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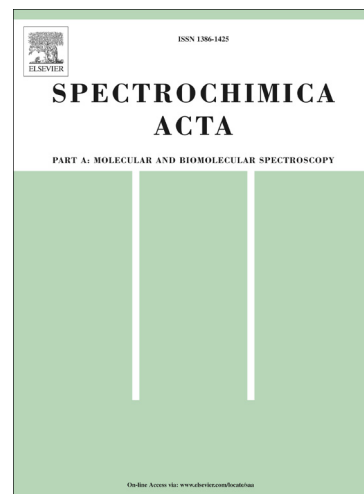
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Spectroscopic and biological activities studies of bivalent transition metal complexes of Schiff bases derived from condensation of 1,4-phenylenediamine and benzopyrone derivatives

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Abstract

Many tools of analysis such as elemental analyses, infrared, ultraviolet-visible, electron spin resonance (ESR) and thermal analysis, as well as conductivity and magnetic susceptibility measurements were used to elucidate the structures of the newly prepared Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from the condensation of 1,4-phenylenediamine with 6-formyl-7-hydroxy-5-methoxy-2-methylbenzo-pyran-4-one (H₂L) or 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one (H₄L). The data showed that all formed complexes are 1:1 or 2:2 (M:L) and non-electrolyte chelates. The Co(II) and Cu(II) complexes of the two Schiff bases were screened for antibacterial activities by the disc diffusion method. The antibacterial activity was screened using *Escherichia coli* and *Staphylococcus capitis* but the antifungal activity was examined by using *Aspergillus flavus* and *Candida albicans*. The Results showed that the tested complexes have antibacterial, except Cu-H₄L, but not antifungal activities.

Keywords: Schiff bases, transition metal complexes, biological activities

1. Introduction

Salen-type ligands, one of the oldest classes of ligands in coordination chemistry, have been used extensively to complex transition metals [1]. The majority of salen ligands reported in the literature are symmetric and available as their N,N'-disubstituted derivatives [2]. Salen-type ligands have been studied widely especially in regard to their use in catalytic synthesis [3, 4]. In addition to, the C=N linkage in azomethine derivatives is an essential structural requirement for biological activity. Several azomethines have been reported to possess remarkable antibacterial [5-9], antifungal [10-12], anticancer [13-16] and diuretic activities [17]. In view of this, we have designed a derivatives of salen type Schiff bases and their complexes. Quite recently, the Schiff bases derived from the condensation of 6-formyl-7-hydroxy-5-

methoxy-2-methylbenzopyran-4-one and 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one with aliphatic diamines (ethylenediamine and trimethylenediamine) and their complexes were previously prepared and characterized [18-21]. In this paper, we report the synthesis and characterization of new transition metal complexes of Co(II), Ni(II) and Cu(II) with Schiff bases derived from condensation of 6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one or 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one and 1,4-phenylenediamine. The complexes have been characterized by several tools of analyses such as elemental analyses, magnetic moment measurements, molar conductance, ESR, IR, UV-Vis spectra as well as thermal gravimetric analysis (TG) have also been studied for some selected metal complexes. The cobalt and copper complexes were assayed by the disc diffusion method for antibacterial and antifungal activity and compared with that of free Schiff bases.

2. Experimental

2.1 Materials and reagents

All chemicals used in this investigation were chemically pure grade (BDH or Aldrich). They included nickel (II) chloride, cobalt (II) acetate, cobalt (II) perchlorate, copper (II) acetate, 1,4-phenylenediamine, 5-methoxy-2-methyl-furanbenzopyran-4-one, potassium dichromate, sulphoric acid, hydrochloric acid. All organic solvents used in this study were either purified by recommended methods [22] or obtained as grade materials from BDH. Doubly distilled H₂O was always used.

2.2. Analysis and physical measurements

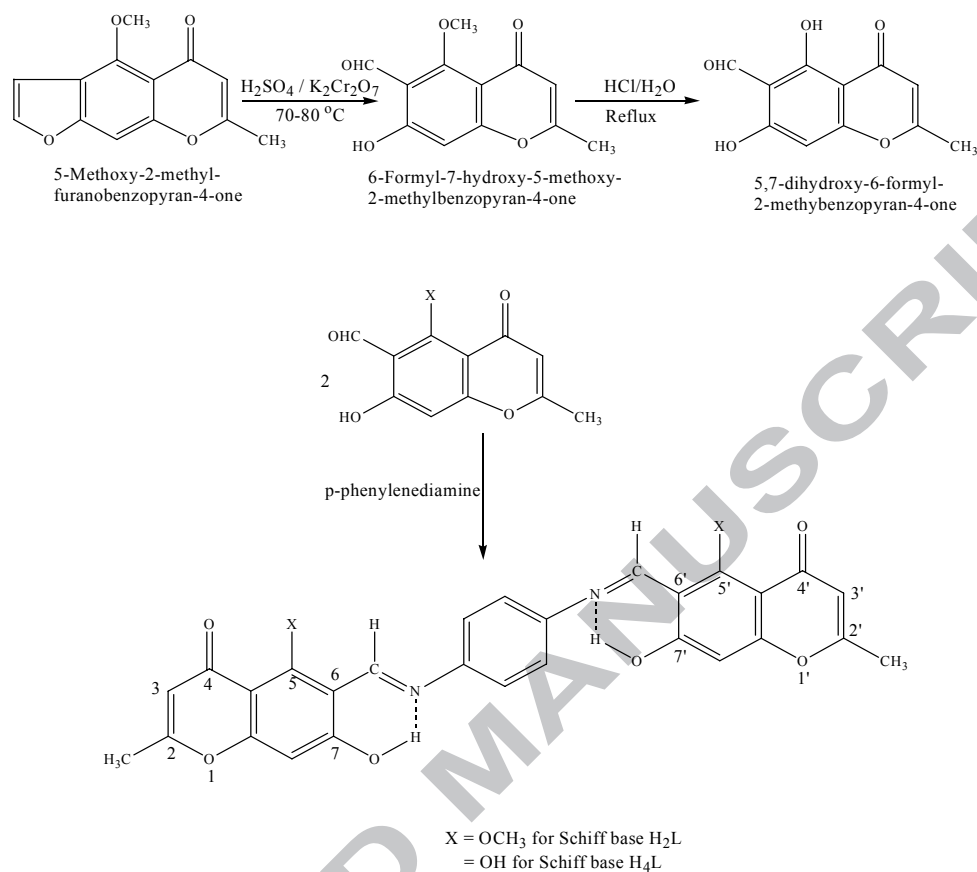
Carbon, hydrogen and nitrogen were analyzed by standard microanalysis methods at Microanalytical center, Cairo University, Giza, Egypt. UV-Vis spectra of the metal complexes in DMF were recorded on UV/Vis-NIR 3101 PC Shimadzu spectrophotometer. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on a Shimadzu FTIR spectrometer. Molar conductivity of 10⁻³ mol/L solutions of the complexes in DMF was measured on the conductivity meter ORION model 150 of 0.6 cell constant. The ESR spectra were recorded for Cu-H₂L and Cu-H₄L on a Bruker EMX spectrometer working with frequency 9.715 GHz and magnetic field set of 3371 E. Thermal analysis has been carried out using Shimadzu-50 Thermal Analyzer from room temperature to 600 °C at a heating rate 10°C min⁻¹. Analysis of the metal ions were carried out by dissolving the complexes in

