



Original Research Article

Synthesis, Characterization, and Biological Activity Study of Some New Metal Ions Complexes with Schiff Base Derived from Vanillin and Ethylenediamine

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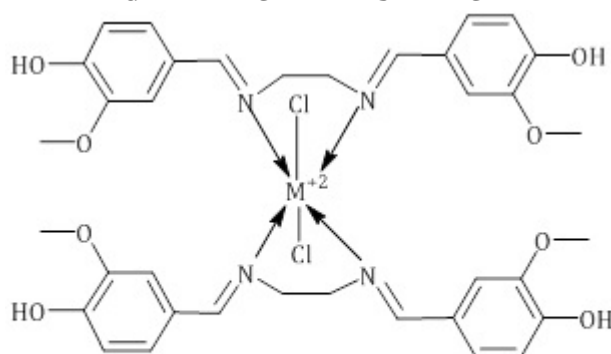
Vanillin

Metal complexes

ABSTRACT

This study describes preparation a new series of complexes from metal ions Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with Schiff base (L) derived from condensation of vanillin with ethylenediamine. Structures of the ligands were identified using IR, UV-Vis, Mass, elemental analysis and ¹H-NMR techniques. All prepared complexes have been identified by recording the melting points, conductivity, FT-IR, UV-Vis spectroscopy, metal analysis by atomic absorption, elemental analysis (CHNO) and measuring magnetic and. All compounds studies biological activity (*E. Coli*, *Staphylococcus aureus*, *Candida albicans* and *Aspergillus niger*), the activity of bacteria was examined and the results showed that their mineral complexes have good antibacterial activities.

GRAPHICAL ABSTRACT



M=Mn, Co, Ni, Cu, Zn

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Introduction

There has recently been considerable interest in chemical complexes with N donors. The increased activity of the Schiff base mineral in this area can be attributed to the striking structural properties and the antimicrobial activity of these donor bonds and the complexes derived from them, which contain N donor atoms and show an extensive bioassay of special atoms, interest in diversity, Chelating activity and the methods by which it binds to metal ions [1-6]. Schiff's bases can be produced by reacting primary amine condensates with carbonyl compounds and contain azomethine ($-C=N$ group) [7-13]. Schiff bases have been used extensively in many fields of biological [14], inorganic domain [15], drug synthesis [16] and as a cross-link in the field of coordination chemistry [17,], which has given rise to many studies from pure synthetic ventures to physicochemical studies. They are essential chelating ligands with a wide range of active uses. [18]. Schiff bases form an important class of drugs [19] and pharmaceutical chemistry, electrochemical processes such as antioxidant agents [20]; it can also be used as numerous biological antibacterials, including, antifungal, antitumor [21,22], anticancer [23-25], antiinflammatory [26,27], antituberculosis [28], antiviral, analgesic [29], antimicrobial [30], agriculture applications insecticides, fungicides, herbicides [31]. The biological activity of Schiff's base derivatives complexes stands out against some Gram-positive and Gram-negative bacteria [32-34].

Material and methods

All chemicals and solvents used were of Analar (AR) grade and were purchased from Sigma-Aldrich companies. Vanillin, ethylenediamine, $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, dimethyl formamide (DMF), methanol solution, ethanol, glacial acetic acid, and dry ether were used.

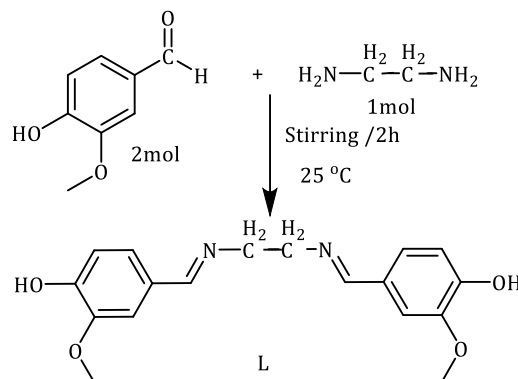
Equipment

The micro-analysis data (CHNO) were performed on Euro-vector EA/3000, single-V.3.0-single. Standard methods were used to estimate metal ion intake. The Fourier Transform Infrared Spectrophotometer was used to obtain FT-IR

spectra in the ranges ($4000-200\text{ cm}^{-1}$) in Japan. At $25\text{ }^\circ\text{C}$ and a concentration of 110^{-3} M , conductance measurements were taken with the conductometer WTW. DMF was used to dissolve all of the complexes. UV-Spectrophotometer, Japan (Shimadzu UV-1800) UV-visible spectrometer in the range of $200-1100\text{ nm}$ was used to obtain electronic spectra of the ligands and their complexes.

