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Synthesis and characterization of Schiff base complexes derived from cephradine: Fluorescence, photostability and photobiological applications

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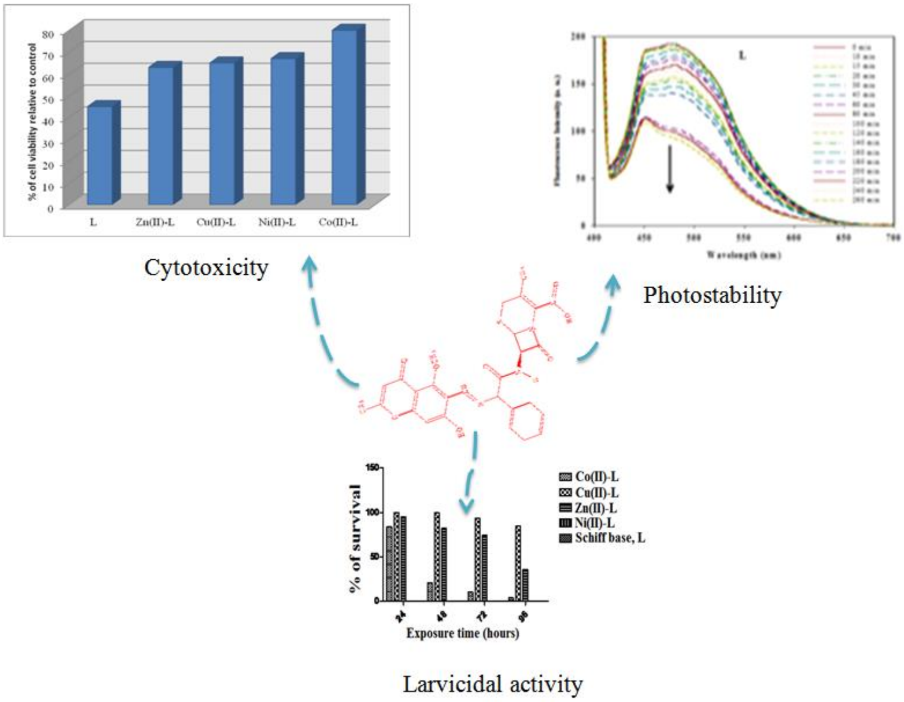
Graphical Abstract



Highlights

1. Preparation and characterization of a new Schiff base and preparation of its Zn(II), Cu(II), Co(II) and Ni(II) complexes
2. Measuring the luminescence properties of the prepared Schiff base and its complexes.
3. Studying the photostability of Schiff base, L, and its Zn(II)-L and Cu(II)-L complexes.
4. Studying the photobilogical activity of cephradine, benzopyran-4-one ,Schiff base L, and all complexes.
5. Studying the In vitro cytotoxicity of the Schiff base and its complexes against Hep G2-cell line.

Abstract

A new Schiff base derived from the condensation of 6-formyl-7-hydroxy-5-methoxy-2-methylbenzo-pyran-4-one (benzopyran-4-one derivative) with cephradine drug (L) was prepared and characterized by elemental analyses and some spectroscopic studies. Also, Zn(II), Cu(II), Co(II) and Ni(II) complexes of that Schiff base were prepared by template reaction. Many tools of analysis such as elemental analyses, infrared, ultraviolet-visible and thermal analysis, as well as electrical conductance and magnetic susceptibility measurements were used to elucidate the structure of these complexes. The data showed that Zn(II)-L and Cu(II)-L complexes are 1:1 (M:L). The ligand was found to be monobasic bidentate. On the other hand, Ni(II)-L and Co(II)-L form binuclear complexes. All the complexes are non-electrolyte. The luminescence properties of the prepared Schiff base and its complexes were measured. The photostability of Schiff base, L, and its Zn(II)-L and Cu(II)-L complexes were also studied. The photobiological activity of cephradine, benzopyran-4-one derivative, Schiff base L and the complexes were studied on mosquito larvae to investigate the extent of their photosensitization efficiency in controlling noxious insects using direct sunlight (larvicidal effect). In vitro cytotoxicity study of the Schiff base and its complexes against Hep G2-cell line was investigated by the MTT assay. The Schiff base, L, exhibits better activity against Hep G2 cell line than the complexes.

Keywords: Schiff base, complexes, luminescence, photostability, cytotoxicity

Introduction

Benzopyrone derivatives (chromones) constitute one of the major classes of naturally occurring compounds, and interest in their chemistry continues unabated because of their applications [1].

Cephalosporins belong to the family of β-lactam antibiotics. The β-lactam antibiotics share approximately 65% of worldwide market of antibiotics [2]. Cephradine is a first-generation cephalosporin class of antibiotic [3]. It contains the (NH_2), (COOH), (NH) and (C=O) functional groups and its molecular model reveals that its structure is suitable for complexation [4]. Cephradine is active in vitro against a broad spectrum of Gram-positive and Gram-negative bacteria, including pathogenic organisms isolated in the clinic [5]. Interaction of various metal ions with antibiotic may enhance or suppress their antimicrobial activity but usually in many cases the pharmacological activity of antibiotics after complexation with metals is enhanced as compared to that of the free ligands [6,7].

Imines or azomethines which are more commonly known as Schiff bases, compounds that contain an azomethine group (-CH=N-). Schiff bases are able to stabilize many different metals in various oxidation states. The complexes of Schiff bases have a large variety of useful applications in many fields such as biological, clinical, analytical and industrial fields [8]. In addition, they have important roles in catalysis and organic synthesis [9,10].

Schiff bases often have the property of luminescence, especially, when their complexes have structure of rigidity plane and rich-electronic conjugation [11-13].Schiff base compounds have occupied an important place in the photometric and fluorescent analysis. For example, the aromatic Schiff base compounds of the salicylidene o-aminophenol type were studied and used as useful fluorimetric reagents for aluminium, magnesium, and other metal ions [14-18].

The Schiff base complexes are among the most known photo-reactive metal complexes [19]. There has been much attention paid to, for example, copper because it is an essential element for life. It is associated with a number of copper-dependent enzymes that are key in biological processes [20,21]. Also, zinc has multifaceted role in biological system as a constituent of proteins and enzymes that belong to cellular signaling pathways [22]. Transition metals have an important place within medicinal biochemistry. On the other hand, it is well known that cephradine is a moderate producer of O_2^{-} under sunlight and UVA irradiation [23]. In another previous study benzopyrone derivatives (chromones) were tested for their photosensitization activity [24].

Accordingly, we prepare a Schiff base compound (L) derived from the condensation of 6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one (benzopyrone derivative) with cephradine. The produced Schiff base was characterized by elemental analyses and spectroscopic studies (IR, ^{1}H-NMR, UV-Vis and mass spectroscopy). Also, its mode of chelation with some metal ions such as Zn(II), Cu(II), Co(II) and Ni(II) was studied using elemental analyses, spectral measurements (UV-Vis, ^{1}H-NMR and IR) and thermogravimetry. In addition, the luminescence properties of this Schiff base and its complexes were studied.

As mentioned before, copper and zinc metal complexes have a wide range of applications and due to the fact that few reports are known in the literature regarding photochemical behavior of Schiff base complexes. We studied the photostability of Schiff base, L, and its zinc and copper complexes in DMSO.

On the other hand, as the urgent need for new agents to control mosquito, which transmit dangerous diseases (E.g. malaria, filariasis, dengue and the viral encephalitis), the extents of photobiological activity of cephradine, benzopyran-4-one derivative, Schiff base, L, as well as the prepared complexes were tested on mosquito larvae to test its larvicidal potential.

Finally, the cytotoxicity of the Schiff base, L, and its complexes were screened against Hep G2-cell line by the MTT assay.

2. Experimental:

2.1. Materials and Methods

All the chemicals used in this investigation were chemically pure grade. All organic solvents used in this study were either purified by recommended methods [25] or obtained as pure grade materials from BDH. Also, doubly distilled H_2O was always used.

2.2. Analysis and physical measurements

Carbon, hydrogen and nitrogen were analyzed by standard microanalysis methods using Automatic analyzer CHNS Vario EL III-Elementar, Germany at Microanalytical center, Cairo University, Giza, Egypt. UV-Vis spectra of the metal complexes in dimethylsulfoxide (DMSO) were recorded on T 80+UV/Vis spectrophotometer PG instruments Ltd. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on a Shimadzu FTIR spectrophotometer. The mass spectra of Schiff bases were recorded with the aid of Q 1000 EX GC-MS Shimadzu (Japan) spectrometer at 70 eV and 100 μA Energy using a direct insertion probe at temperature 90-110 °C. Mass spectra of the complexes were performed using GC MS-QP 2010 Shimadzu Ultra gas chromatograph-mass spectrometer. Molar conductivity of 10^{-3}mol/L solutions of the complexes in DMSO was measured on the conductivity meter ORION model 150 of 0.6 cell constant. Thermal analysis has been carried out using Shimadzu-50 Thermal Analyzer from room temperature to 800 °C at a heating rate 10°C min^{-1}. Analysis of the metal ions was determined from the weight of the metal oxide or carbonate residue after thermal decomposition. Magnetic susceptibilities of the chelates were measured at room temperature using a magnetic susceptibility Cambridge England Sherwood Scientific. The effective magnetic moments were calculated from the expression $\mu_{eff} = 2.828(X_M T)^{1/2}$ B.M., where X_M is the molar susceptibility corrected using Parcel's constants for diamagnetism of all atoms in the complexes [26]. The fluorescence measurement was made on Perkin Elmer precisely LS 55 fluorescence spectrometer equipped with quartz cuvette of 1 cm path length. The excitation and emission slit widths were 10 nm and scan speed 500 nm/min.

2.3. Photostability measurements

The photostability measurement was carried out in quartz spectrophotometric cell at room temperature in a laboratory by irradiation of 5 mL of solution immediately using LT 18w/073 Backlight blue lamb. The degradation of sample was studied by absorption spectra using T 80+UV/Vis spectrophotometer PG instruments Ltd and fluorescence spectra on a Perkin Elmer precisely LS 55 fluorescence spectrometer.

2.4. Synthesis of the Schiff-base

The Schiff base (L) was prepared, Scheme 1, by adding 349 mg of cephradine to 234 mg of 6-Formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one. The fused mixture was stirred with a glass rod on hot sand bath until it solidified. The product was crystallized from methanol, then dried in a desiccator and subjected to elemental analysis.

2.5. Preparation of metal complexes:

Due to the solubility problem of the prepared Schiff base, the metal complexes were prepared using template reaction by adding (349 mg, 1 mmole) cephradine dissolved in ethanol (30 mL) to hot ethanolic solution of (234 mg, 1 mmole) 6-Formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one. The mixture then refluxed for 30 min. A hot ethanolic solution (10 mL) of $Zn(CH_3COO)_2.2H_2O$, $Cu(CH_3COO)_2.H_2O$, ($Ni(ClO_4)_2.6H_2O$) or $Co(ClO_4)_2.6H_2O$ (1 mmole) then added to this mixture and refluxed for another 30 min, the product was isolated by filtration and washed with hot ethanol. The obtained complexes were desiccated under $CaCl_2$ anhydrous.