concentrated nitric acid followed by hydrogen peroxide, neutralizing the diluted aqueous solutions with sodium hydroxide to pH 5.5 and the metal content was determined by recommended method [23] or were determined by the weight of the complex 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 $\mu_{\text{eff}} = 2.828(X_M T)^{1/2}$ B.M., where X_M is the molar susceptibility corrected using Parcel's constants for diamagnetism of all atoms in the compounds [24].

2.3. Synthesis

2.3.1. Synthesis of the Schiff-bases

The Schiff base H₂L was prepared by adding 5 mmole of 20 mL ethanolic solution of 1,4-phenylenediamine gradually with continuous stirring to a solution of 10 mmole of 6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one which prepared from 5-methoxy-2-methylfuranobenzopyran-4-one as previously mentioned [25]. While, the Schiff base H₄L was prepared by addition of 1,4-phenylenediamine (5 mmole) in 20 ml ethanol dropwise with continuous stirring to 10 mmole of ethanolic solution of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one (prepared as previously mentioned [25]). The reaction mixtures were stirred at room temperature for at least 30 min and the solids obtained were filtered off, washed with ethanol and recrystallized from dimethylformamide. Scheme 1 illustrates the synthesis of the Schiff bases H₂L and H₄L.



Scheme 1. Preparation of the Schiff bases

2.3.2. Synthesis of the metal complexes

The solid chelates were prepared by mixing a hot ethanolic solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with the Schiff bases sufficient to form 1:1, 1:2 and 2:1 (M:L) complexes. The reaction mixture was stirred on a water bath. The solid chelates were filtered off and washed several times with second distilled water and ethanol until the filtrate becomes colorless. The obtained complexes were kept in a vacuum desiccator and subjected to elemental analysis.

3. Results and discussion

Elemental analyses and some physical properties of the isolated pure complexes are listed in Table 1. The analytical results demonstrate that all the

prepared complexes have 1:1 or 2:2 (M:L) stoichiometry. The molar conductance measurements in DMF of all the 1:1 (M:L) chelates are in the range 11.7-34.8 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$. These values are lower than those expected for an electrolyte. These observations indicate a non-electrolytic nature of all complexes [26] in DMF at room temperature. The solid complexes are soluble in DMF and DMSO. The structures and properties were also characterized by FT-IR, UV-Vis, ESR spectroscopy, thermal analysis (TGA) and magnetic moment measurements.

3.1. IR spectra

The most important bands occurring in the IR spectra of the free ligands and their complexes have been compared in order to ascertain the bonding sites in the chelating ligands, Table 2. The IR spectra of H₂L and H₄L ligands show a broad band at 3433 and 3430 cm^{-1} due to phenolic OH stretching, respectively. The bands at 1658 and 1340 cm^{-1} are assigned as $\nu(\text{C}=\text{O})$ of benzopyrone carbonyl in position four and $\nu(\text{C}-\text{N})$ vibration, respectively. The stretching vibration for the $(\text{C}=\text{N})$ (azomethine) in the free Schiff bases H₂L and H₄L was observed at 1608 and 1632 cm^{-1} , respectively. H₂L and H₄L ligands display bands at 1167 and 1170 cm^{-1} which can be assigned to C-OH stretching vibration. On the complexation, the band due to $\nu(\text{C}=\text{N})$ in the IR spectrum of H₂L Schiff base exhibit an upward shift by about 9 cm^{-1} in case of Co_a-H₂L. On other hand, this band disappeared in the IR spectra of the complexes of Cu-H₂L, Co_p-H₂L and Ni-H₂L complexes. The $\nu(\text{C}=\text{N})$ stretching shows upward shift by about 12-15 cm^{-1} in the IR spectra of the complexes of H₄L. This reveals that the azomethine group is one of the coordination sites of the Schiff base ligands H₂L and H₄L [27]. This is also confirmed by the appearance of bands in the range 473-486 cm^{-1} due to the formation of the $\nu(\text{M} \rightarrow \text{N})$. The shifting towards higher value for the band due to C-OH stretching vibration in the spectra of complexes confirms the participation of the oxygen anion of the hydroxyl group in position seven in the C-O-M bond. This mode of bonding is supported by the appearance of new absorption band at 547-559 cm^{-1} , which is not observed in the spectrum of the free ligands. This band is assignable to $\nu(\text{M}-\text{O})$ [28]. The band due to the stretching vibration of the carbonyl group in position four of benzopyrane-4-one moiety shows no significant change in all the complexes indicating that the C=O group did not participate in the chelate formation. The IR spectra of all the complexes show new absorption bands in the region 3375-3416 cm^{-1} indicating the presence of the water or ethanol molecules inside the coordination sphere of the