Synthesis of Schiff Base

In the separation funnel, we place a (1 mol) of ethylene diamine in 10 ml ethanol was slowly added (dropping) by a separation funnel with stirring at room temperature to (2 mol) to (2 mol) of vanillin (dissolving in 20ml ethanol round bottom flask) after color changed to yellow. Stirring lasted for 2 hours, the forming of the yellow precipitate, rinsed off with ethanol (10 ml) dried in an oven for 1 hour (render = 65%), certain characteristics are given in Table 1 and the reaction is shown as scheme 1.



Scheme 1: Synthesis of Schiff base

Synthesis of complexes

$Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ chloride solution, ions (1Mole) in 10ml methanol were combined immediately with the ship base L solution in the same solvent. For all complexes, the molar ratio of metal: ligand was 1:2. The aforementioned combination was removed for 24 hours, the product was filtered, and the material was dried in the air to obtain the crystals. Some attributes are shown in Table 1.

Stoichiometric Determination of Complexes [1]

The continuous variation (JOB) method was used to make sure about the correlation ratio between ions and ligand in equilibrium media.

Table 1: L and Metal Yield percentages and CHNO analysis

| Compound | Yield% | Analysis (calculated) | | | | | |
|-------------------------------------|--------|-----------------------|----------------|----------------|------------------|----------------|----------------|
| | | C% | H% | N% | O | Cl | M |
| Ligand (L) $C_{18}H_{20}N_2O_4$ | 70 | 66.58 (65.84) | 6.07 (6.14) | 8.21 (8.53) | 19.14 (19.49) | ----- | ----- |
| Mn(L) ₂ Cl ₂ | 72 | 53.23 (53.83) | 5.41 (5.32) | 7.49 (7.39) | 17.09 (16.87) | 7.29 (7.24) | 9.49 (9.35) |
| Co (L) ₂ Cl ₂ | 66 | 55.99 (55.44) | 5.35 (5.41) | 6.93 (6.99) | 15.73 (15.97) | 7.26 (7.35) | 8.74 (8.85) |
| Ni(L) ₂ Cl ₂ | 70 | 53.05 (53.57) | 5.46 (5.29) | 7.53 (7.35) | 16.52 (16.79) | 7.91 (7.70) | 9.48 (9.30) |
| Cu (L) ₂ Cl ₂ | 69 | 53.79 (53.23) | 5.02 (5.26) | 7.37 (7.30) | 16.32 (16.68) | 8.07 (8.28) | 9.43 (9.24) |
| Zn(L) ₂ Cl ₂ | 71 | 53.67 (53.10) | 5.01 (5.24) | 7.26 (7.29) | 16.38 (16.64) | 8.38 (8.50) | 9.31 (9.22) |

Result and Dissection

FT-IR Spectra of Ligand

The method for synthesis of (L) is illustrated in Scheme 1 and 2. The FT-IR spectra of the ligand showed the disappearance of the bundles of the (C=O) of the aldehyde in the region of (1693) cm^{-1} and the amino group (-NH₂) in the region (3358-

3284) cm^{-1} and the emergence of new beams, which were the bundles of the right group, and the absorption beams of the imine group of the prepared ligand were in the range (1631) cm^{-1} , belonging to the azomethene group [35]. Figure 1 and Table 2 display the values of the infrared spectra of the prepared ligand.