2.6. Photobiological activity assessment:

The photobiological activity of cephradine, benzopyran-4-one derivative, Schiff base, L, and the prepared complexes was carried out on mosquito larvae.

48 beakers (100 ml) of 20 mosquito larvae each were used in this experiment. 42 beakers assigned for all replicates of treated samples, three beakers for light control (untreated samples but exposed to sunlight) and three beakers for normal control. Samples treatment was carried out by homogenously spreading of the powder form of treatment agents on the water surface of treatment beakers. The treated samples were divided into two groups. First group (21 beakers) was exposed to sunlight for the whole daytime of four consecutive days and the second group (21 beakers) was kept in dark for the same period (dark toxicity). The percentages of mosquito larvae survival were determined every 24 h of experimental period. All experiments were carried out in triplicate and the mean results were given

2.7. Cell cultures and treatments

Liver cancer cell line, Hep G2, was used for experiment at passages 2 to5. Hep G2 cells were cultured in DMEM (Dulbecco's modified Eagle's medium) supplemented with 10% FBS (fetal bovine serum), 1% L-glutamine, 100U/ml penicillin streptomycin. Cells were maintained at 37 ºC in a humidified incubator with 5 % CO_2.

2.7.1. Cell labeling

Liver cancer cell line (Hep G2-cell line) was treated with the Schiff base, L, and its complexes diluted in growth media at different concentrations. The culture was then incubated for 24 h (full dose) in complete medium at 37 °C in humid air with 5% CO_2. Then, the cells were washed 3 times in PBS (phosphate-buffered saline) and centrifuged 5 minutes at 300 r min^{-1}. After centrifugation, the cells were re-suspended in PBS. The number of cells and cell viability was determined by the MTT. Adherent cells were repeatedly washed with fresh PBS to remove loosely attached or extracellular particles until the eluted PBS appeared particles free under light microscope.

2.7.2. Cell viability/cytotoxicity assay

The cytotoxicity of the Schiff base, L, and its complexes against Hep G2-cell line was investigated by the MTT assay. They were incubated together for 24 h. Then, the cells were washed with PBS. After that, the cells were incubated with MTT solution at 37°C for 2 h, and the dye was dissolved by dimethyl sulfoxide (DMSO) for 15 min. Absorbance was examined at 570 nm and cell viability was calculated as a percentage of control cells without materials and tested cells. Each experiment was repeated at least three times independently.

3. Results and discussion

Elemental analyses and some physical properties of the isolated pure Schiff base and its complexes are listed in Table 1. The elemental analyses data are consistent with the calculated results from the empirical formula of each compound. The obtained data reveal that the metal chelates are formed in the ratios of 1:1, Zn(II)-L and Cu(II)-L, and 2:1, Ni(II)-L and Co(II)-L, (M: L). These metal complexes are stable, non-hygroscopic, partially soluble in most organic solvents and soluble in DMF and DMSO. The molar conductance values of Schiff base, L, chelates in DMSO range from 0-50 ohm^{-1} cm^{2} $mole^{-1}$ may be taken as evidence for the non-electrolytic nature of these chelates [27] indicating that no anions are present outside the coordination sphere.

3.1. Characterization of Schiff base

3.1.1. Mass and ^{1}H-NMR spectra of Schiff base

Mass spectrum of Schiff base L exhibits the molecular ion peak at m/e = 566 (M+1). Confirming its formula weight is equal to its molecular weight Figure 1.

The ^{1}H-NMR spectrum of Schiff base, L, in DMSO-d_6, Figure 2, displays resonance at $\delta = 2.30$ ppm with integration value for six protons due to two methyl groups in benzopyran-4-one and cephradine moieties [28]. The signal observed at 4.10 ppm was assigned to O-CH_3 group but the signal at 8.32 ppm was assigned to azomethine (CH=N) proton. The signal at 8.24 ppm may be due to the amide group (HNC=O) [29]. The signal for COOH proton in the spectrum of uncomplexed cephradine at 10.30 ppm [29].This signal observed in Schiff base at 10.20 ppm. The signal of β-lactam (2H) appeared at 8.20 ppm [29]. The signal of phenolic OH group present in the benzopyran-4-one moiety appears at 15.60 ppm.

3.1.2. IR spectrum of Schiff base

The IR spectrum of pure cephradine showed stretching vibration at 3350-3230 cm^{-1} due to amino group [30,31].The stretching vibrations at 3350-3230 cm^{-1} were absent in the IR spectrum of investigated Schiff base L. This indicates that amino group of cephradine and aldehyde group in benzopyran-4-one derivative have condensed to produce the -CH=N- group.

The IR spectrum of Schiff base shows a broad band at 3398 cm^{-1} due to phenolic OH stretching. The broadness is due to intramolecular hydrogen bonding between the phenolic group and the azomethine group. There are two strong absorption bands in the lower frequency region [32] which can be attributed to the OH deformation modes. Such bands are O-H deformation and O-C stretching vibration. The first band (O-H deformation) occurs in the range 1114-1157 cm^{-1}, while the second one (C-O stretching) arises in the region 1170-1225 cm^{-1} [33]. In the present study, the IR spectrum of free Schiff base shows bands at 1111 and 1180 cm^{-1} due to OH deformation and O-C stretching, respectively.

Bands at 1755, 1651, 1611, 1431 cm^{-1} were assigned to $\nu(C=O)_{\beta\text{-lactam}}$, $\nu(C=O)_{\text{benzopyrone}}$, $\nu(CH=N)_{\text{azomethine}}$, ternary N- atom (β-lactam nitrogen), respectively. The asymmetric and symmetric COO^- frequencies are appeared at 1520 and 1350 cm^{-1}, respectively, in the IR spectrum of the Schiff base.

The elemental analyses (Table 1), IR, ^{1}H-NMR and mass spectra verified the molecular structure shown in Scheme 1 of the Schiff base.

3.2. Characterization of the complexes

3.2.1. Mass spectrometry

The mass spectra of complexes, Figure 3, show molecular ion peaks, which are in good agreement with the expected values and corresponding to the molecular weight of the respective compounds. Mass spectra of Zn(II)-L (M.Wt. 718.59) gives peak at m/z = 718, while that of Cu(II)-L complex (M. Wt 716.78) shows a moleculer ion peak at m/z = 716. Ni(II)-L (M. Wt. 916.92) and Co(II)-L (M. Wt. 917.37) complexes show well-defined parent peaks at m/z = 916 and 917, respectively. The presence of these peaks confirms the structure of the complexes.

3.2.2. Infrared spectroscopy

The most important infrared spectral bands of the investigated metal complexes in the present study are summarized in Table 2. A comparison of the IR spectrum of the free Schiff base L and its complexes allow us to determine the coordination sites that could be involved in chelation Figure 4.

The band observed in the spectra of the complexes in the range 3377-3414 cm^{-1} considerably support the presence of water molecules in the complexes [34].The band at 1111 cm^{-1} due to the OH deformation in the spectrum of the free ligand L shows a remarkable negative shift within the 1092-1080 cm^{-1} region in all the spectra of complexes. The shift, Table 2, in the band due to phenolic C-O stretching vibration appears in the IR spectra of all complexes, indicating the involvement of oxygen of the hydroxyl group of benzopyran-4-one moiety after deprotonation. The band due to stretching vibration of azomethine group ν(CH=N) at 1611 cm^{-1} is shifted to higher wave numbers (1620-1632 cm^{-1}) in the IR spectra of all complexes, indicating the participation of the azomethine nitrogen in coordination. This confirms that the chelation occurs through nitrogen of azomethine group and deprotonated phenolic oxygen of benzopyrone moiety in all complexes.

The asymmetric stretching vibration of cephradine carboxylate group ν(COO$^-$) cannot be assigned due to the interfering with ν(CH=N)$_{\text{azomethine}}$ but the band at 1350 cm^{-1} in free ligand due to the symmetric stretching vibration of carboxylate group shifted to 1327 and 1330 cm^{-1} in the

IR spectra of (1:2) (L:M) Ni(II)-L and Co(II)-L complexes, respectively. Also, the frequency of the ternary N-atom (β-lactam nitrogen) shifted to 1450 and 1454 cm^{-1} in Ni(II)-L and Co(II)-L complexes, respectively. This suggests that for binuclear (1:2) (L:M) complexes (Ni(II)-L and Co(II)-L), the chelation of second metal ion occurs between the carboxylate oxygen and β-lactam nitrogen.

The band at 1651 cm^{-1} in the free Schiff base (L) of $\nu(C{=}O)_{benzopyrone}$ shows no change in Cu(II)-L complex but suffers shift to higher wave number in other complexes. Also, the band of $\nu(C{=}O)_{\beta\text{-lactam}}$ shifted to lower frequency and obscured by the $\nu(C{=}O)_{benzopyrone}$ in all complexes. The shift in these bands may be ascribed to the electronic changes in the ligand molecule after chelation. Where, cephradine forms complexes with transition metal ions in which the β-lactam carbonyl stretching frequency decreases by 10-30 cm^{-1} depending upon the nature of the metal ion [35] despite the lack of participation `of this group in chelate formation. Also, a number of workers have studied complexes of cephalosporins with Mg, Mn, Fe, Ni, Co and Zn etc. and showed that these metals form 1:1 with cephalosporins [36,37] and the spectral studies indicate that the linking of the drug molecule with the metal ions is through the nitrogen of the β-lactam thiozolidine ring and carboxylate ion forming a five membered ring. The site of metal ion coordination for cephradine is thus, not different from other cephalosporins. Furthermore, coordination between the carboxylate oxygen and β-lactam nitrogen was selected for penicillanic acid [35].

In the low frequency region, new bands observed in the IR spectra of all chelates in the region 459-467 cm^{-1} may be attributed to νM-N [37]. But,the new band observed at 528-556 cm^{-1} in the infrared spectra of the complexes may be attributed to νM-O stretching [38]. This indicates that both phenolic oxygen and nitrogen of azomethine group are involved in the formation of all chelates. Also the presence of these two bands with high intensity confirms the second center of chelation (carboxylate oxygen and β-lactam nitrogen) in (1:2) (L:M) Ni(II)-L and Co(II)-L complexes.

Charge balance for the divalent positive transition metal ions can be achieved by the participation of OH^- in the coordination sphere of the metal ion from solution in Zn(II)-L and Cu(II)-L complexes but that for the divalent positive cobalt and nickel ions can be achieved by the participation of perchlorate ion. The presence of a coordinated perchlorate group is shown by the appearance of bands at 1178, 1056, 964 and 629 cm^{-1} in Co(II)-L and at 1178, 1049, 955 and 633 cm^{-1} in Ni(II)-L [39].