complexes. In addition, the band at 837-830 cm^{-1} in the IR spectra of complexes due to the OH bending of the coordinated water molecules suggests that water molecules are coordinated to the metal ions [28]. Moreover, strong evidence for the presence or absence of water of crystallization and / or coordinated water supported by the thermogram of the complexes. The two bonding sites in case of H_2L and H_4L Schiff bases are the oxygen of the deprotonated hydroxyl groups of benzoprone moiety in position seven and the azomethine nitrogen leading to a stable six membered chelate ring. 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 all complexes except $\text{Co}_p\text{-H}_2\text{L}$ complex. In this complex chloride ion could be detected by elemental analysis and the IR spectrum is indicative of the presence of coordinated perchlorate ion. The presence of a coordinated perchlorate group in the IR spectrum of $\text{Co}_p\text{-H}_2\text{L}$ complex at group is shown by the appearance of bands at 1160, 1035, 945-and 648 cm^{-1} in the IR spectra [29]. The studies reveal that the bis-Schiff bases H_2L and H_4L behave as monobasic bidentate chelating agents through the oxygen of the deprotonated hydroxyl groups in position seven of the benzopyrone moieties and azomethine nitrogen atoms.

3.2. Electronic spectra and magnetic moment studies

The electronic absorption spectra of Schiff bases and their complexes are shown in Figs. 1 and 2. Due to the limited solubility of the complexes in most organic solvents, the electronic spectra are scanned using a saturated solution of dimethylformamide (DMF). The electronic absorption spectra of the two ligands (H_2L and H_4L) exhibit shoulder at 30769 cm^{-1} due to the $\pi \rightarrow \pi^*$ transition within the azomethine ($\text{CH}=\text{N}$) group. This shoulder disappeared in the spectra of complexes as a result of the participation of azomethine nitrogens in coordination. The band appears at 25316 and 25510 cm^{-1} in the electronic spectra of H_2L and H_4L , respectively, is assigned to an intramolecular charge transfer (CT transition) involving the whole molecule. The electronic spectra of all complexes show bands in the range of 25510-27027 cm^{-1} , Table 3, which may be due to a LMCT transition. The measured μ_{eff} values of $\text{Cu-H}_4\text{L}$ is 1.74 BM, this value suggests the square-planar geometry [30]. On the other hand, $\text{Cu-H}_2\text{L}$ complex shows magnetic value of 2.21 B. M., this value is higher than the spin-only value of 1.73 B. M. for one unpaired electron and indicates that this complex is dimeric. In addition, Ni(II) forms complexes with H_2L and H_4L ligands

with different geometries. The observed diamagnetism of Ni-H₂L suggests its square-planar geometry but the magnetic moment of Ni-H₄L complex (3.2 M. B.) lies within the region expected for octahedral geometry. The room temperature magnetic susceptibility measurement shows that the μ_{eff} values are 2.49 and 2.89 BM for Co_p-H₂L and Co_p-H₄L respectively. These values indicate the presence of one unpaired electron for square planar stereochemistry around Co(II) d⁷ complexes [31]. Co(II) acetate with H₂L and H₄L complexes show unusual magnetic moment values (6.36 and 6.07 BM) which could be considered as 2:2 (M:L) complexes where two ligand molecules are coordinated to two metal ions.

3.3. ESR spectra

To obtain further information about the stereochemistry and the metal-ligand bonding and to determine the magnetic interaction in the metal complexes, the powder ESR spectra of Cu-H₂L and Cu-H₄L complexes were recorded at room temperature with frequency 9.715 GHz and magnetic field set of 3371 G. The spin-Hamiltonian parameters of the two complexes were calculated, Table 4. The solid state ESR spectra of the two complexes exhibit axially symmetric g-tensor parameters with $g_{\parallel} >$

$g_{\perp} > 2.003$ indicating that the copper site has a dx²-dy² ground state characteristic of

tetradedral, square planar or octahedral stereochemistry [32]. The values of g_{av} were

calculated according to the equation $g_{\text{av}} = 1/3 (g_{\parallel} + 2g_{\perp})$ and the results are given in

Table 4. The g_{\parallel} value is an important function for indicating the covalent character of M-L bond. Kivelson and Neiman have reported that g_{\parallel} value < 2.3 for covalent character of metal-ligand band and g_{\parallel} value > 2.3 for ionic character. For the two copper complexes, the g_{\parallel} is less than 2.3 revealing an appreciable covalent character for M-L bond [33]. Based on IR, electronic spectra and ESR data, Cu-H₂L complex has octahedral structure but Cu-H₄L complex has square planar structure. In the axial

symmetry, the g -values are related by the expression $G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$ where G is the exchange interaction parameter. According to Hathway [34], if the value of G is greater than 4, the exchange interaction is negligible in the solid state, whereas, when is less than 4, considerable exchange interaction is indicated in the solid state complex. A forbidden magnetic dipolar transition for Cu-H₂L complex is observed at half-field (c.1500 G, $g = 4.0$) but the intensity is very weak. Its spectrum is similar to that of binuclear Cu(II) complexes [35]. The appearance of a half-field signal confirms the magnetic interaction between the two Cu(II) ions in 2:2 (M:L) Cu-H₂L complex; this is not observed in Cu-H₄L complex, which is mononuclear. Superhyperfine structure for this complex is not observed at a high-field excluding any interaction of the nuclear spins of the nitrogen ($I = 1$) with the unpaired electron density on Cu(II). The exchange interaction parameter, G , in Cu-H₂L complex is less than four (3.3), suggesting that a copper-copper exchange interaction exist. The low magnetic moment, 2.21 B. M., for the binuclear Cu-H₂L complex indicates the presence of strong exchange interaction in the solid state. The G value for Cu-H₄L complex is greater than four (4.15) suggests the absence of exchange coupling between Cu(II) center in the solid state [32].

3.4. Thermogravimetric analysis (TG) of the solid complexes

The results of the thermal analysis of the complexes are given in Table 5. Thermal studies have been carried out using a thermogravimetric TG technique. The experimental mass losses were calculated from the TG curves and the calculated ones were obtained from the suggested formula based on the obtained data of the elemental analyses. Fig. 3 illustrates the thermal behavior of the some chelates. All complexes were thermally decomposed within the temperature 25-600 °C.

