1440 | 1587 | 1639 | 531 | 485 |
| M3 | 3423 | 1417 | 1587 1544 | 1618 | 586 | 450 |
| M4 | 3396 | 1471 1419 | 1583 1546 | 1653 | 588 | 465 |

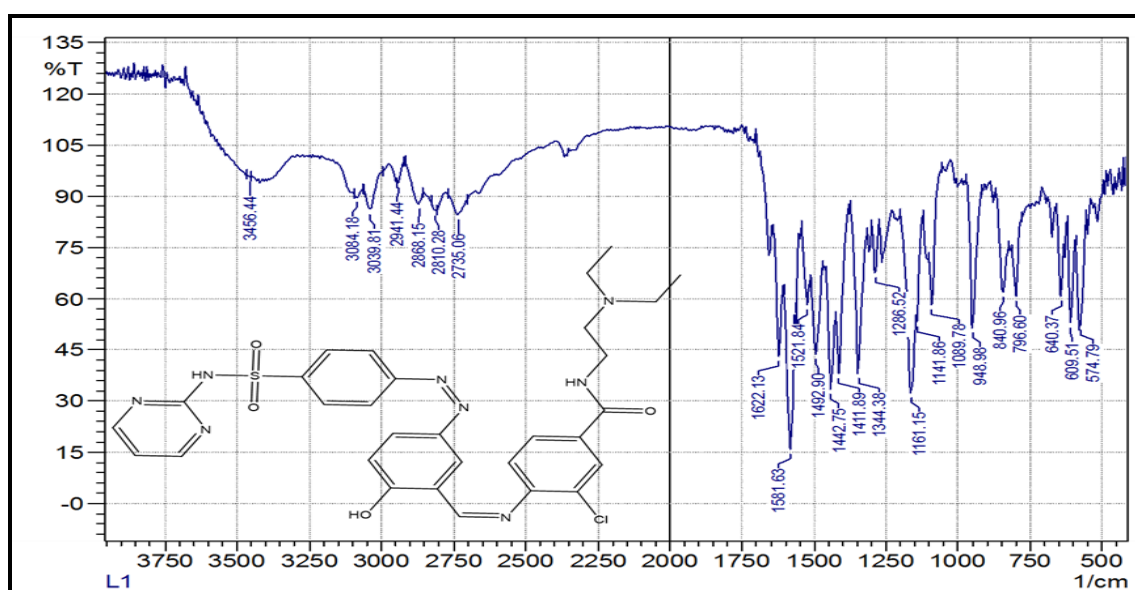


Figure (1): IR spectrum of the ligand.

