

**Synthesis, Characterization and Biological Activity Studies of New Metal Ion Complexes With Schiff Base Derived from (Z)-3-Hydrazineylidene-1-Phenylpyrazolidine and Evaluating Them as Antioxidants**

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## RESEARCH ARTICLE

# Synthesis, Characterization and Biological Activity Studies of New Metal Ion Complexes With Schiff Base Derived from (Z)-3-Hydrazineylidene-1-Phenylpyrazolidine and Evaluating Them as Antioxidants

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## ABSTRACT

The research includes the preparation of several complexes of the transition elements and zinc where M(II) = Co, Ni, Cu, and Zn, containing the 3d shell, with ligand (LH) was synthesized by treating the (Z)-3-hydrazineylidene-1-phenylpyrazolidine and Salicylaldehyde. Ligand (LH) was identified using FT-IR spectra, <sup>1</sup>H-<sup>13</sup>C-NMR, UV-Vis spectroscopy, elemental microanalysis CHN and mass spectrometry. The complexes were studied and identified with elemental microanalysis CHN, FT-IR spectroscopy, UV-Vis spectroscopy, conductivity measurement, and magnetic sensitivity. The result showed that, these complexes were classified as homogeneous tridentate complexes with the formula [M(LH)(H<sub>2</sub>O)<sub>2</sub>Cl] or [M(LH)<sub>2</sub>]. xH<sub>2</sub>O. The physical measurements indicated that the prepared complexes are non-electrolyte and showed that the ligand is tridentate when coordinated with metal ions through the nitrogen of azomethine (-C=N-), oxygen atom of (O-H) and the nitrogen(N-H) of Pyrazolidinone octahedral geometry for all complexes with good yield. This study emphasized the importance of using a metal complexation method to stabilize ligands and increase their bioactivity. The biological screening of the complexes demonstrates that the Schiff base metal complexes exhibit remarkable efficacy in combating microorganisms, by utilizing *Pseudomonas*, *E. coli*, *strepto* and *staph* as bacterial strains using doxycycline, tetracycline, clindamycin, rifampin, clarithromycin, levofloxacin, amikacin, ceftriaxone, vancomycin, ampicillin as reference to determine Pharmacological resistance to negative and positive bacteria. Hence, their results were good in inhibition. Then, the potential of these prepared compounds as antioxidants was determined by inhibiting free radicals using DPPH as a free radical.

**Keywords:** Biological activity, 1-Phenyl-3-Pyrazolidinone, Evaluation as antioxidants, Salicylaldehyde, Schiff bases complexes

## Introduction

The Schiff bases are important chemical compounds that have been widely studied because of their biological activity.<sup>1</sup> Firstly, it was reported by the German scientist Hugo Schiff.<sup>2</sup> Where it leads condensation of primary amines and active carbonyl groups can result in the formation of Schiff's bases.<sup>3</sup>

They are also known as imines with the general structure R<sub>1</sub>-CH=N-R<sub>2</sub>, where R<sub>1</sub> and R<sub>2</sub> are linear or cyclic alkyl or aryl groups that may be differently substituted.<sup>4</sup> The Schiff rule is one of the links that is consistent with metal ions across the azomethine nitrogen and is formed from primary amines with the carbonyl group of aldehydes (RHC=O) or ketones (R<sub>2</sub>C=O).<sup>5</sup> Whereas the aromatic aldehydes

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with active electron exchange are more stable than the aliphatic aldehydes because aliphatic aldehydes are easy to polymerize. Schiff bases considered it is a significant family of ligands that have been thoroughly explored<sup>6,7</sup> and particularly those that include heterocyclic compounds containing the azomethine group, as they have basic characteristics since the azomethine ( $-C = N$ ) nitrogen atom has an electron pair on it, and they frequently have pentagonal or hexagonal rings with the metal ion.<sup>8</sup> The provision of electron-rich couples, such as N, O atoms, to transitional metals has made them even more important because of their physical, chemical, biological, therapeutic, and other activities.<sup>9</sup> Schiff bases, or their reduced counterparts, have a considerable chelating affinity for metal ions, which allows them to stabilize a variety of transition metal complexes.<sup>10</sup> Schiff base derivatives are used in industry and medicine for a broad range of applications, including pharmaceuticals. They can also be viewed as raw materials for the production of necessary medications, such as anti-cancer, anti-tumor, and antibiotics. These Schiff bases react with hydrazine hydrate to generate amine compound.<sup>11</sup> and they have been utilized as chemicals, analytical guides, and anti-corrosion agents. The new Schiff base ligand synthesized in this study, the reaction of the organic substance 1-Phenyl-3-Pyrazolidinone, known as phenidone, with hydrazine, where 1-Phenyl-3-Pyrazolidinone has the preventive effect of many types of neurotoxic disease and neuroinflammation.<sup>12</sup> In this work is used as a ligand to give sites that can be donors for the formation of complexes with Co (II), Ni (II), Cu (II), and Zn (II). All of the ligand's complexes have been completely described.