The TG curve of Co_a-H₂L complex shows the first degradation step within the temperature range 50-130 °C with an estimated mass loss of 5.56% (calc. 5.69%) corresponding to the loss of four molecules of lattice water. But the TG curve of Co_a-H₄L displays 8.33% (calc. 8.67%) mass loss in the temperature range 50-180 °C which corresponding to the loss of six water molecules of hydration. Thermal degradation of the organic molecule of the two complexes starts above 240 °C. Further heating of the two complexes result in continuous mass-loss till a constant mass where the CoO residue is formed as a final product.

The TG curve of Co_p-H₂L chelate exhibits 5.00% mass loss in the temperature range 50-130 °C, which correlated to two water molecules outside the coordination sphere. The mass loss in the range 130-330 °C is attributed to the loss of one coordinated ethanol molecule. Thermal degradation of the organic molecule starts above 340 °C. Complete decomposition of the organic molecule ending at 595 °C with formation of CoO as a final product.

For Ni-H₄L chelate the mass loss occurring at 8.00% (calc. 8.07%) corresponds to the loss of three coordinated water molecules in the temperature range 150-300 °C. The organic part of the complex decomposes in two steps with the formation of intermediates which finally decompose to the stable NiO at 597 °C.

3.5. Kinetics of thermal decomposition of the complexes

The kinetic and thermodynamic parameters of the thermal degradation process were calculated from the integral method proposed by Coats-Redfern model [36]. The Horowitz and Metzger [37] equation $C_s = (n)^{1/n}$, where C_s is the weight fraction of the substance present at DTG peak temperature, T_s , was used for the determination of the value of the reaction order, and given by

$$C_s = \frac{(m_i - m_{\infty})}{(m_o - m_{\infty})}$$

Where: m_s is the remaining weight at T_s , m_o and m_{∞} are the initial and final weights of the substance, respectively.

Coats-Redfern equation for $n = 1$:

$$\log \left[\frac{-\log(1-x)}{T^2} \right] = \log \left(\frac{AR}{\beta E_a} \right) \left(1 - \frac{2RT}{E_a} \right) - \left(\frac{E_a}{2.303 RT} \right)$$

Where β is the heating rate, x is the fraction decomposed, A is Arrhenius pre-exponential, R is the universal gas constant, T is the absolute temperature and E_a is the activation energy. The term $\left(\frac{AR}{\beta E_a} \right) \left(1 - \frac{2RT}{E_a} \right)$ is practically constant and the value of $\left(1 - \frac{2RT}{E_a} \right) \approx 1$. Hence, a plot of $\log \left[\frac{-\log(1-x)}{T^2} \right]$ vs. $\frac{1000}{T}$ gave a straight line with a slope equal $\left(\frac{-E_a}{2.303 RT} \right)$ in which activation energy can be calculated and an intercept equal $\log \left(\frac{AR}{\beta E_a} \right)$ in which Arrhenius pre-exponential factor can be also calculated.

The estimated values of C_s for the thermal decomposition of the complexes were found in the range of 0.35-0.37 (Table 6). Thus indicates that the decomposition of a series of H₂L and H₄L complexes was suggested to be first order, $n=1$, [38]. So

the values of the activation energy (E_a), Arrhenius constant (A), the activation entropy (S^*), the activation enthalpy (H^*) and the free energy of activation (G^*) are calculated by applying Coats-Redfern equation for $n=1$ and given in the Table 6 where:

$$H^* = E - RT$$

$$S^* = R \ln[Ah/KT]$$

$$G^* = H^* - TS^*$$

From the obtained results, it is apparent that G values of the complex acquire highly positive magnitudes. The high value of the energy of activation of the complexes revealed the high stability of the investigated complexes due to their covalent character [39]. The positive sign of ΔG revealed that the free energy of the final residue is higher than that of the initial compound and all the decomposition steps are non-spontaneous processes. The lowest value for ΔG of Co_p-H_2L indicates that this ion has the highest tendency for interaction with the ligand. The enthalpy values are positive for the investigated complexes supporting that a high temperature is favourable for the complexation and the process is endothermic. The negative values of ΔS for the degradation process indicates that more ordered activated complex than the reactants and the decomposition reaction is slow [40]. The correlation coefficient of the Arrhenius plots of the thermal decomposition steps were found to be in the range 0.98-0.99 which indicates good fitness of the linear function.