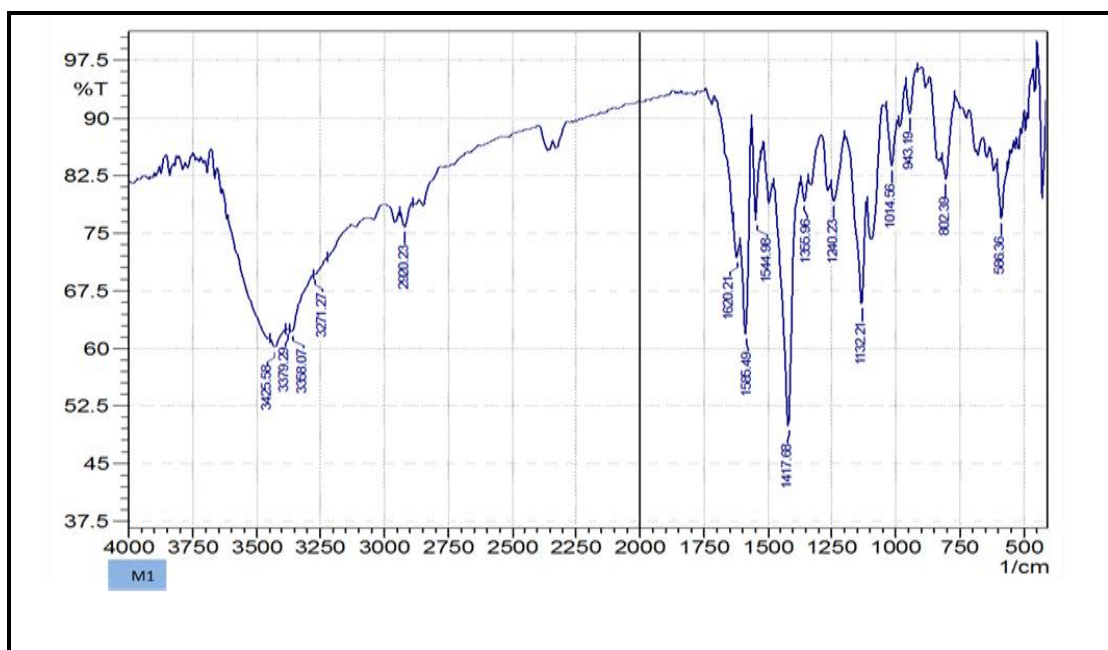


Figure (2): IR spectrum of M1.

$^1\text{H-NMR}$ spectrum of azoschiff base ligand

The $^1\text{H-NMR}$ spectrum of the azoschiff base ligand figure(3) was measured using in DMSO as a solvent. The azoschiff base spectral results show peaks at $\delta = 7.27-7.28$ ppm attributed to the phenyl ring. The single peaks at $\delta = 8.64$ ppm and 10.49 ppm due to the NH and OH groups in ligand respectively. The azoschiff base ligand show single peak at $\delta = 8.68$ ppm which is assigned to the presence of protons of azomethine group.^[23,24] The singlet peak at 2.5 ppm due to the existence of DMSO solvent. The result shows in table(3).

Table 3: $^1\text{H-NMR}$ data of the azo-schiff base (L).

| Group | δ (ppm) |
|-----------------------------|----------------|
| CH ₃ (methyl) | 1.5-1.0 |
| CH ₂ (methylene) | 3.5-3.0 |
| CH(1-benzene) | 7.23-8.74 |
| CH (azomethine) | 8.68 |
| NH (amide) | 8.64 |
| CH(1-benzene) | 9.3 |
| OH | 10.49 |
| NH (amine) | 11.4 |