## Materials and methods

### Materials

The chemicals used in this study are: 1-Phenyl-3-Pyrazolidinone (Sigma Aldrich), hydrazine hydrate (Sigma Aldrich), salicylaldehyde (Sigma Aldrich), Dimethyl formamide (DMF),  $NiCl_2 \cdot 6H_2O$ ,  $CuCl_2 \cdot 2H_2O$ ,  $CoCl_2 \cdot 6H_2O$ , and  $ZnCl_2$ .

### Instrumentation

The melting point of the prepared compounds was measured by a Stuart (SMP10) electrothermal melting point apparatus. Using an infrared spectra device of type (Shimadzu-8000S) and disc (KBr) for ligand and (CsI) for complexes, in the range ( $4000-200$ )  $cm^{-1}$ . The John Mathey device was used to measure magnetic sensitivity. Mass compensation is also based on the mass100p\_Shimadzu contribution. A

Bruker 400-MHz-meter was used for the reported  $^1H$ -NMR, and a Perkin\_Elmer\_automatic instruments model\_240B was used for the elemental microanalysis. A Shimadzu\_(A-A)\_680G AA\_spectrometer was used to determine the composition of the minerals. The WTW meter was used in order to ascertain the molar conductivity, and the Shimadzu UV-Vis equipment was utilized in order to acquire the UV-visible spectra, ultraviolet spectrophotometer A 160, covering the wavelength range of 190.00–1100 nm.