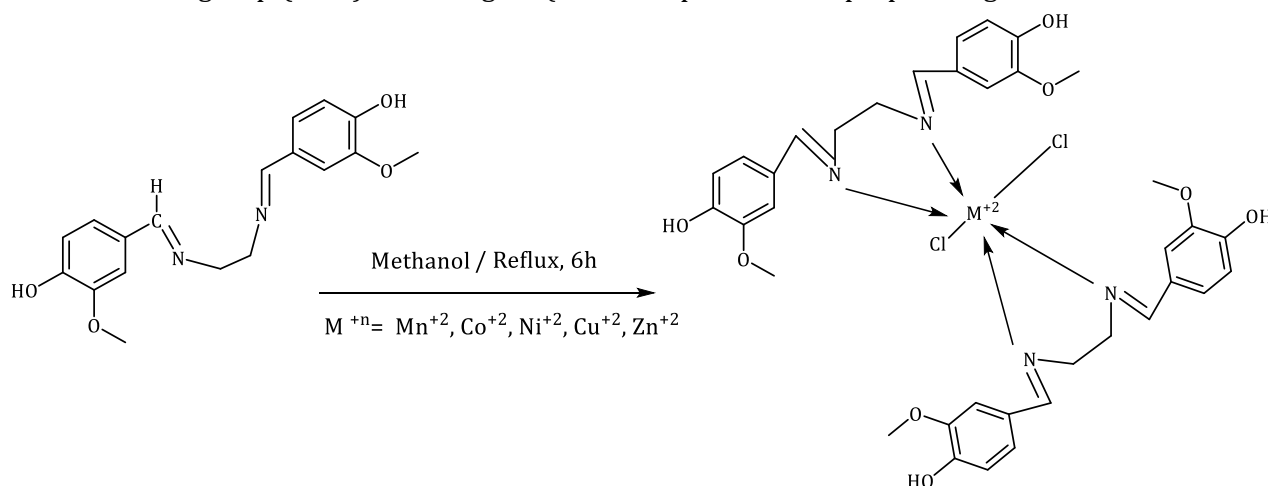
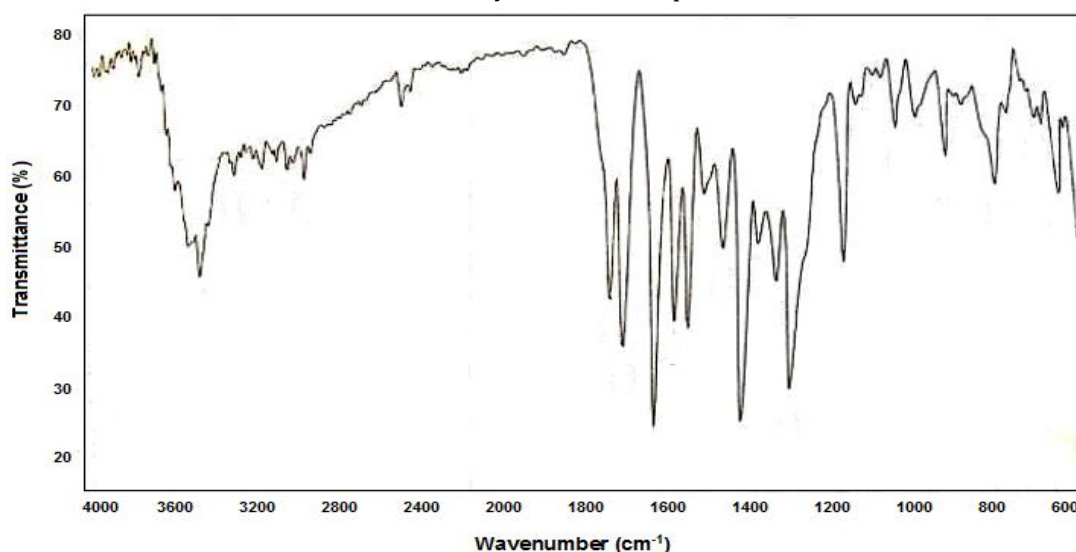
**Scheme 2:** Synthesis of complexes**Figure 1:** IR spectra for Ligand L