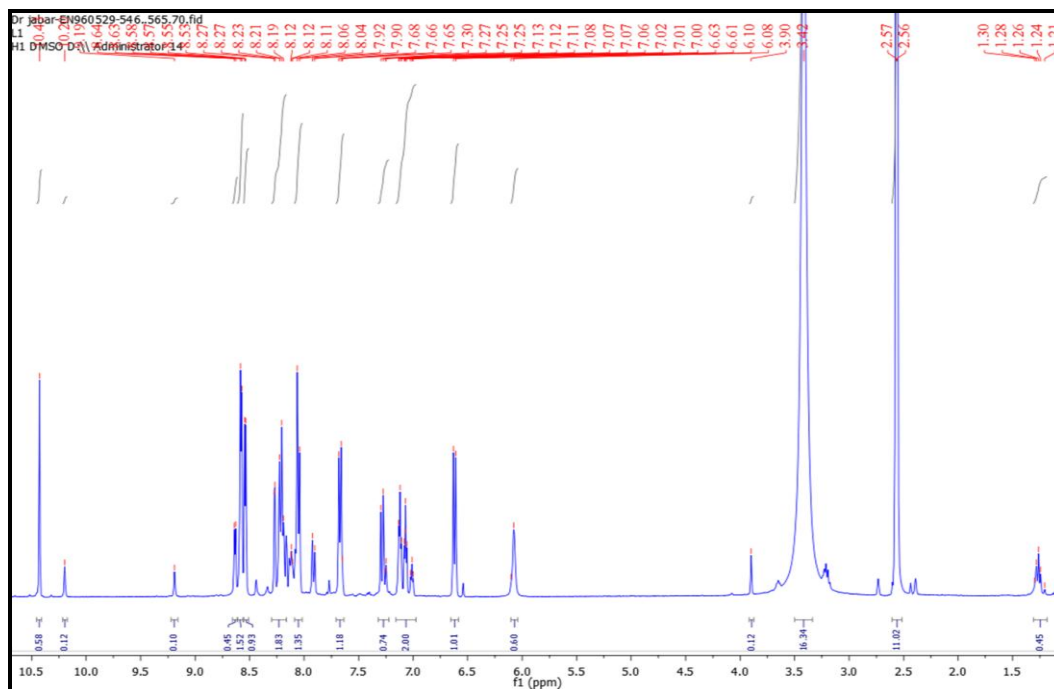
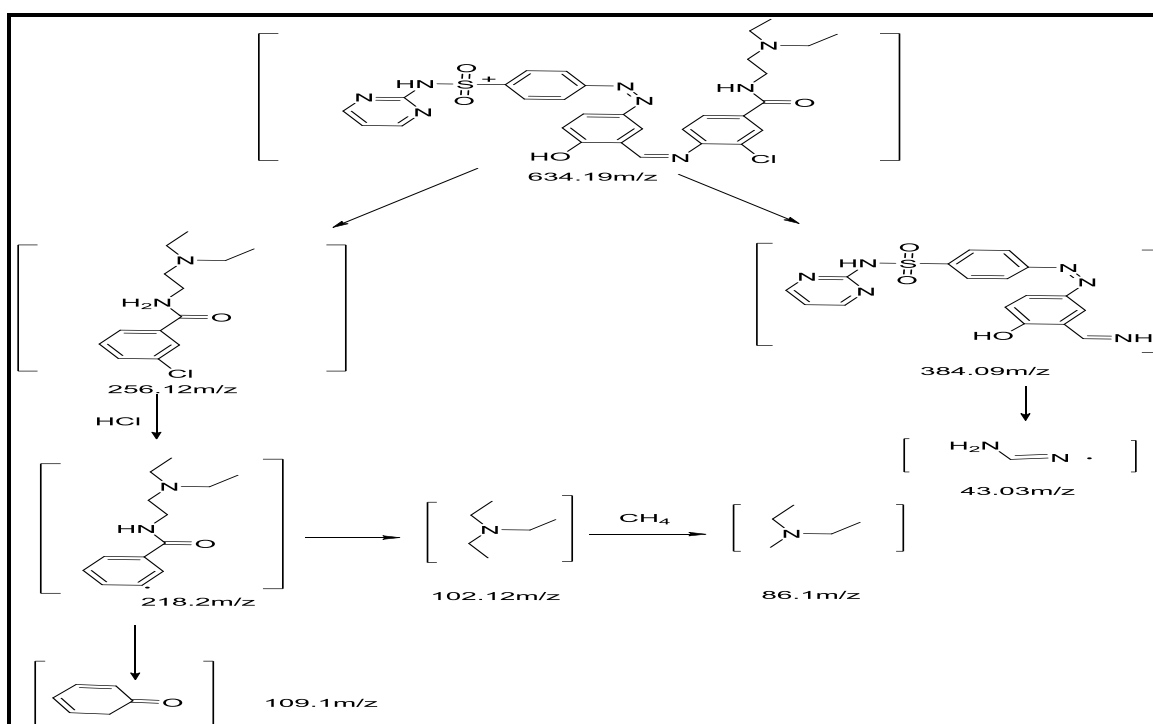


Figure (3): $^1\text{H-NMR}$ spectrum fragmentaino of azo-schiff base ligand.

Mass spectrum of the novel azo-schiff base ligand

The mass spectral fragmentations of azo-schiff base ligand (I) shown in scheme-2 and figure 4. The base peak of azo-schiff base ligand at $m/e = 635.14$ is attributed to the original molecular weight of the ligand under investigation. scheme 3 show the mechanism of fragmentation.



Scheme 2: Fragmentation of L.