3.2.3. ^{1}H-NMR

A substantial support for the structure of complexes is gained by considering the changes for the ^{1}H-NMR spectrum of Zn-L chelate, Figure 5, in comparison with the free ligands L.
The signal at 2.30 ppm in the ^{1}H-NMR spectrum of ligand L is not influenced by the chelation. In the spectrum of Zn (II)-L complex, the signal appeared at 3.40 ppm may be assigned to the water molecules in this chelate.
The azomethine (CH=N) signal at 8.32 ppm for Schiff base,L, is found at 8.64 ppm in Zn(II)-L complex. This indicates that this group is coordinated to the Zn(II) ion without proton displacement. On other hand, β-lactam proton signal at 8.20 ppm in the spectrum of the Zn(II)-L complex is not influenced by the chelation. The signal of amide (HNC=O) appears in the spectrum of complex at 8.27 ppm.

The signal of COOH group appeared highfield (9.4 ppm) may be due to the increase in conjugation during coordination. The signal of phenolic –OH group present in the benzopyran-4-one moiety is not observed in the spectrum of the complex, this is confirms the bonding of phenolic oxygen at position seven to the metal ion (C-O-M). The same result was confirmed by the IR spectra.

3.2.4. Electronic spectra and magnetic susceptibility measurement

The electronic spectra of Schiff base L and its complexes, Figure 6, were recorded in dimethyl sulfoxide (DMSO) .The position of the band maxima and the magnetic moment values of the complexes are listed in Table 3.

The electronic spectrum of the ligand exhibits one broad intense band at 376 nm (26596 cm^{-1}) assigned to the charge transfer transition.

The spectrum of Zn(II)-L complex does not contain d-d transition but there are two bands at 367 nm (27247cm^{-1}) and 444 nm (22522 cm^{-1}). The band at 27247 cm^{-1} displaced to lower value compared with the corresponding band in the spectrum of the free ligand, which proves the coordination of the ligand to the metal ion. The band at 22522 cm^{-1} can be attributed to the LMCT transition, which is compatible with this complex having an octahedral structure [40,41] The Zn(II)-L complex was found to be diamagnetic as expected.

The Metal-ligand charge transfer (MLCT) transitions were reported to be in the range 400-448 nm which can be assigned to the combination of $^2B_{1g} \rightarrow ^2E_g$ and $^2B_{1g} \rightarrow ^2B_{2g}$ transition in a distorted square planar environment for copper complexes [42,43]. In the present study, the spectrum of Cu(II)-L complex shows band at 412 nm (24272 cm^{-1}) which supports distorted square planer geometry for this complex. The observed magnetic momentum value of Cu(II)-L complex is 1.74 BM [44].

The magnetic moment value for (2:1) (M:L) Ni(II)-L complex is 2.28 B.M per metal ion. This μ_{eff} is lower value relative to that for Ni(II) complex in distorted tetrahedral geometry (3.2-4.0 B.M) [45]. This can be explained on the bases of antiferromagnetic interaction [46]. The electronic spectrum of Ni(II)-L complex shows one band at 445 nm (22472 cm^{-1}) which is shifted from that of the parent ligand 376 nm (26596 cm^{-1}) upon complex formation.

The magnetic moment (2.64 B.M per metal ion) for Co(II)-L complex falls in the region reported for one unpaired electron existing for both square planar and low spin octahedral geometries. The absence of octahedral characteristic bands excludes the low spin octahedral configuration and the existence of band at 455 nm (21978 cm^{-1}) due to the $^1A_{1g} \rightarrow ^1B_{1g}$ transition [47] may supports the square planar geometry. The band of the ligand appears at 374 nm (26738 cm^{-1}) in the electronic spectrum of this complex.

3.2.5. Thermogravimetric analysis (TG)

In the present investigation, the thermal stability of the complexes was investigated using TG technique at a heating rate of 10 ^oC/ min in nitrogen atmosphere over the range from ambient temperature to 800 ^oC, Figure 7. The data in Table (4) provides information concerning thermal decomposition of these complexes in solid state.

In the TG curve of Zn(II)–L complex, the first step displays a gradual mass loss of 2.70 % (calc. 2.50^oC) within the temperature range of 30–69 ^oC which may be attributed to the loss of one molecule of water of crystallization, whereas, the second step shows a mass loss of 7.50 % (calc. 7.51^oC) which is due to the loss of three molecules of coordinated water molecules within temperature range 69–208 ^{o}C. Then the mass loss continues due to the decomposition of organic part of the complex until a constant mass at 569 °C corresponds to the formation of $ZnCO_3$ residue.

In TG curve of Cu(II)-L complex, the initial mass loss of 7.32 % (calc. 7.53%) occurring in the temperature range 54-145 ^{o}C represents the loss of three molecules of hydrated water. The second stage corresponds to a mass loss of 2.31 % (calc. 2.51%) within the temperature range 145–190°C represents the loss of one coordinated water molecule. The third stage, 240–440 °C with a found mass loss of 82.5% is reasonably accounted for the decomposition of the organic part of the complex leaving out $CuCO_3$ as a residue.

For Ni(II)-L complex The mass loss of 4.01% (calc. 3.93%) within the temperature range 82-145 °C represents the loss of two molecules of coordinated water. The decomposition is completed at 623.3^{o}C leading to the formation of the stable nickel oxide (NiO) residue.

The TG curve of Co(II)–L complex shows mass loss of 4.00% (calc. 3.93%) within the temperature range of 29-185 °C which is due to the loss of two coordinated water molecules. Beyond 525 °C, the residue attains a constant composition corresponding to $CoCO_3$ (Found 26.5%, calc. 25.93%).

Based on the results of elemental analyses, IR, electronic spectra, magnetic moment, molar conductance measurements, and thermogravimetric analysis, it can be concluded that Schiff base behaves as mononegative NO bidentate ligands, coordination occurring via the azomethine nitrogen and the deprotonated phenolic oxygen atoms of the benzopyrane-4-one ring Scheme 2. In binuclear complexes, the second metal ion coordinates to the ligand through carboxylate oxygen and β-lactam nitrogen, as shown in Scheme 3.

3.3. Photoluminescence study of Schiff base and its complexes:

In the present study, the luminescence properties of the free Schiff base L and its complexes (Zn(II)-L, Cu(II)-L, Ni(II)-L and Co(II)-L) were studied at room temperature (298 K) in DMSO, Figure 8.

The free Schiff base L, 10^{-5} mol/L, exhibited blue photoluminescence with a maximum emission at 450 nm upon excitation at 396 nm. The fluorescence of the ligand is probably due to the intraligand $\pi \rightarrow \pi^*$ transition.

The emission spectrum of Zn(II)-L ($5x10^{-7}$ mol/L) shows two bands at 433 and 703 nm. In Zn(II) complex no emission originating from metal-centered (MLCT or LMCT) excited states are expected, since the Zn(II) ion is difficult to oxidize or reduce due to its stable d^{10} configuration [48]. Thus, the emission observed in Zn(II)-L complex can be obtained only by the organic ligand. The different emission properties between the free Schiff base and Zn(II)-L complex can be likely ascribed due to the presence of the zinc ion which plays an essential role in the increasing of ligand conformational rigidity and coplanarity, accordingly reduces the energy gap between the π and π^* molecular orbital of the ligand [49].

The spectrum of Cu(II)-L complex (10^{-4}mol/L) shows emission band at 443 nm. This intense fluorescence band is stronger and blue shifted than that of the free ligand. This emission may be assigned to the intraligand fluorescence since the free ligand exhibited a similar emission under the same condition [48]. Another band appears at 726 nm in the spectrum of this complex which may be due to intramolecular charge transfer between the triplet level of the ligand and the emitting level of the ion.

The emission intensity of the Zn(II)-L and Cu(II)-L complexes is stronger than that of the ligand.

On the other hand, the emission spectra of Ni(II)-L and Co(II)-L complexes show bands at 474 and 515 nm, respectively. These bands are shifted to the red region and have lower intensity than that of the free ligand. Significant differences in position of emission maxima and intensity from that of the ligand establish the complexation process.

The enhancement of the fluorescence may be attributed to the chelation of a ligand to metal ion which effectively increases the rigidity of the ligand and thus reduces the loss of energy by thermal vibrational decay [50]. Enhancement of fluorescence through complexation is of much interest as it opens up the opportunity for photochemical applications of these complexes.

The photoluminescence data for the ligand and its complexes are summarized in Table 5.

3.4. Photostability studies using absorption and fluorescence spectra:

Photodecomposition tests of Schiff base, L, Zn(II)-L and Cu(II)-L compounds were conducted in DMSO. These compounds were exposed to UV radiation using LT 18w/073 Backlight blue lamp. The lamp was allowed to stabilize for 10 min prior to experiments. The change in the absorption and fluorescence spectra was performed at different time intervals during irradiation period.

The Schiff base L, Zn(II)-L and Cu(II)-L complexes undergo photodegradation due to absorption of photonic energy from the UV range. It was found that UV irradiation induced a gradual decrease of the absorption over the whole measured spectral range, Figure 9. This may be due to the UV irradiation of Schiff base (L), Zn(II)-L and Cu(II)-L compounds cause their irreversible photochemical decomposition-bleaching [51].

Also, the change in the fluorescence spectra of the same compounds by UV irradiation was achieved at different times during irradiation period, Figure 10. The irradiation induced a clear decrease in the fluorescence intensity with time of Schiff base, L, Zn(II)-L and Cu(II)-L compounds.

3.4.1. Kinetics of the photochemical decomposition

The rate constant of photodegradation of Schiff base (L), Zn(II)-L and Cu(II)-L compounds was estimated kinetically by plotting the curve between log(A_o/A_t) and irradiation time (min), Figure 11, according to the following equation [52]:

$$\log \frac{A_o}{A_t} = \frac{k}{2.303}\, t$$

Where A_o and A_t are the absorptions before and after irradiation for time (t), k is the apparent rate constant.

The graphical method was employed to predict the order of the reaction. The plot of (logA_o/A) with irradiation time (t) gives straight line which indicates that reaction is first-order. The photodegradation rate constant, k (min^{-1}), is calculated using the slope.

By replacing A_t with $A_o/2$, the reaction half time ($t_{1/2}$) can be calculated by:

$$t_{1/2}=\frac{0.693}{k}$$

Also, the rate of photodegradation was determined by fitting the fluorescence intensities of the compounds to the equation:

$$\ln\frac{F_o}{F_t}=k\,t$$

Where, F_o and F_t are the fluorescence intensities at λ_{em}(nm) of the main band at times zero and t, respectively, k is the apparent rate constant.

The curve of $\ln(F_o/F_t)$ versus irradiation time (min), Figure 12, gives straight line with a slope equal to the rate constant of photodegradation (k). Half-lives ($t_{1/2}$) of these compounds were also calculated.