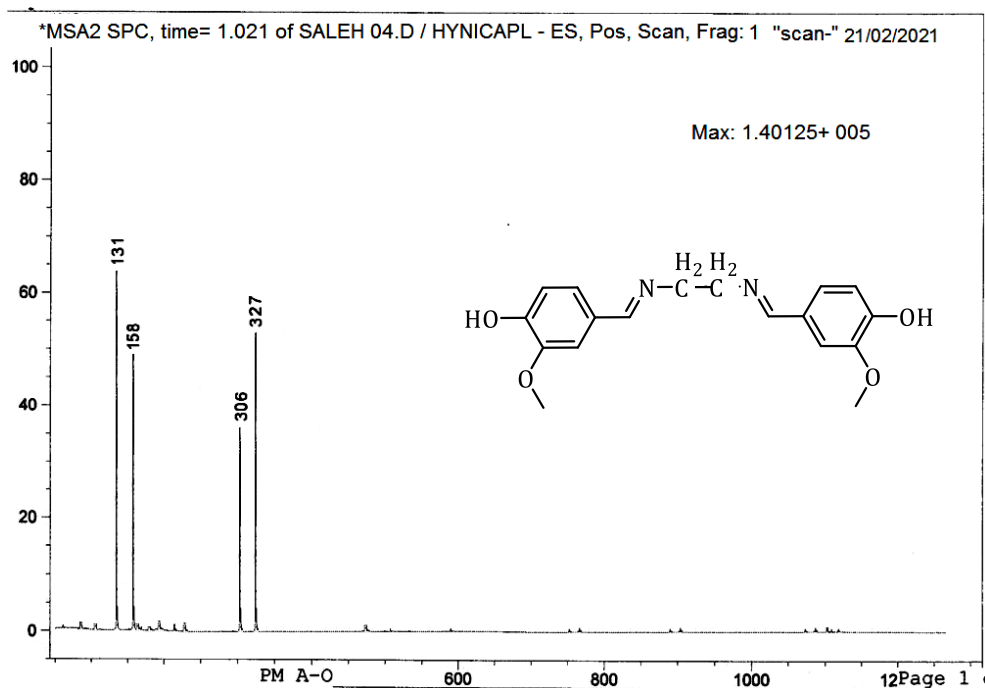
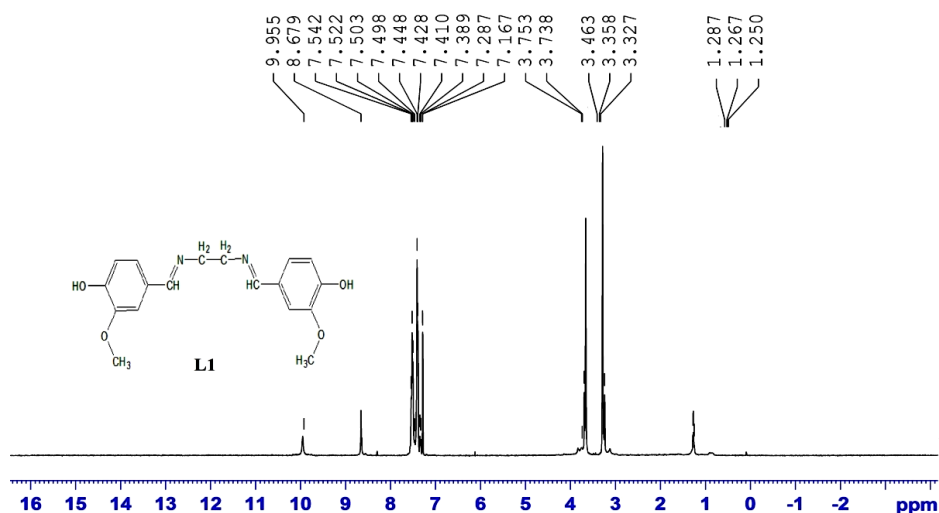
Table 2: FT-IR data of Ligand and its metal complexes (cm⁻¹)

| Compound | $\nu(\text{C}=\text{N})$ | νOH | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{Cl})$ |
|--|--------------------------|-----------------|--------------------------|---------------------------|
| Ligand (L) $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$ | 1631(s) | 3414(b) | - | |
| $\text{Mn}(\text{L})_2\text{Cl}_2$ | 1647(s) | 3408(b) | 434(w) | 381(m) |
| $\text{Co}(\text{L})_2\text{Cl}_2$ | 1667(s) | 3476(b) | 428(m) | 320(m) |
| $\text{Ni}(\text{L})_2\text{Cl}_2$ | 1673(s) | 3413(b) | 418(m) | 320(m) |
| $\text{Cu}(\text{L})_2\text{Cl}_2$ | 1672(s) | 3450(b) | 416(m) | 306(m) |
| $\text{Zn}(\text{L})_2\text{Cl}_2$ | 1650(s) | 3477(b) | 453(m) | 360 |