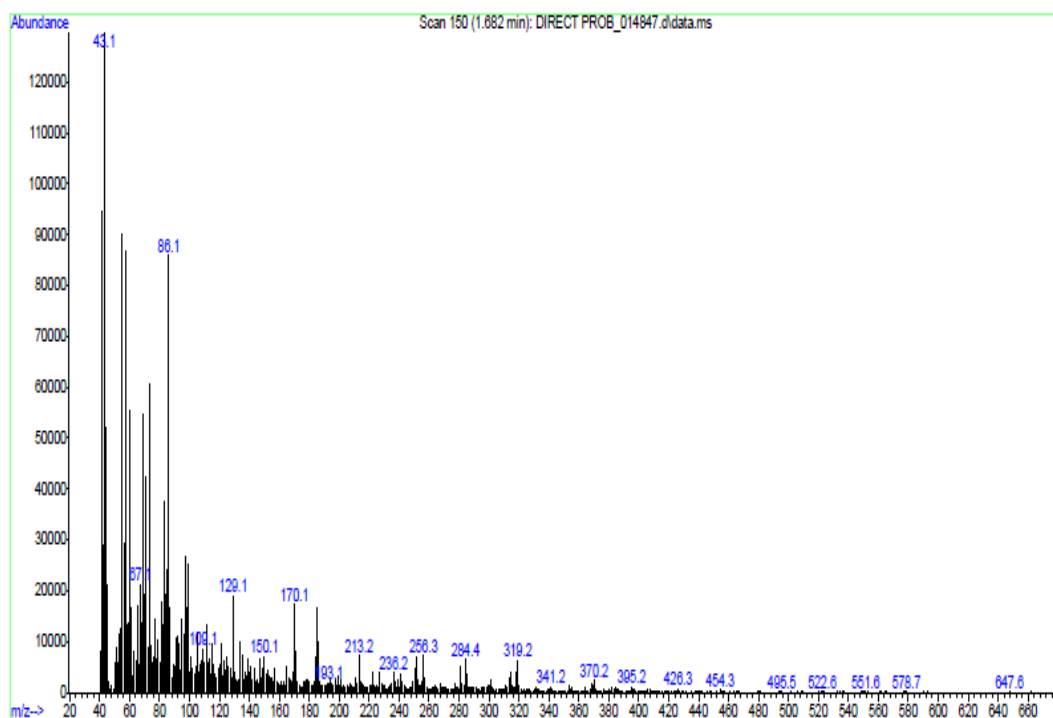


Figure (4): Mass spectra of L.

Metal:Ligand Ratio

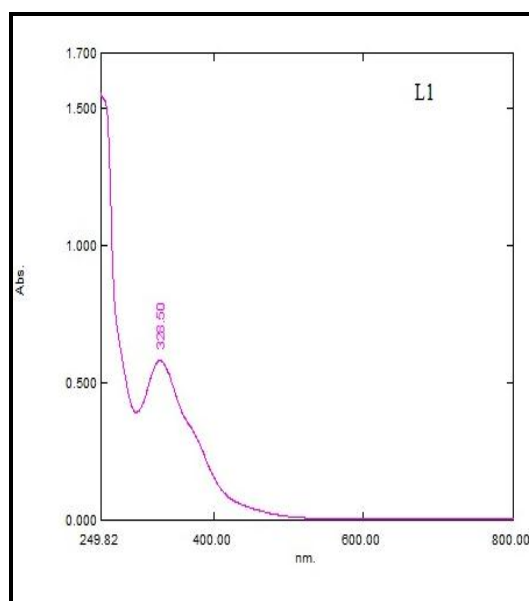
The metal: ligand ratios of chelates complexes were determined by the method of molar ratio at wavelength of maximum absorption (λ_{max}). The azoschiff base ligand (L) was found to form [1:2] M:L chelates with metal ions, these result are in a greement with values reported for some azoschiff base complexes.^[25,26]

Electronic absorption spectra

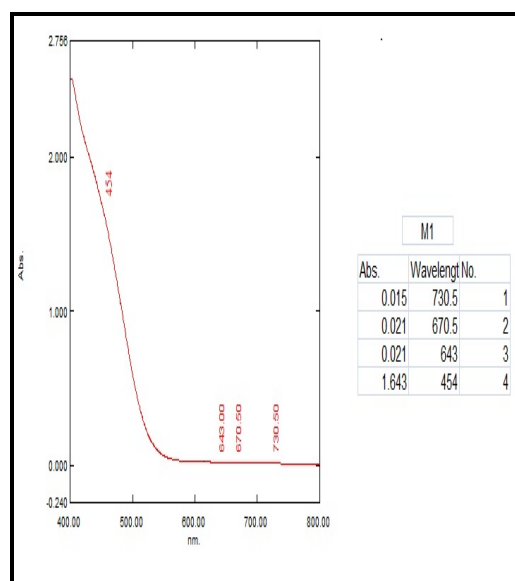
The UV–Vis spectral data of the ligands and their complexes are given in table 4. The aromatic peaks of () ligand at (350-380) and (240-298) nm, which may be ascribed to, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, intra ligand charge transfer ransitions respectively, due to presence of conjugation in the ligand molecule. The electronic spectra of the ligand and complexes (fig.6-8) show two intense transition peaks < 440 nm which are assigned to ligand centered transitions, along with intense peak at longer wavelength (450-460) nm that can be referred to the combination of MLCT [$d\pi(M^{2+}) \rightarrow \pi^*(L)$] transitions where $\pi^*(L)$.^[26-27]