4. Antimicrobial activity of some complexes

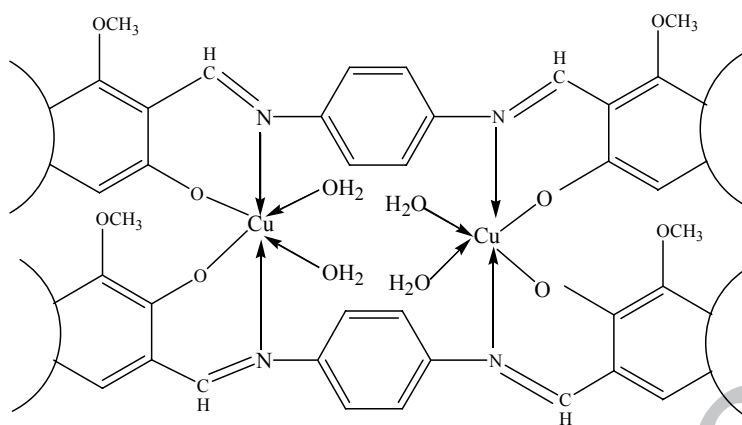
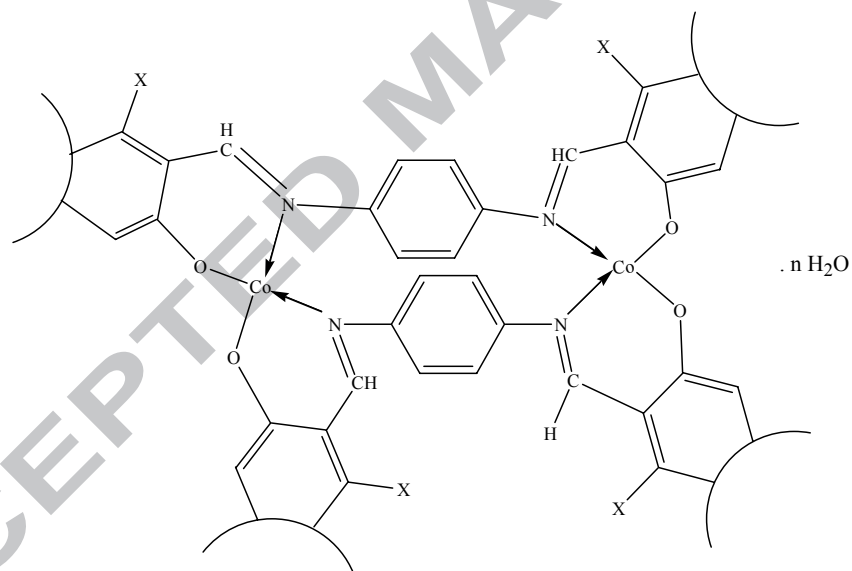
In azomethine derivatives, the C=N linkage is an essential structural requirement for biological activity. The free Schiff bases H_2L and H_4L were screened for antibacterial activities by micro-plate assay technique [25]. *Escherichia coli* and *Staphylococcus capitis* were exposed to different concentrations of the Schiff bases. As mentioned previously [25] the antibacterial effect of these Schiff bases on Gram-negative were higher than that on Gram-positive bacteria moreover, the Schiff base H_2L which contain OCH_3 on position five has higher antibacterial activity than H_4L that contain OH group on the same position [25]. These Schiff bases have no antifungal activity. In the present study, the antimicrobial activities Cu(II) and Co(II) acetate complexes of these two Schiff bases were carried out in order to enhance their antimicrobial effect according to the conventional agar diffusion method by tetracycline as a standard [41,42] using *Staphylococcus aureus* as Gram-positive and *Escherichia coli* as Gram-negative bacteria, *Aspergillus flavus* (aflatoxin

producing fungus) and *Candida albicans*. The antibacterial inhibition zone values are summarized in Table 7. As shown in the table the tested complexes have no antifungal activity. Co_a-H₂L complex has the highest antibacterial activity, on the other hand, Cu-H₄L complex don't have any bacterial activity on the tested microorganisms. So the complexation lowered the efficiency of the Schiff bases as antibacterial agents where the free Schiff bases have higher antibacterial effect [25] than the complexes.

5. Conclusion

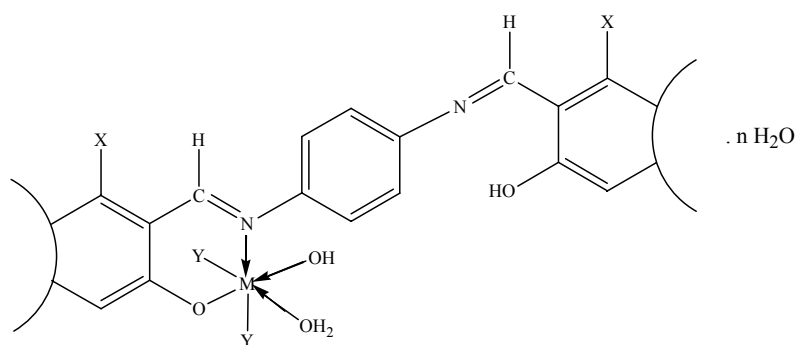
Cu(II), Ni(II) and two different salts of Co(II), cobalt (II) acetate and cobalt (II) perchlorate, metal complexes of Schiff bases derived from the condensation of 1,4-phenylenediamine with 6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one (H₂L) or 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one (H₄L) were prepared and characterized by different spectroscopic techniques and TG and molar conductance and magnetic moment measurements. The metal complexes exhibited different geometrical arrangements such as square planar and octahedral arrangements. In case Cu-H₂L, Co_a-H₂L and Co_a-H₄L, two ligand molecules are coordinated to two metal ions (2:2; M:L). The antimicrobial activities Cu(II) and Co(II) acetate complexes of the two Schiff bases were carried out. The tested complexes have no antifungal activity. Co_a-H₂L complex has the highest antibacterial activity, on the other hand, Cu-H₄L complex don't have any bacterial activity on the tested microorganisms.

The geometric structure, schemes 2-4, of the prepared complexes can be shown as follows:

Scheme 2. The proposed structure of Cu-H₂L complex

| Complex | X | n |
|-----------------------------------|------------------|---|
| Co _a -H ₂ L | OCH ₃ | 4 |
| Co _a -H ₄ L | OH | 6 |

Scheme 3. The proposed structure of Co_a-H₂L and Co_a-H₄L complexes



| Complex | X | Y | n |
|-----------------------------------|------------------|------------------|---|
| Ni-H ₂ L | OCH ₃ | - | 0 |
| Ni-H ₄ L | OH | H ₂ O | 0 |
| Cu-H ₄ L | OH | - | 0 |
| Co _p -H ₄ L | OH | - | 2 |

Scheme 4. The proposed structure of Ni-H₂L, Ni-H₄L, Cu-H₄L and Co_p-H₄L and complexes

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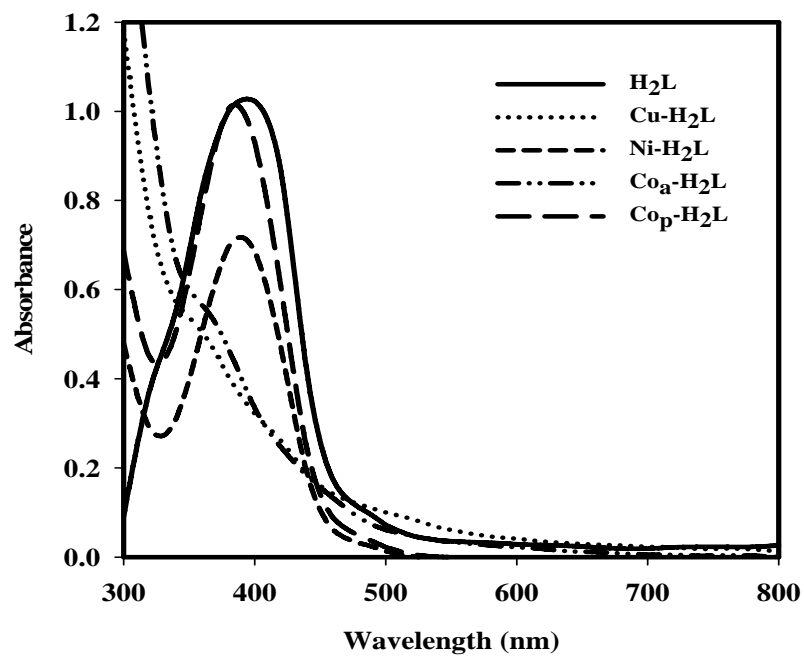