Mass spectral data and ¹H-NMR

Figure 2 shows Mass spectroscopy (LC-MS) using (SIM) technology, which defines the molecular mass of material to be studied at m/z 337.0 (M^+)/($\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$)⁺ without fragmentation of the base ship ligand detected, which is in line with

anticipated values of $m/z=328$ refer. Figure 3 shows ¹H-NMR (CDCl_3 -400MHz) $\delta=$ 9.955 (s, 2H, 2*OH), 8.679 (s, 2H, 2*CH=N), 7.176-7.547 (m, 6H, 2*Ar-H), 3.738-3.753 (s, 4H, 2*CH₂), 3.327-3.463 (s, 1H, 2*OCH₃), 1.25-1.27 (solvent+H₂O).

**Figure 2:** LC-mass spectra for Ligand L**Figure 3:** ¹H NMR spectra for Ligand L

Spectra of complexes (FT-IR)

All chemical FT-IR spectrum allocations are given in Table 2. In the L (1631) cm^{-1} complex the imine group (C=N) band moved to the highest frequencies of all complexes indicating nitrogen connections, from (C=N) with the metal [36]. A new band in the range (306-381) cm^{-1} emerged because of vibrations in the group stretch [37], with a group stretch (M-N) in the bordered area between (416-434 cm^{-1}) which confirmed that the metal is associated with the (N) atom [1]. The table shows the infrared spectrum values for the complexes (2).

Electronic Spectra, Magnetic Moments and Molar Conductance of Complexes

Most of the complexes of the transition elements show absorbance at certain wavelengths of the spectrum, because most of these complexes are colored. The electron spectrum of the prepared complexes was recorded in the range (200–1100 nm) using DMF solvent [18].

The distinction between the UV-Vis spectra of ligand with complexes shows a displacement was observed. It ranged between (10-20) nm and there was a difference between the spectra of the solutions of ligand and the metal ion, as well as

the clear difference in the colors of the mixing solutions from the solutions of the ligand and the metal ion before mixing, which is clear evidence of a coordination between them [38]. Table 3 and Figure 4 give the all-electronic spectral, magnetic moments, and Molar Conductance data of the prepared compounds. The results of the magnetic susceptibility gave values for the magnetic moment which correspond to the suggested shape.

Measuring the inhibitory effect of compounds on bacteria

All the available ligand and the metal chelates were tested against *Staphylococcus aureus*, *E.coli*, *Candida albicans* as well as *Aspergillus niger* in antibacterial and anti-fungal activities. The bulk of the composites have therefore shown biological activity against gram-positive bacteria and gram-negative bacteria. The compounds were highly inhibited against gram-positive *S. aureus*, while activities with gram-negative *Candida albicans* with the highest concentration (20 mg/mL) of the most widely used compound were shown to be relatively lower in comparison with *E. coli*, *Staphylococcus aureus*, and *Aspergillus niger* (Table 4 and Figure 5).