The results of photodegradation (k) and half life time ($t_{1/2}$) obtained by the two methods are given in Table (6). These values are in good agreement.

The rate of photodegradation of L lesser than that of Zn(II)-L and Cu(II)-L complexes; this means that the complexes are less photostable than the free Schiff base but Cu(II)-L more stable than Zn(II)-L. The stability of the metal complexes can be explained by Falk "stability factor" (including charge number of the metal ion, effective radius of the metal ion in Å and the Pauling electronegativity) [53] According to the Falk equation, the stability of the complexes is ordered as: Zn(II)-complex < Cu(II)-complex [53].

3.5. Photobiological activity assessment:

The photobiological activity of cephradine, benzopyran-4-one derivative, Schiff base, L, and the all complexes were studied on mosquito larvae to investigate the extent of their photosensitization efficiency in controlling noxious insects using direct sunlight (larvicidal effect). The experiment also was carried out in the dark (dark toxicity). Figure 12 (A,B), shows the photosensitizing effect of compounds. Figure 13 (A,B), shows the effect of the same agents in dark conditions (dark toxicity). Both figures reflect the extent of photosensitizing activity and dark toxicity of the compounds.

Schiff base has high photosensitizing activity comparing to its dark toxicity. In Figure 12 A, Schiff base, L, shows the highest photosensitizing activity as a function of mosquito larvae survival percentage (0%). Schiff base, L, is better than the cephradine and benzopyran-4-one derivative. Among the complexes, Ni(II)-L has high photosensitizing activity which induce high percentage of larva mortality (100%, Figure 12 B). The photosensitizing activity of Ni(II)-L complex is much better than its dark toxicity, Figure 13 B. The order of the larvicidal effect of the compounds after exposure to the sunlight as follow:

Schiff base > benzopyran-4-one derivative > cephradine and Schiff base = Ni(II)-L > Co(II)-L > Zn(II)-L > Cu(II)-L

3.6. In vitro cytotoxicity studies of Schiff base and its complexes

Cytotoxicity of Schiff base L, and its complexes was studied on Hep G2 cell line with different concentrations. Analysis of the data of the cytotoxicity using MTT assay showed that the tested compounds have promising activity at concentration of 25 µmol L^{-1}. In particularly, Schiff base, L, inhibit 55% from Hep G2 cell line. Zn(II)-L, Cu(II)-L and Ni(II)-L complexes show inhibition of 37%, 35% and 33%, respectively. On other hand, Co(II)-L shows the lowest cytotoxic activity where it inhibits only 20% from Hep G2 cell line. In general, the Schiff base, L, exhibits better activity against Hep G2 cell line than the complexes, Figure 14.

4. Conclusion

Based on the results of elemental analyses, mass spectrometry, IR, electronic spectra, magnetic moment, molar conductance measurements, and thermogravimetric analysis, it can be concluded that Schiff bases behave as mononegative NO bidentate ligands in all complexes.

The coordination occurs via the azomethine nitrogen and the deprotonated phenolic oxygen atoms of the benzopyrane-4-one ring. In binuclear complexes (2:1) (M:L) (Ni(II)-L and Co(II)-L), the second metal ion coordinates to the ligand through carboxylate oxygen and β-lactam nitrogen.

The Schiff base, L, and its complexes each displays intense fluorescence at room temperature. Significant differences in position of emission maxima and intensity from that of the ligand establish the complexation process.

Furthermore, the photostability studies of Schiff base, L, Zn(II)-L and Cu(II)-L compounds showed that the rate of photodegradation of Schiff base, L, lesser than that of Zn(II)-L and Cu(II)-L complexes. This means that the complexes are less photostable than the free Schiff base.

Also, the photobiological activity (larvicidal effect) of cephradine, benzopran-4-one, Schiff base, L and all complexes were studied on mosquito larvae to investigate the extent of their photosensitization efficiency in controlling noxious insects using direct sunlight. Schiff base, L, and Ni(II)-L show the highest photosensitizing activity as a function of percentage of mosquito larva mortality (100%). The order of the larvicidal effect of the compounds after exposure to the sunlight as follow: Schiff base > benzopyran-4-one derivative > cephradine and Schiff base = Ni(II)-L > Co(II)-L > Zn(II)-L > Cu(II)-L

Finally, cytotoxicity of Schiff base L, and its complexes was studied on Hep G2 cell line. The Schiff base, L, exhibits better activity against Hep G2 cell line than the complexes.

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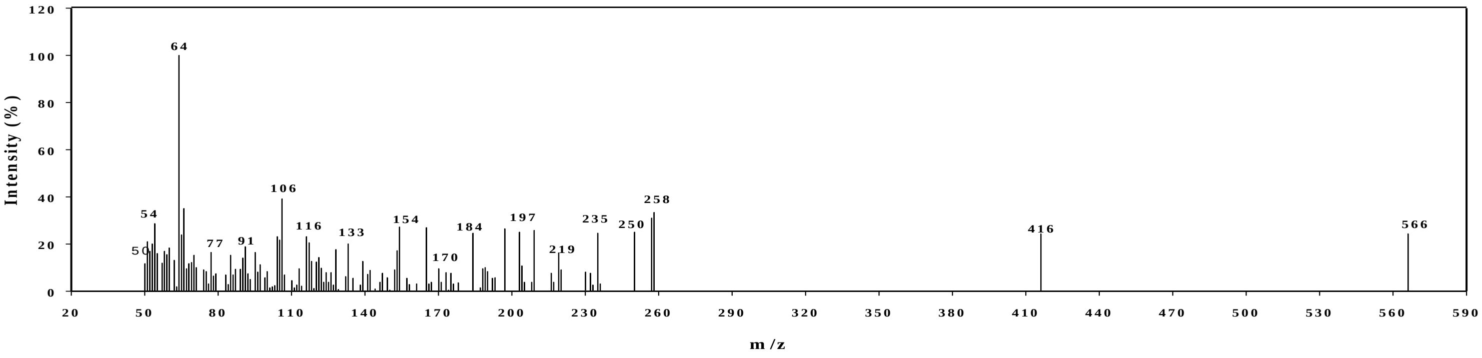