Table (4): Electronic Spectra and molar conductance of azo, L and complexes.

| Complexes | λ_{\max} (nm) ($\pi \rightarrow \pi^*$) | ($n \rightarrow \pi^*$) λ_{\max} (nm) | λ_{\max} (nm) for complexes | Molar Conductivity (S.cm ² .mol ⁻¹) |
|-----------|--|--|--|--|
| Z | 370.50 | - | | --- |
| L | 311 | 363 | | -- |
| M1 | 334, 309 | 341, 339 | 454, 643, 670.5, 730.5 | 18 |
| M2 | 310 | 328 | 567 | 15 |
| M3 | 307 | 317 | 569 | 17 |
| M4 | 327 | 398 | 454, 701 | 37 |



Figure(6):- The absorption spectrum of ligand.



Figure(7):- The absorption spectrum of M1.

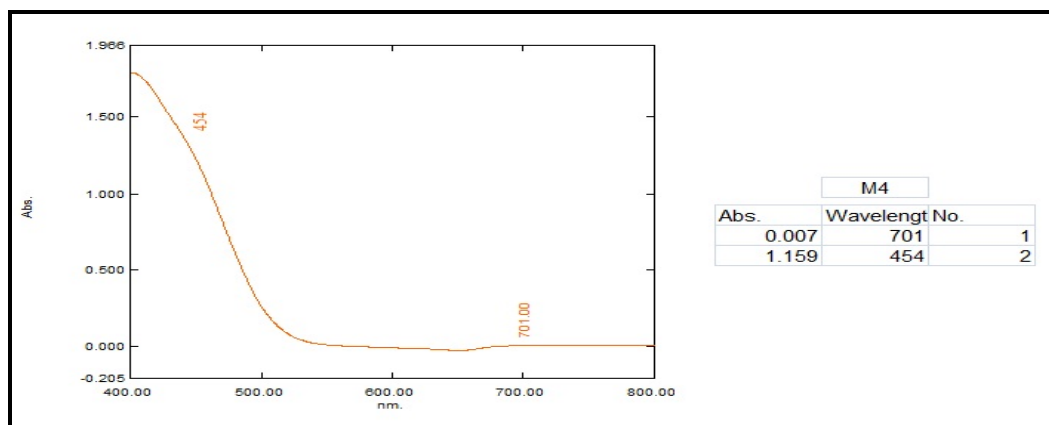


Figure (8): The absorption spectrum of M4.

Molar Conductivity Measurements

By using the relation $\Lambda_m = K/C$, the molar conductance of the complexes (Λ_m) can be calculated, where C is the molar concentration of the metal complex solutions, K = specific conductivity of the complex. The chelates were dissolved in DMSO, the molar conductivities of 10^{-4} M of their solutions at $25^\circ\text{C} \pm 2^\circ\text{C}$ were measured. Table (1) these complexes are, non-electrolytes.^[27] Except Cr(III), complex, it has molar conductance of $37 \Omega^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^{-2}$ indicating electrolytic nature (1:1) of the complex.^[28]

Biological Studies^[30]

The organisms used in the present investigation included Gram positive bacteria (*Staphylococcus aureus*) and Gram negative bacteria (*Escherichia coli*). The results of the bactericidal screening of the synthesized compounds are have no activity.

CONCLUSION

New CoII, NiII, CuII, and Cr(III), metal complexes with Azo-Schiff base derived L from reaction of azoaldehyde with (2-(diethylamino)ethyl 4-aminobenzoate) have been synthesized. All the complexes are insoluble in water but soluble in DMF, as well as all of them are non-electrolyte. The structure of the complexes based on Uv-Vis, IR, mass spectroscopy were proposed that the Azo-Schiff base Ligand L behave as bidentate which coordinated with the metal ions through N, O atoms. The synthesized ligand and its metal complexes were screened for their biological activity against bacterial species, Gram positive bacteria (*Staphylococcus aureus*) and Gram negative bacteria (*Escherichia coli*).

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