Table 3: Some physical data electronic spectra for (L) and complexes in DMF

| Compound | Mp&Dec. Point °C | Conductivity $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ 25 °C | Magnetic Moment (B.M) | Color | Absorption Bands (nm) | Assigned Transition |
|-------------------------------------|---------------------|--|-----------------------------|--------------------|--------------------------|---|
| Ligand (L) | 229-230 | 4 | - | yellow | 284 | $\pi \rightarrow \pi^*$ |
| | | | | | 405 | $n \rightarrow \pi^*$ |
| Mn(L) ₂ Cl ₂ | 224 d | 17 | 5.82 | dark yellow | 24096 | Charge Transfer |
| Co (L) ₂ Cl ₂ | 230 d | 25 | 4.7 | light green | 10277 | $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$ (F) |
| | | | | | 16000 | $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$ (p) |
| | | | | | 23529 | Charge Transfer |
| Ni(L) ₂ Cl ₂ | 232 d | 12 | 3.2 | yellowish green | 10638 | $^3\text{A}_{2g}$ (F) \rightarrow $^3\text{T}_{2g}$ (F) |
| | | | | | 13986 | $^3\text{A}_{2g}$ (F) \rightarrow $^3\text{T}_{1g}$ |
| | | | | | 20000 | $^3\text{A}_{2g}$ (F) \rightarrow $^3\text{T}_{1g}$ (P) |
| Cu(L) ₂ Cl ₂ | 294 d | 8 | 1.9 | olive | 15037, 16129 | $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ |
| Zn (L) ₂ Cl ₂ | 241 d | 8 | Dia | yellow | 26600 | Charge Transfer |

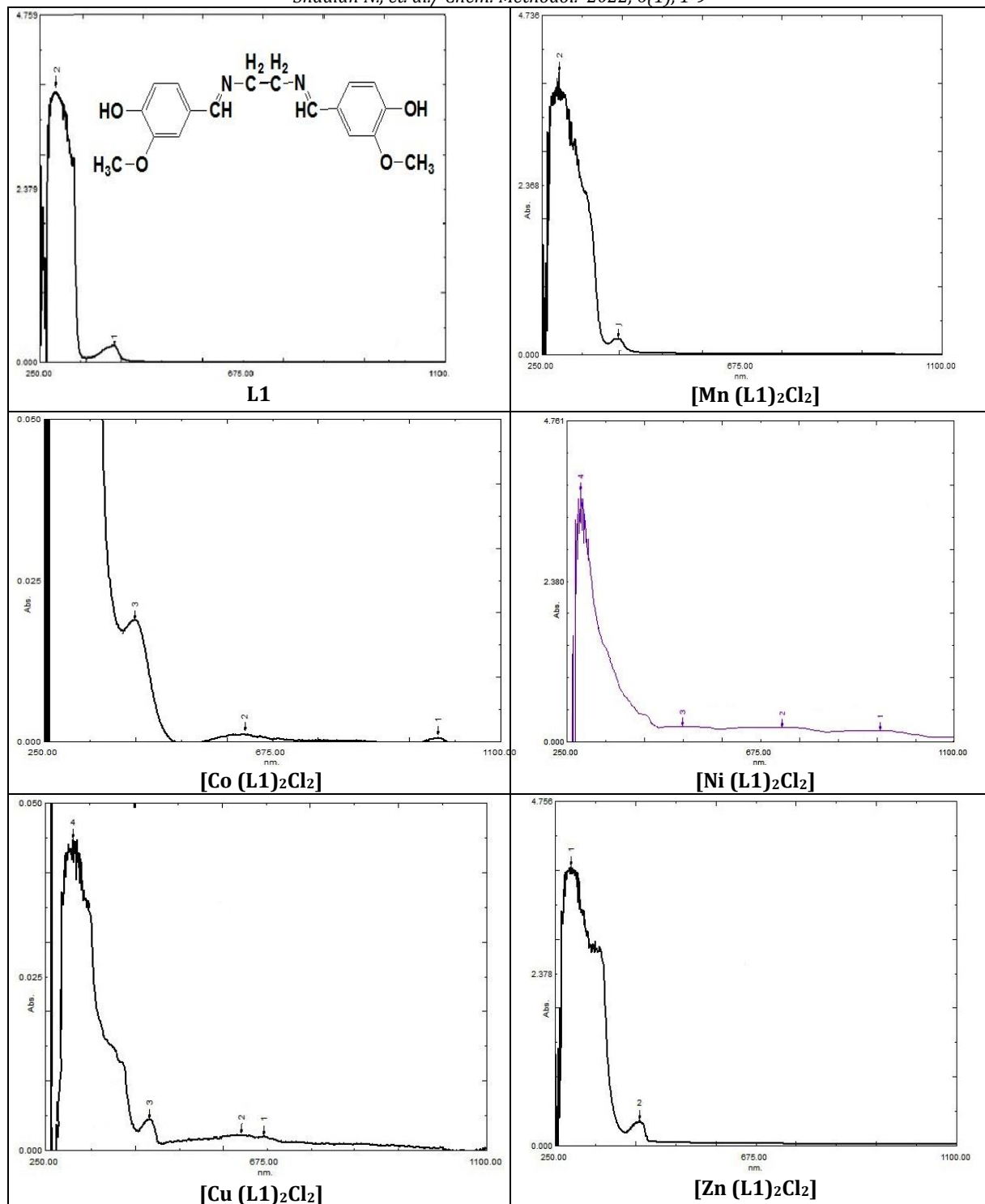
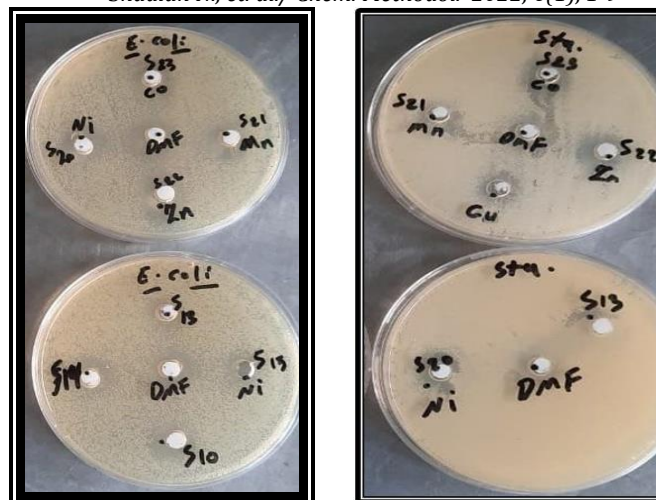