Fig. 1. Electronic absorption spectra of H₂L ligands and its complexes

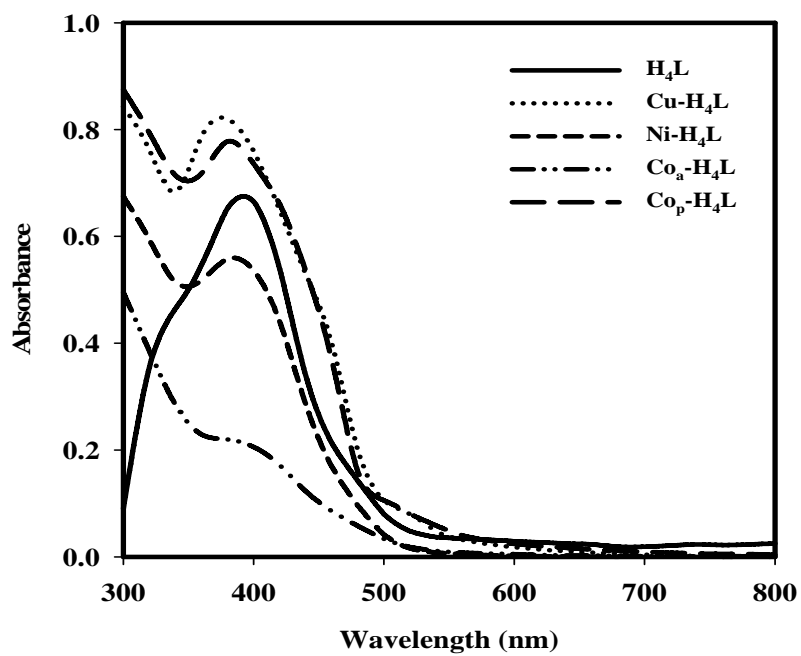


Fig. 2. Electronic absorption spectra of H₄L ligands and its complexes

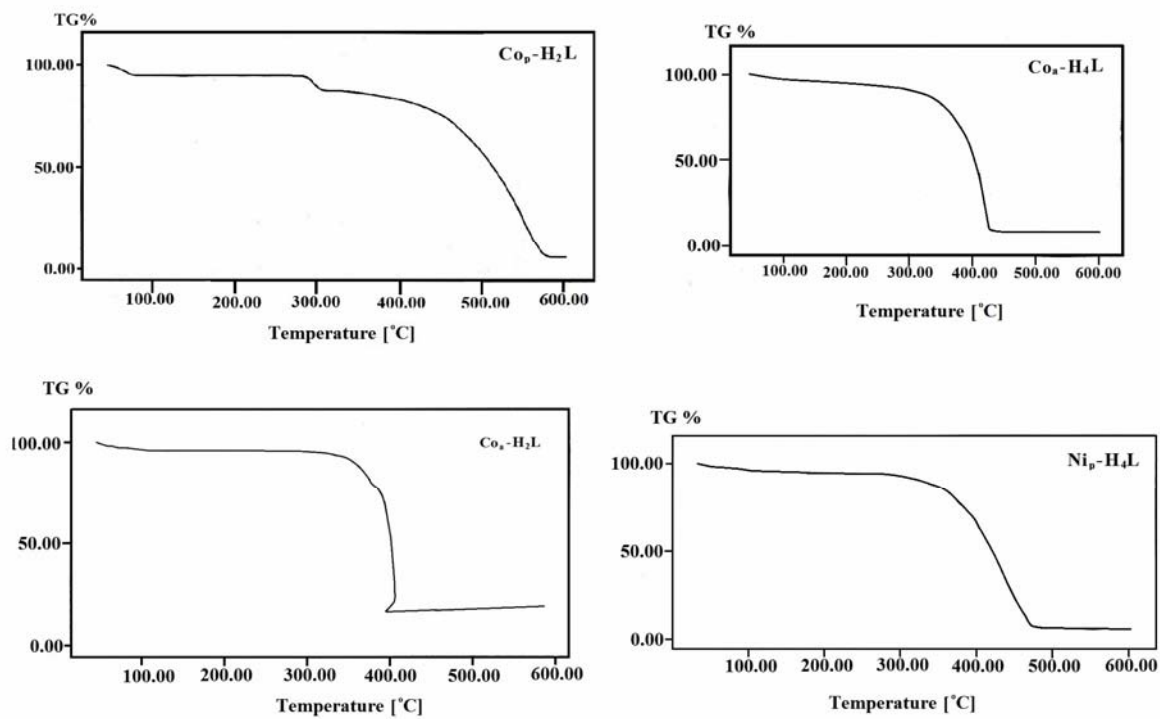


Fig. 3 TG plot of $\text{Co}_p\text{-H}_2\text{L}$, $\text{Co}_a\text{-H}_2\text{L}$, $\text{Co}_a\text{-H}_4\text{L}$ and $\text{Ni}_p\text{-H}_4\text{L}$ complexes