Figure 1: Mass spectrum of Schiff base L

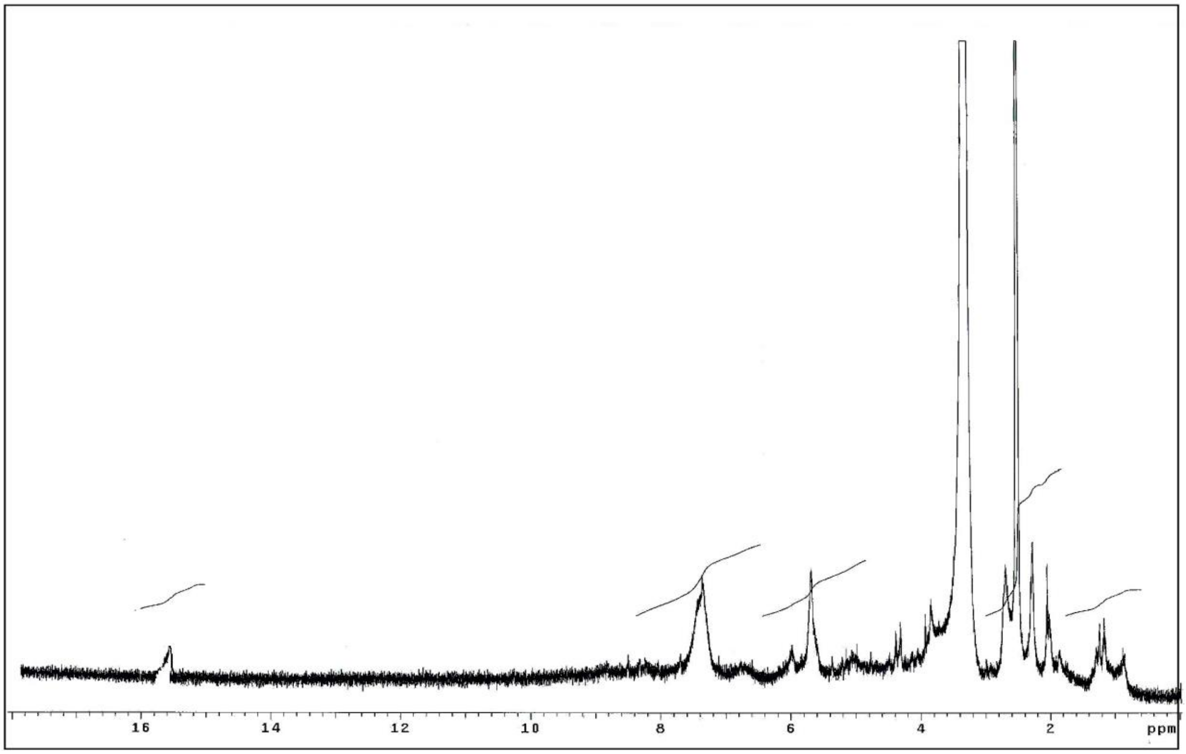


Figure 2: ^{1}H-NMR spectrum of Schiff base, L

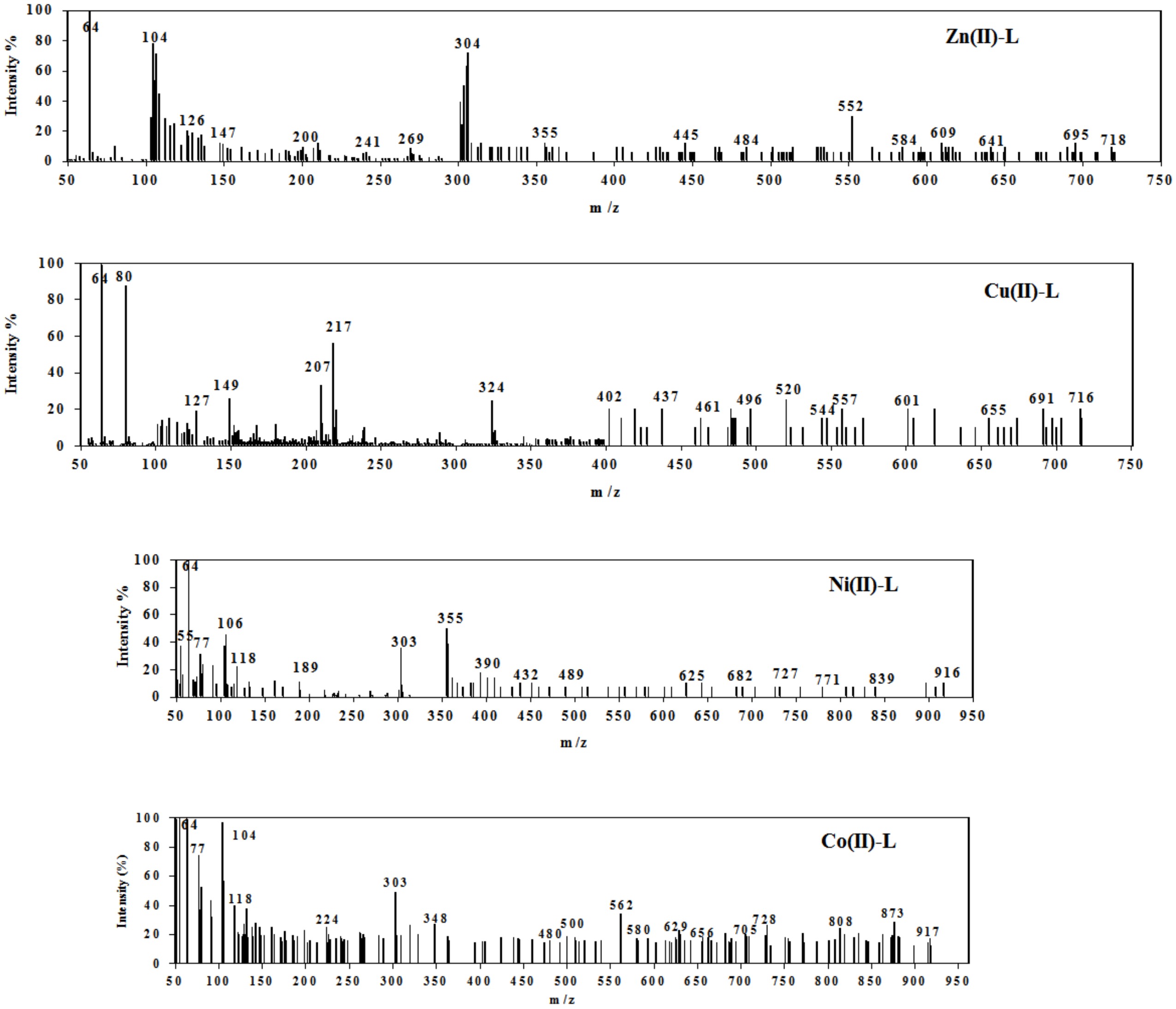


Figure 3: Mass spectra of the complexes

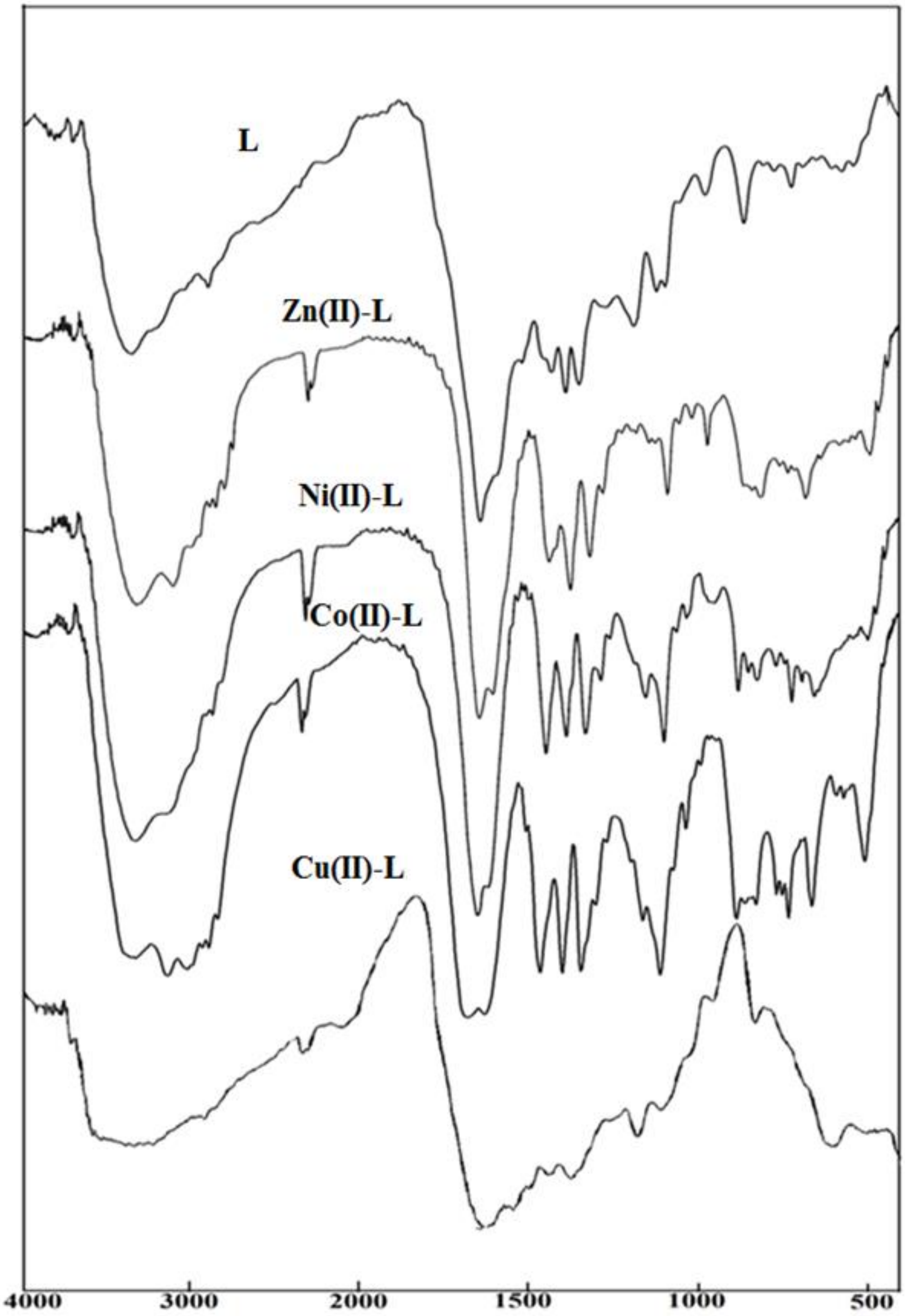


Figure 4: IR spectra of Schiff base, L, and its complexes

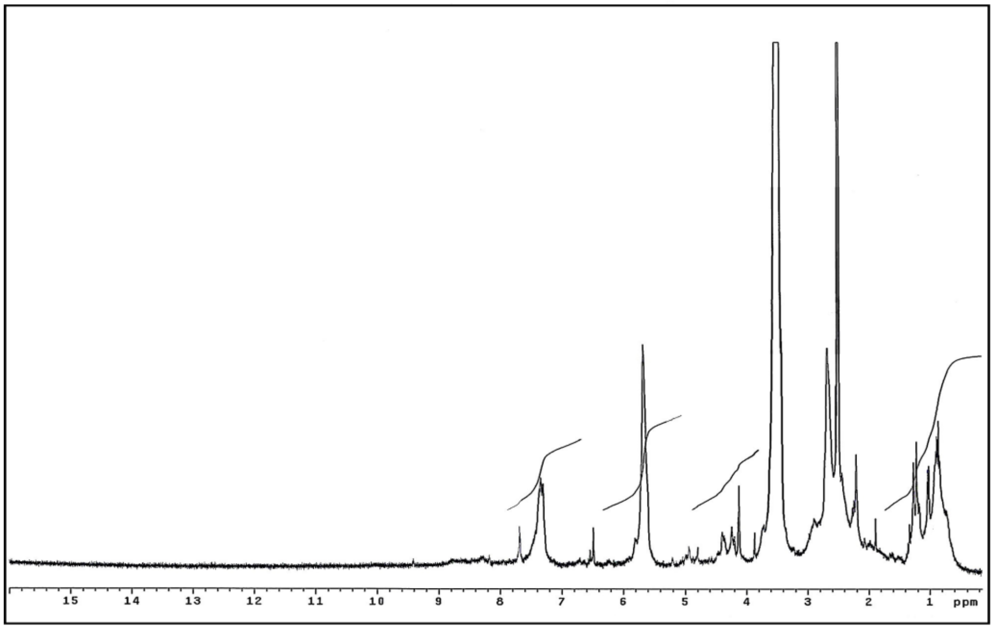


Figure 5: ^{1}H-NMR spectrum of Zn(II)-L complex

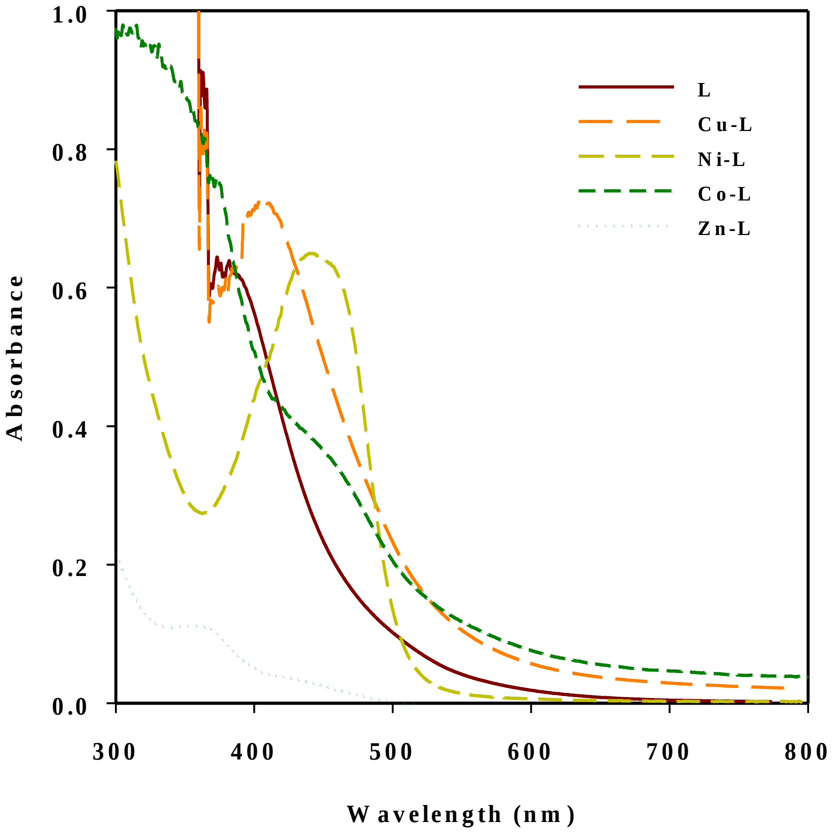


Figure 6: the Electronic absorption spectra of Schiff base,L, and its metal complexes