Figure 4: UV-VIS spectra for L and complexes

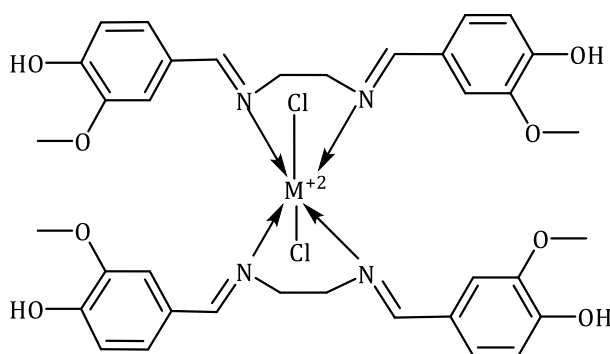
Table 4: Antibacterial activity of Schiff base ligand and complexes

| Sample | E. coli | Staphylococcus aureus | Candida albicans | Aspergillus niger |
|-------------------------------------|----------------------|-----------------------|------------------|-------------------|
| | Inhibition Zone (mm) | | | growth Zone (mm) |
| Ligand (L) | | | | |
| Mn (L) ₂ Cl ₂ | 13 | 10.6 | 7 | 17 |
| Co (L) ₂ Cl ₂ | 13 | 18 | 9 | 17 |
| Ni (L) ₂ Cl ₂ | 15 | 13 | 15 | 11 |
| Cu (L) ₂ Cl ₂ | 12 | 15 | 12 | 13 |
| Zn (L) ₂ Cl ₂ | 12 | 14 | 11 | 17 |
| DMF | 11 | 0 | 10 | 9 |



(Staph and coli-E)

Figure 5: Antibacterial activity of Schiff base ligand and complexes



M=Mn, Co, Ni, Cu, Zn

Figure 6: Suggested structure for complexes

Conclusion

We have observed new ligand compounds and their complexes from the first series of the transition of metals. The collected data demonstrated that the ligand behaves like didentate ligand of N_2 . From the electronic spectra, infrared spectrum and magnetic measurements, it is inferred that most of all complexes contain hexa coordinates and have octahedral geometry (Figure 6). Molar conductivity measurements of the prepared complexes indicate complexes with neutral base (non electrolyte),

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Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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