Table 1: Analytical and physical data of the metal complexes of Schiff bases

| Ligand or complex | Symbol | Formula | Molar conductance $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ | (Calc.) Found | | | | |
|---|-----------------------------------|--|--|------------------|----------------|----------------|----------------|----------------|
| | | | | % C | % H | % N | % M | % Cl |
| H ₂ L | H ₂ L | C ₃₀ H ₂₄ O ₈ N ₂ | - | 66.32 (66.66) | 4.40 (4.48) | 4.95 (5.18) | - | - |
| [Cu(L)(H ₂ O) ₂] ₂ | Cu-H ₂ L | C ₆₀ H ₅₂ Cu ₂ N ₄ O ₂₀ | 32.6 | 56.88 (56.47) | 3.67 (4.08) | 4.20 (4.39) | 9.89 (9.97) | - |
| [Co _a (L)] ₂ .4H ₂ O | Co _a -H ₂ L | C ₆₀ H ₅₂ Co ₂ N ₄ O ₂₀ | 19.0 | 55.35 (56.88) | 4.06 (4.11) | 4.20 (4.43) | 9.17 (9.31) | - |
| [Co _p (HL)(ClO ₄) _{1/2} (C ₂ H ₅ OH)].2H ₂ O | Co _p -H ₂ L | C ₃₂ H ₅₁ CoN ₂ O ₁₅ Cl | 15.4 | 52.25 (52.63) | 4.65 (4.52) | 4.20 (3.84) | 7.86 (7.39) | 2.71 (2.43) |
| [Ni(HL)OH(H ₂ O)] | Ni-H ₂ L | C ₃₀ H ₂₆ NiN ₂ O ₁₀ | 32.2 | 57.00 (56.99) | 4.60 (4.11) | 4.68 (4.43) | 9.07 (9.28) | - |

The metal salt used in the preparation was: a = metal acetate, p = metal perchlorate

Table 1 continued

| | | | | | | | | |
|--|-----------------------------------|--|------|------------------|----------------|----------------|------------------|---|
| H ₄ L | H ₄ L | C ₂₈ H ₂₀ N ₂ O ₈ | - | 65.69 (65.62) | 3.79 (3.93) | 5.37 (5.47) | - | - |
| [Cu(H ₃ L)OH(H ₂ O)] | Cu-H ₄ L | C ₂₈ H ₂₂ CuN ₂ O ₁₀ | 34.8 | 55.13 (55.12) | 3.82 (3.61) | 4.46 (4.59) | 10.01 (10.42) | - |
| [Co _a (H ₂ L)] ₂ .6H ₂ O | Co _a -H ₄ L | C ₅₆ H ₄₈ Co ₂ N ₄ O ₂₂ | 11.7 | 53.80 (53.93) | 3.85 (3.85) | 4.90 (4.49) | 9.61 (9.46) | - |
| [Co _p (H ₃ L)OH(H ₂ O)].2H ₂ O | Co _p -H ₄ L | C ₂₈ H ₂₆ CoN ₂ O ₁₂ | 19.7 | 53.40 (52.42) | 4.15 (4.06) | 4.50 (4.37) | 9.00 (9.19) | - |
| [Ni(H ₃ L)OH(H ₂ O)] ₃ | Ni-H ₄ L | C ₂₈ H ₂₆ NiN ₂ O ₁₂ | 22.0 | 52.90 (52.25) | 3.95 (4.06) | 4.50 (4.37) | 8.64 (9.16) | - |

Table 2: Important IR bands of the ligands and their metal complexes

| Compounds | $\nu(\text{H}_2\text{O})$ $\nu(\text{OH})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}-\text{N})$ | $\nu(\text{C}-\text{O})$ | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{N})$ |
|---|---|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| H_2L | 3433 | 1602 | 1658 | 1340 | 1187 | - | - |
| $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]_2$ | 3416 | - | 1658 | 1315 | 1235 | 559 | 484 |
| $[\text{Co}_a(\text{L})]_2 \cdot 4\text{H}_2\text{O}$ | 3383 | 1611 | 1653 | 1264 | 1229 | 558 | 486 |
| $[\text{Co}_p(\text{HL})(\text{ClO}_4)_{1/2}(\text{C}_2\text{H}_5\text{OH})] \cdot 2\text{H}_2\text{O}$ | 3501 | - | 1658 | 1302 | 1226 | 547 | 473 |
| $[\text{Ni}(\text{HL})\text{OH}(\text{H}_2\text{O})]$ | 3380 | - | 1658 | 1304 | 1227 | 549 | 473 |
| H_4L | 3430 | 1632 | 1656 | 1341 | 1170 | - | - |
| $[\text{Cu}(\text{H}_3\text{L})\text{OH}(\text{H}_2\text{O})]$ | 3404 | 1627 | 1655 | 1343 | 1267 | 556 | 474 |
| $[\text{Co}_a(\text{H}_2\text{L})]_2 \cdot 6\text{H}_2\text{O}$ | 3361 | 1619 | 1663 | 1344 | 1222 | 555 | 474 |
| $[\text{Co}_p(\text{H}_3\text{L})\text{OH}(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ | 3379 | 1620 | 1656 | 1341 | 1223 | 553 | 470 |
| $[\text{Ni}(\text{H}_3\text{L})\text{OH}(\text{H}_2\text{O})_3]$ | 3381 | 1619 | 1657 | 1342 | 1267 | 553 | 473 |

Table 3: Electronic absorption bands and magnetic moments of the Schiff bases and their metal chelates

| Compounds | ν cm ⁻¹ | BM |
|-----------------------------------|------------------------|------|
| H ₂ L | 30769, 25316 | - |
| Cu-H ₂ L | 27027 | 2.21 |
| Ni-H ₂ L | 25706 | 0.00 |
| Co _a -H ₂ L | 26882 | 6.36 |
| Co _p -H ₂ L | 25906 | 2.49 |
| H ₄ L | 30769, 25510 | - |
| Cu-H ₄ L | 26809 | 1.74 |
| Ni-H ₄ L | 25706 | 3.21 |
| Co _a -H ₄ L | 25510 | 6.07 |
| Co _p -H ₄ L | 26109 | 2.89 |

Table 4: Electron spin resonance data of Cu (II) complexes

| Complex | g_{\parallel} | g_{\perp} | g_{av} | G |
|---------------------|-----------------|-------------|----------|------|
| Cu-H ₂ L | 2.09 | 2.03 | 2.06 | 3.13 |
| Cu-H ₄ L | 2.18 | 2.04 | 2.09 | 4.15 |