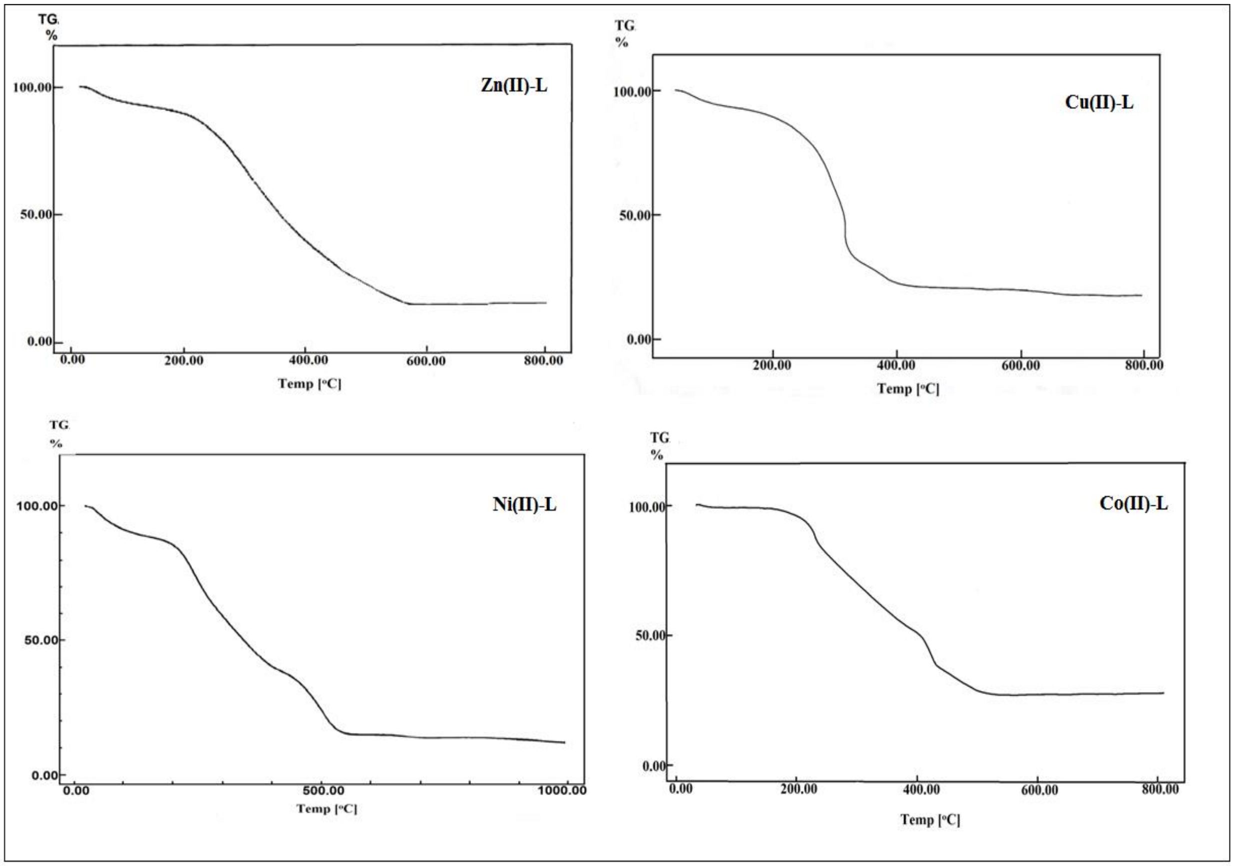


Figure 7: TG curves of the complexes

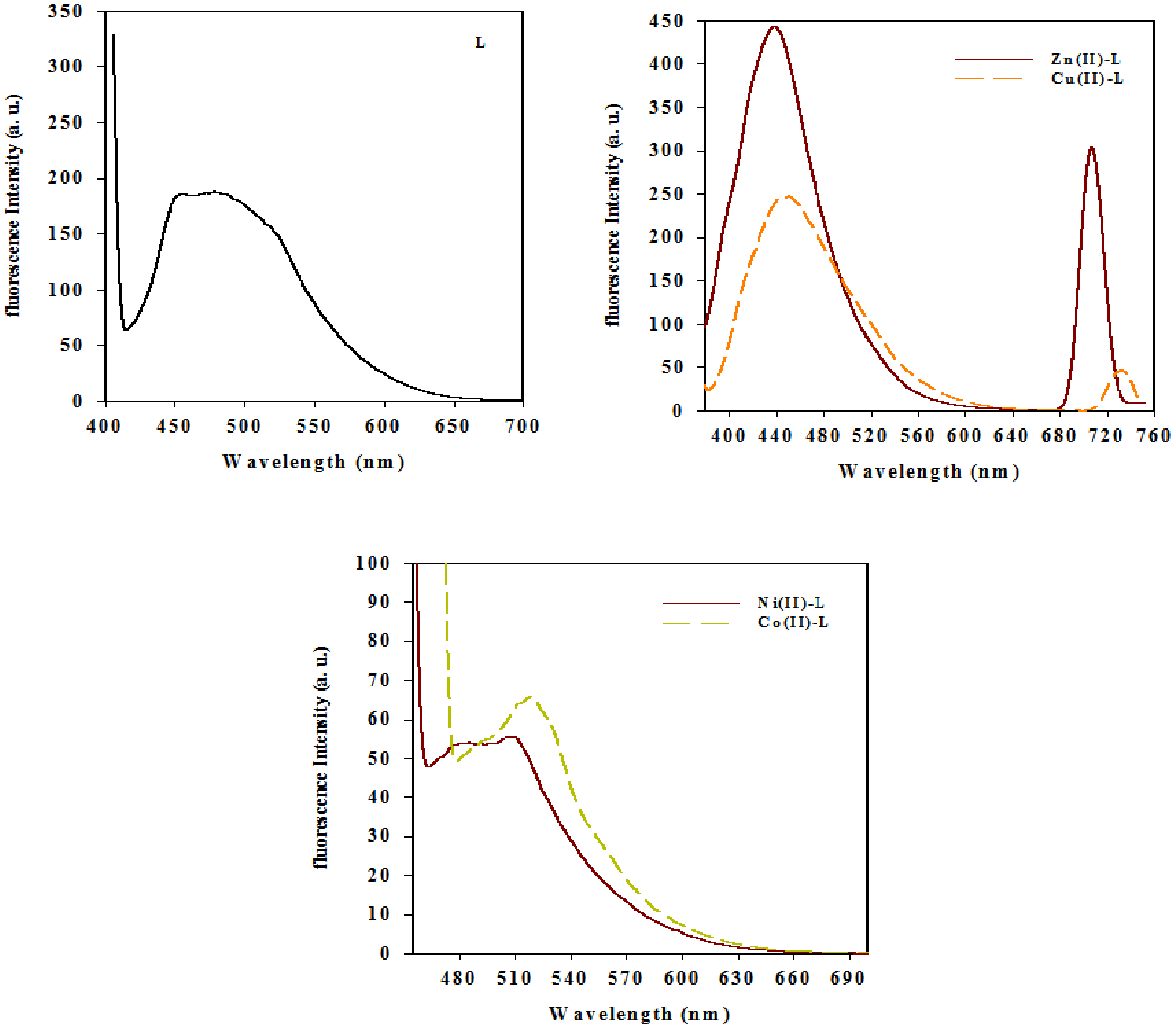


Figure 8: Fluorescence spectra of Schiff base, L, and its complexes in DMSO

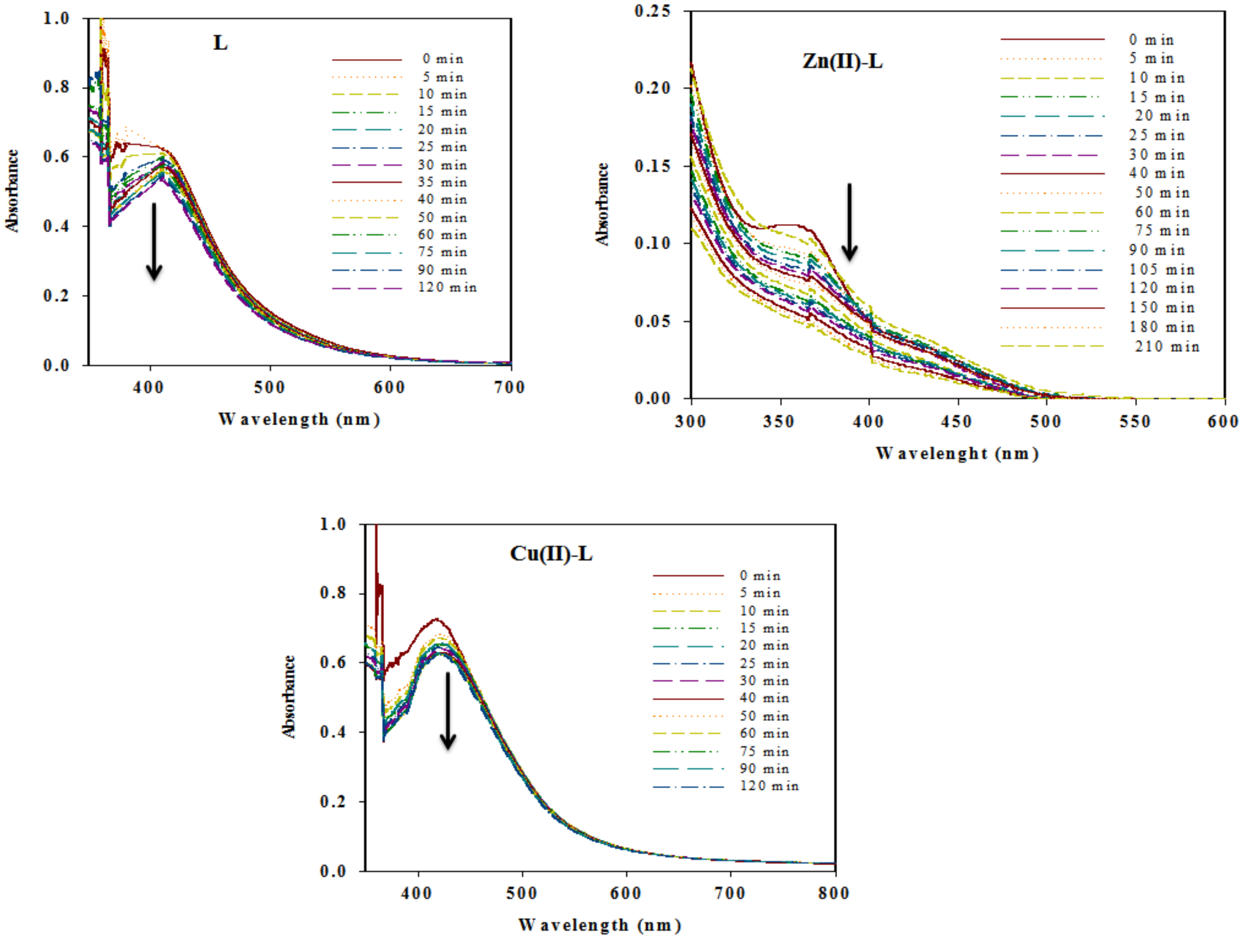


Figure 9: Electronic absorption spectra of Schiff base, L, Zn(II)-L and Cu(II)-L in DMSO at various irradiation times

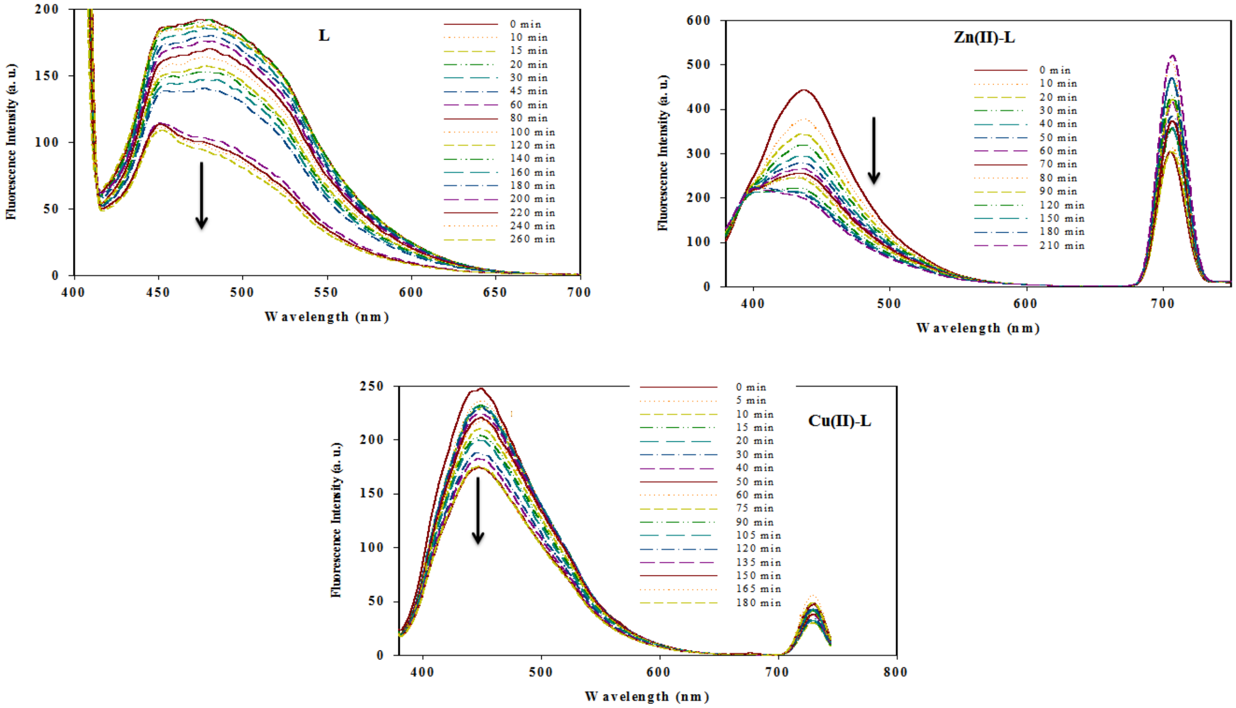


Figure 10: Fluorescence spectra of Schiff base, L, Zn(II)-L and Cu(II)-L in DMSO at various irradiation times

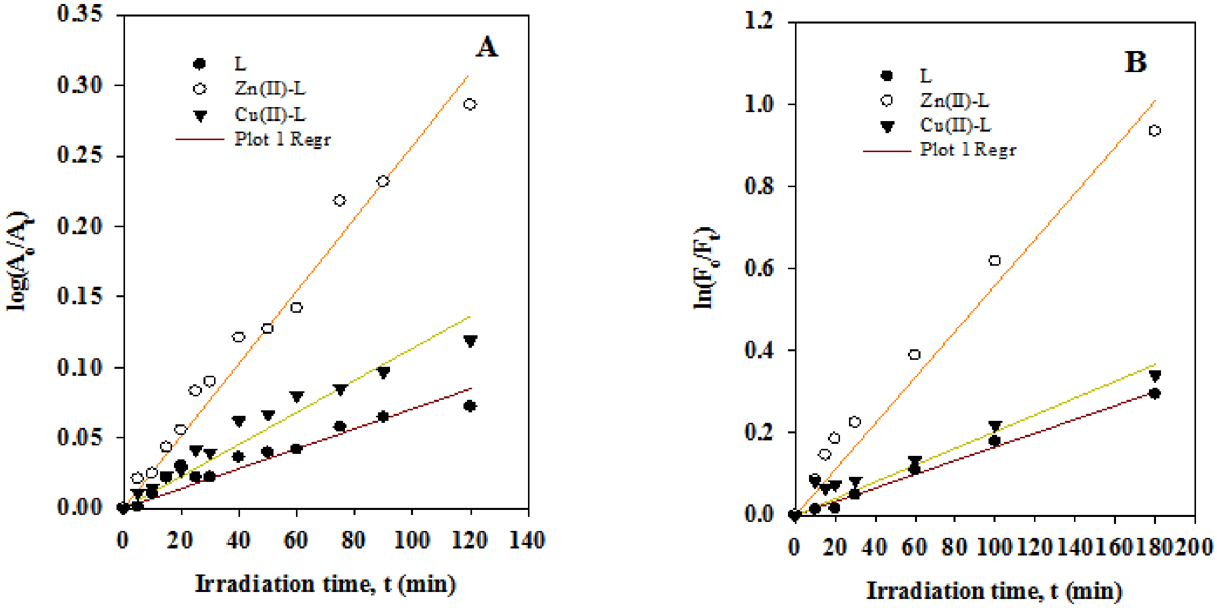


Figure 11: First order kinetic plots for the photochemical decomposition of Schiff base (L), Zn(II)-L and Cu(II)-L in DMSO under UV-B irradiation by absorption spectra (A) and fluorescence spectra (B).

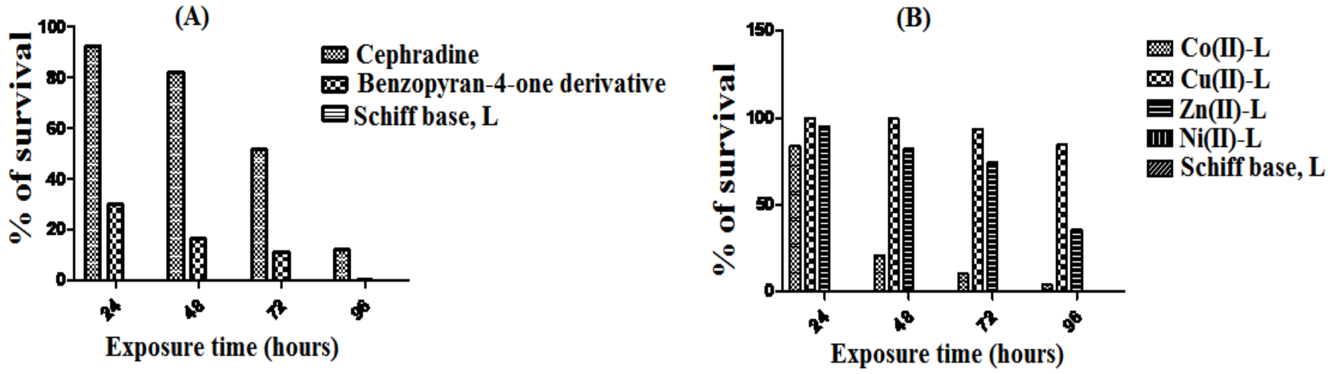


Figure 12 (A): Photosensitizing effect of cephradine, benzopyran-4-one derivative and Schiff base

(B): Photosensitizing effect of Schiff base and its complexes on mosquito larvae

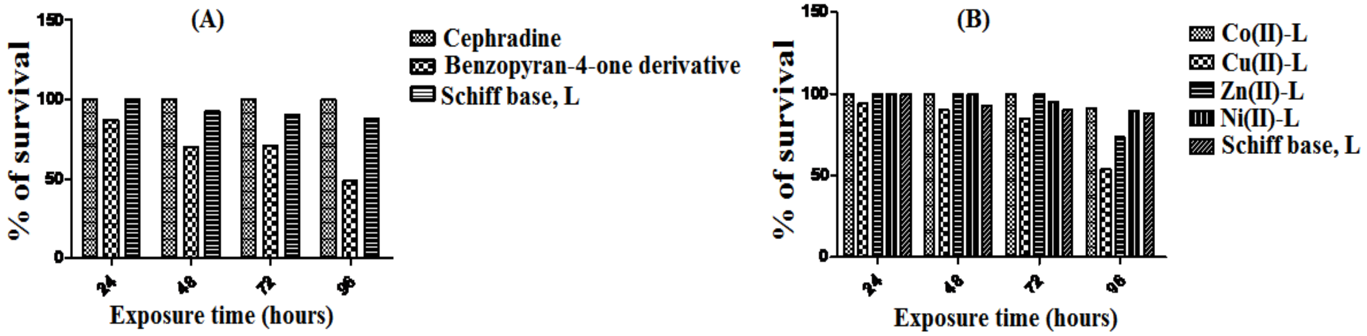


Figure 13 (A): Dark toxicity of cephradine, benzopyran-4-one derivative and Schiff base