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Table 5: Thermal behavior of some solid chelates with Schiff bases

| Complexes | Symbol | M:L | Dehydration stage | | | Decoordination stage | | | Metal oxide residue % | | |
|---|----------------------------------|-----|-------------------|---------------|-------|----------------------|---------------|-------|-----------------------|-------|-------|
| | | | Temp. range | % weight loss | | Temp. range | % weight loss | | Temp. °C | Calc. | Found |
| | | | | Calc. | Found | | Calc. | Found | | | |
| $[\text{Co}_a(\text{L})]_2 \cdot 4\text{H}_2\text{O}$ | $\text{Co}_a\text{-H}_2\text{L}$ | 2:2 | 50-130 | 5.69 | 5.56 | - | - | - | 570 | 11.84 | 11.66 |
| $[\text{Co}_p(\text{HL})(\text{ClO}_4)_{1/2}(\text{C}_2\text{H}_5\text{OH})] \cdot 2\text{H}_2\text{O}$ | $\text{Co}_p\text{-H}_2\text{L}$ | 1:1 | 50-130 | 4.93 | 5.00 | 130-330 | 6.30 | 6.11 | 595 | 10.26 | 10.00 |
| $[\text{Co}_a(\text{H}_2\text{L})]_2 \cdot 6\text{H}_2\text{O}$ | $\text{Co}_a\text{-H}_4\text{L}$ | 2:2 | 50-180 | 8.67 | 8.33 | - | - | - | 596 | 12.03 | 12.22 |
| $[\text{Ni}(\text{H}_3\text{L})\text{OH}(\text{H}_2\text{O})_3]$ | $\text{Ni-H}_4\text{L}$ | 1:1 | - | - | - | 150-300 | 8.07 | 8.00 | 597 | 11.17 | 11.00 |

Table 6: Kinetic data of the thermal decomposition of some H₂L and H₄L metal chelates

| Complex | Symbol | Decomposition Temp. (K) | E _a (KJmol ⁻¹) | A (S ⁻¹) | H* (KJmol ⁻¹) | S* (Jmol ⁻¹ K ⁻¹) | G* (KJmol ⁻¹) | Cs | Correlation Coefficient r ² |
|---|-----------------------------------|----------------------------|--|-------------------------|------------------------------|---|------------------------------|------|--|
| Co _a (L) ₂ .4H ₂ O | Co _a -H ₂ L | 493-673 | 122.31 | 5.03 E ⁸ | 116.77 | -85.04 | 173.40 | 0.36 | 0.98 |
| [Co _p (HL)(ClO ₄) _{1/2} (C ₂ H ₅ OH)].2H ₂ O | Co _p -H ₂ L | 573-853 | 71.79 | 3.33 E ⁶ | 67.07 | -125.40 | 138.18 | 0.37 | 0.98 |
| [Co _a (L) ₂ .6H ₂ O | Co _a -H ₄ L | 513-698 | 72.77 | 3.53 E ⁵ | 67.09 | -145.62 | 166.55 | 0.37 | 0.99 |
| [Ni(H ₃ L)OH(H ₂ O) ₃] | Ni-H ₄ L | 613-723 | 83.11 | 1.53 E ⁵ | 77.28 | -152.77 | 184.36 | 0.35 | 0.99 |

Table 7: Biological activities of Cu(II) and Co(II) complexes of two Schiff bases

| Sample | Inhibition zone diameter (mm/mg sample) | | | |
|---------------------------------------|---|--|------------------------------------|----------------------------------|
| | <i>Escherichia coli</i> (G ⁻) | <i>Staphylococcus aureus</i> (G ⁺) | <i>Aspergillus flavus</i> (Fungus) | <i>Candida albicans</i> (Fungus) |
| Control: DMSO | 0.0 | 0.0 | 0.0 | 0.0 |
| Tetracycline (Antibacterial agent) | 31.0 | 29.0 | - | - |
| Amphotericin B (Antifungal agent) | - | - | 19.0 | 21.0 |
| Cu-H ₂ L | 10.0 | 12.0 | 0.0 | 0.0 |
| Co _a -H ₂ L | 13.0 | 12.0 | 0.0 | 0.0 |
| Cu-H ₄ L | 0.0 | 0.0 | 0.0 | 0.0 |
| Co _a -H ₄ L | 12.0 | 11.0 | 0.0 | 0.0 |

Research highlights

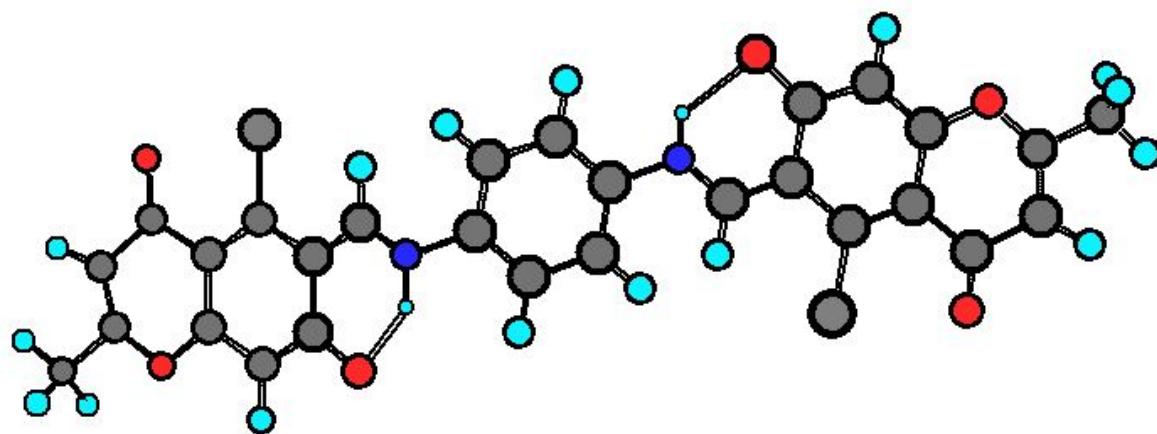
The structure of the prepared complexes was studied using many tools of analysis.

The metal complexes exhibit different geometrical arrangements.

All formed complexes are 1:1 or 2:2 (M:L) and non-electrolyte chelates.

The tested complexes show antibacterial activity.

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Benzopyran-4-one derivative

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