(B): Dark toxicity of Schiff base and its complexes on mosquito larvae

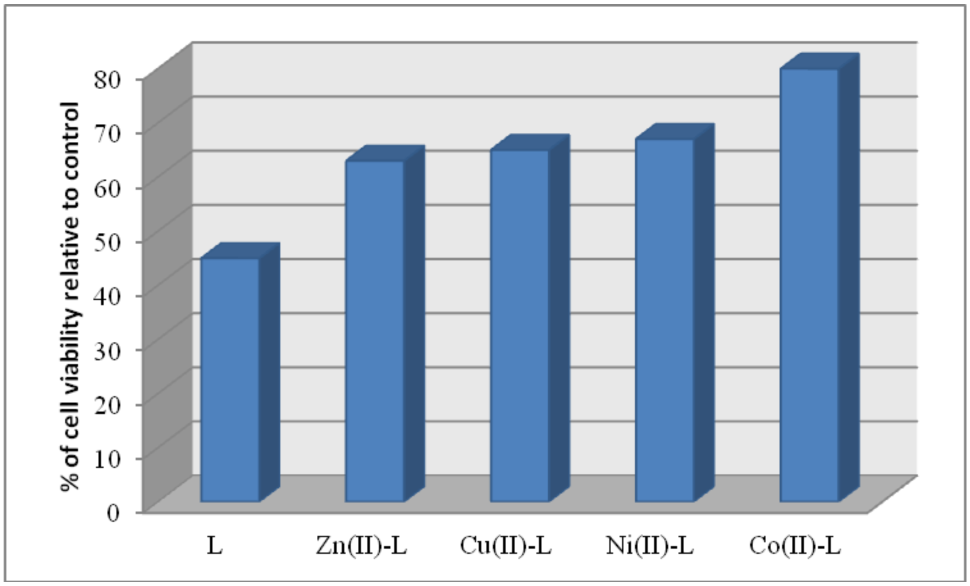
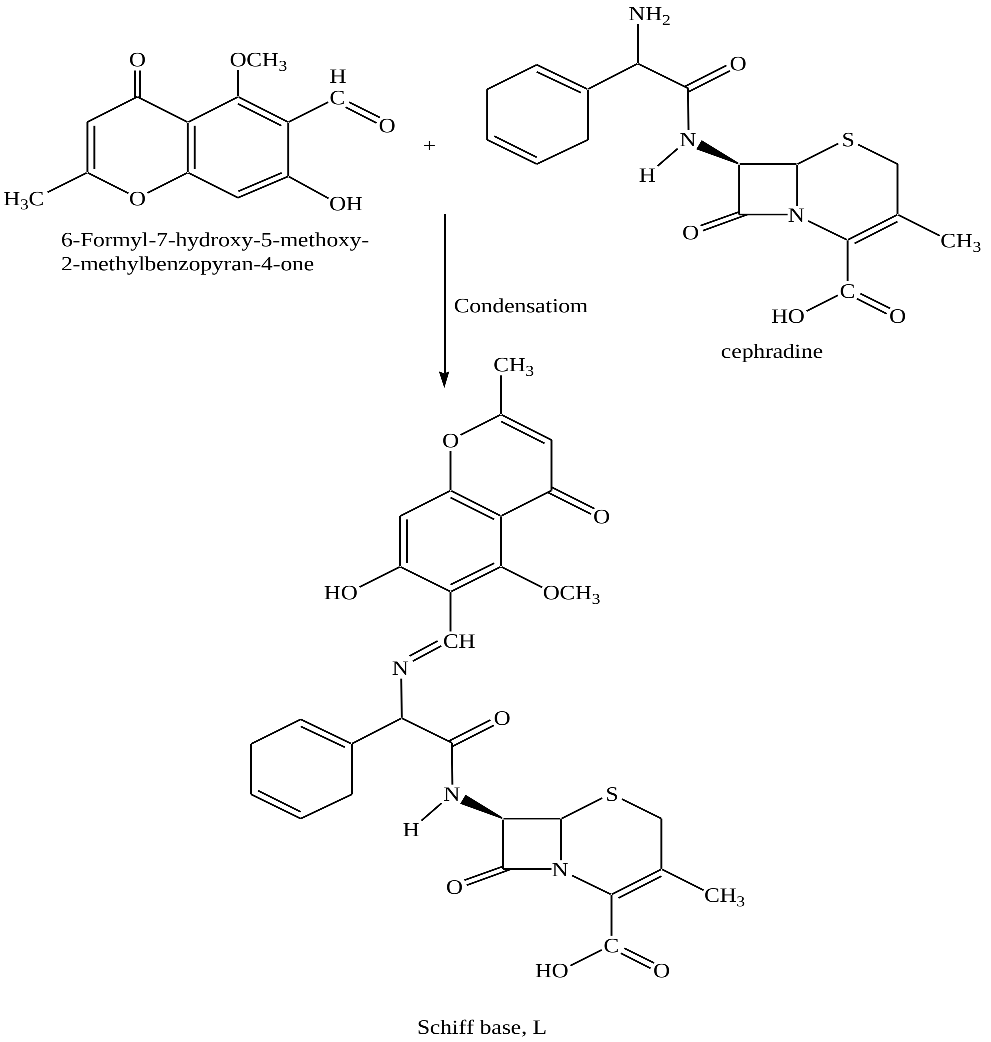
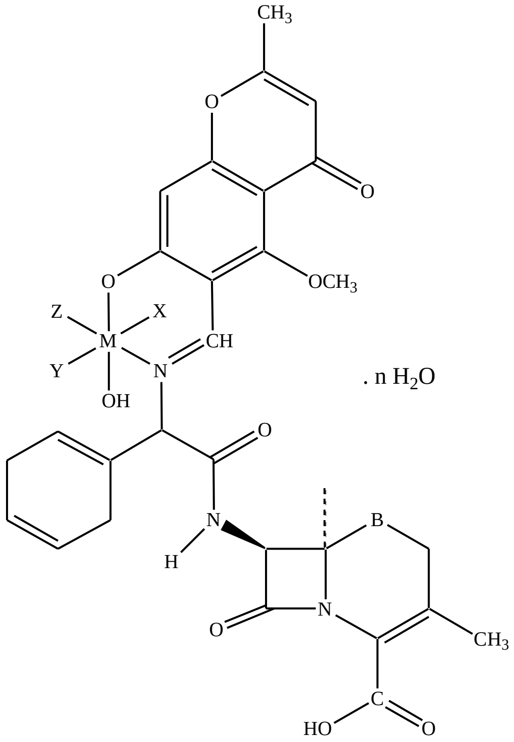


Figure 14: The percentage of cell viability of cells of the Schiff base, L, and its complexes in Hep G2 cell line

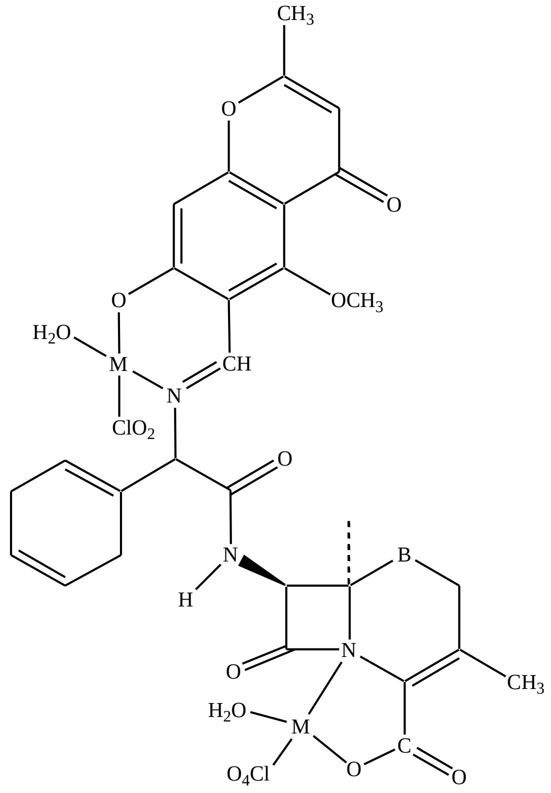


Scheme 1: Preparation of Schiff base, L



Complex	X	Y	Z	N
Zn(II)-L	H_2O	H_2O	H_2O	1
Cu(II)-L	H_2O	-	-	3

Scheme 2: the proposed structure of 1:1 (L:M) complexes



Complex	M
Ni(II)-L	Ni
Co(II)-L	Co

Scheme 3: The proposed structure of binuclear complexes

Table (1): The elemental analyses data of the Schiff base (L) and its complexes

Symbol	Compound	M.Wt	M:L	Λ ohm^{-1} cm^{2} mole^{-1}	C% Calc. (Found)	H% Calc. (Found)	N% Calc. (Found)	M% Calc. (Found)	%Cl Calc. (Found)
L	$L.2H_2O$	601.62	-	-	55.90 (56.68)	5.19 (5.48)	6.98 (6.87)	-	-
Zn(II)-L	$[Zn\ L.OH.3H_2O].H_2O$	718.59	1:1	11.70	46.80 (46.92)	4.91 (4.80)	5.84 (5.78)	9.09 (8.87)	-
Cu(II)-L	$[Cu\ L.OH.H_2O].3H_2O$	716.78	1:1	13.80	46.92 (46.55)	4.92 (4.24)	5.86 (5.65)	8.86 (9.00)	-
Ni(II)-L	$[Ni_2\ L_1.(ClO_4)_2.2H_2O]$	916.92	2:1	13.80	36.70 (36.35)	3.19 (3.46)	4.58 (4.62)	12.80 (12.77)	7.73 (7.47)
Co(II)-L	$[Co_2\ L.(ClO_4)_2.2H_2O]$	917.37	2:1	41.20	36.63 (37.04)	3.19 (3.49)	4.58 (4.67)	12.85 (13.13)	7.73 (7.58)

Table (2): assignment of IR-bands of Schiff base and its metal chelates

Compound	ν cm^{-1}							
	ν(OH)	$\nu(C=O)_{benzopyrone}$	ν(CH=N)	$\nu(COO^{-)})_{symmetric}$	ν(C-O)	δOH	ν M-O	ν M-N
Schiff base L	3398	1651	1611	1350	1180	1111	-	-
Zn(II)-L	3414	1674	1632	1350	1167	1088	533	467
Cu(II)-L	3402	1651	1628	1350	1185	1080	535	459
Ni(II)-L	3413	1662	1632	1327	1146	1092	556	467
Co(II)-L	3377	1677	1620	1330	1139	1088	528	467

Table (3): Magnetic moment and electronic spectral data of the Schiff base L and its complexes:

Compound	λ_{max} (cm^{-1})	μ_{eff} (B.M)
Free ligand (L)	26596	
Zn(II)-L	27247,22522	0.00
Cu(II)-L	24272	
Ni(II)-L	22472	2.28*
Co(II)-L	26738,21978	2.64*

* per metal ion

Table (4): Thermogravimetric analysis data of metal chelates of Schiff base L:

Chelates	M:L	Dehydration stage			Decoordination stage			Metal carbonate residue%		
		Temp. range	% Weight loss		Temp. range	%weight loss		Temp. °C	Calc.	Found
			Calc.	Found		Calc.	Found			
[Zn L.OH.3H_2O].H_2O	1:1	31-69	2.50	2.70	69-207	7.51	7.50	569	17.39	17.10
[Cu L.OH.H_2O].3H_2O	1:1	54-145	7.53	7.32	145-190	2.51	2.31	440	17.23	17.50
[Ni_2 L.$(ClO_4)_2$.2H_2O]	2:1	-	-	-	82-145	3.93	4.01	623	16.29*	16.25*
[Co_2 L.$(ClO_4)_2$.2H_2O]	2:1	-	-	-	29-185	3.93	4.00	525	25.93	26.50

* metal oxide residue

Table (5): fluorescence data of Schiff base (L) and its metal complexes

compound	$\lambda_{(ex)}$	λ_{em}(nm)	F.I.
Free ligand (L)	396	450	108.52
Zn(II)-L	353	433	439.01
		703	297.55
Cu(II)-L	364	443	245.38
		725	43.56
Ni(II)-L	444	474	53.66
Co(II)-L	460	515	64.77

Table (6): Kinetic parameters for photodegradation of Schiff base, L Zn(II)-L and Cu(II)-L:

	By Absorption spectra		By fluorescence spectra	
compound	k (min^{-1})	$t_{1/2}$ (min)	k (min^{-1})	$t_{1/2}$ (min)
Schiff base (L)	$1.68 x 10^{-3}$	412.58	$1.66 x 10^{-3}$	417.56
Zn(II)-L	$5.92 x 10^{-3}$	117.08	$5.86 x 10^{-3}$	118.28
Cu(II)-L	$2.61 x 10^{-3}$	265.57	$2.30 x 10^{-3}$	301.37