## Methods

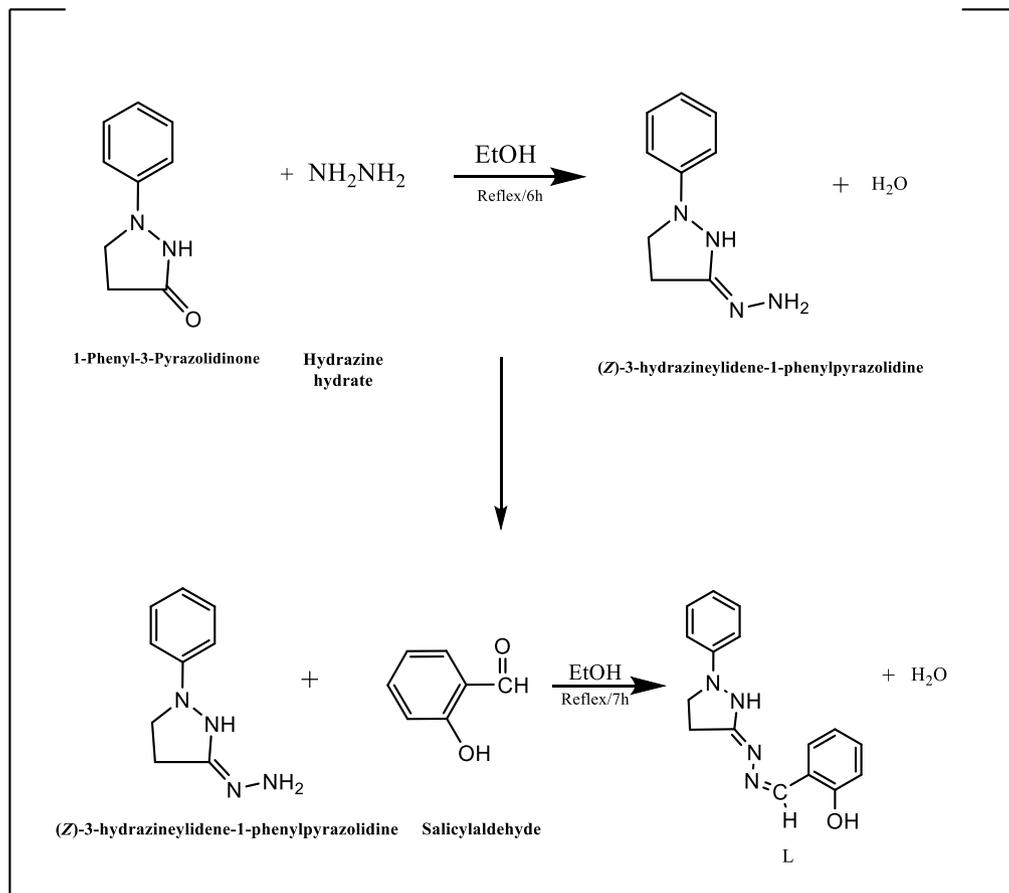
### Ligand-preparation steps

Step 1: (2 g, 0.01233 mole) of 1-Phenyl-3-Pyrazolidinone was dissolved in 10 ml of absolute ethanol and (10 ml, 0.19976 mole) of hydrazine hydrate was added by dropping and stirring continuously to a mixture and followed by an addition of 3 drops of glacial acetic acid. The mixture stays at a boil, refluxing at  $80^\circ C$ , until it homogenizes for 6 hours. After the reaction ends, the mixture was filtered and washed with ethanol and dry ether. The product was recrystallized with a mix of 40:60 methanol: ethanol and after being filtered and dried for 24 hours, [Scheme 1](#).

Step 2: (1.53 g, 0.00788 mol) from compound A was dissolved in 10 ml of ethanol absolute, and then (0.9623 ml, 0.00788) mol of salicylaldehyde was added, followed by an addition of three to five drops of glacial acetic acid, and stirred until all the ingredients are mixed. The reaction's mixture was stirred for 7 hours throughout the reflexing process. After the reaction is over, the mixture was filtered and washed with ethanol and dry ether, and the material is left to dry at room temperature. The re-crystallized powder had a melting point (M.P) of  $165-168^\circ C$  and a yield of 81% [Scheme 1](#):

### Preparation of the metal complex from the prepared ligand

(0.1 g, 0.000335 mol) of the ligand was dissolved in a 250 ml flask with a circular bottom in 10 ml of methanol and 5 drops (DMF), pure 99%. And then (0.0797 g, 0.000335 mol) of metal was dissolved in 10 ml of methanol based on the equivalent weights per salt as in [Table 1](#). And it mixed with the ligand before that, a few drops of triethylamine were added and stayed in reflux process for 7 hours. The change in color of the mixture indicates that the complex is prepared. The mixture is left to stabilize at the temperature of the room after the reaction is over. And then which it is filtered and washed using dry

**Table 1.** Equivalent weights of metal salts.

| Complex symbol                             | Salt formula                         | M. wt. for salt | Quantity in grams |
|--|--------------------------------------|-----------------|-------------------|
| [Co(LH) <sub>2</sub> ].H <sub>2</sub> O    | CoCl <sub>2</sub> .6H <sub>2</sub> O | 237.93          | 0.0797            |
| [Ni(LH) <sub>2</sub> ].2H <sub>2</sub> O   | NiCl <sub>2</sub> .6H <sub>2</sub> O | 237.69          | 0.1193            |
| [Cu(LH)(H <sub>2</sub> O) <sub>2</sub> Cl] | CuCl <sub>2</sub> .2H <sub>2</sub> O | 170.48          | 0.0571            |
| [Zn(LH)(H <sub>2</sub> O) <sub>2</sub> Cl] | ZnCl <sub>2</sub>                    | 136.29          | 0.0684            |

**Table 2.** Physical properties of the Ligand and complexes.

| Compound formula                                      | Color          | m.p. °C | M. wt. | Yield% |
|---|----------------|---------|--------|--------|
| LH/[C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O] | White bright   | 165–168 | 280.33 | 81     |
| [Co(LH) <sub>2</sub> ].H <sub>2</sub> O               | glowing yellow | 218–220 | 635.59 | 59     |
| [Ni(LH) <sub>2</sub> ].2H <sub>2</sub> O              | Light green    | 300d    | 653.37 | 55     |
| [Cu(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]            | Dark brown     | 300d    | 414.35 | 76     |
| [Zn(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]            | White          | 288–290 | 416.18 | 71     |

ether and cold distilled water. And it left it to dry, then the melting point is measured.

## Results and discussion

The reaction between one mole of (Z)-3-hydrazineylidene-1-phenylpyrazolidine and one mole of Salicylaldehyde resulted in the excellent yielding production of the tridentate ligand. The produced ligands and their complexes were identified by the use of infrared spectrum, microscopic examination of the elements, the proton NMR spectrum (just for ligand), Mass Spectroscopy (just for ligand), and the molar conductivity. Some physical properties of the Ligand and complexes in Table 2.

### Microanalysis of the elements

Carbon-hydrogen and nitrogen micro-elemental analysis was performed on all prepared compounds and the results of these analyses are in Table 3. The values obtained in practice with the theoretically calculated values were a significant convergence between them, which confirms the correctness of the proposed formula for complexes.<sup>13</sup>

### <sup>1</sup>H-NMR Spectral of Schiff Bases Ligand

Nuclear magnetic resonance spectroscopy is a method for determining the chemical surroundings of

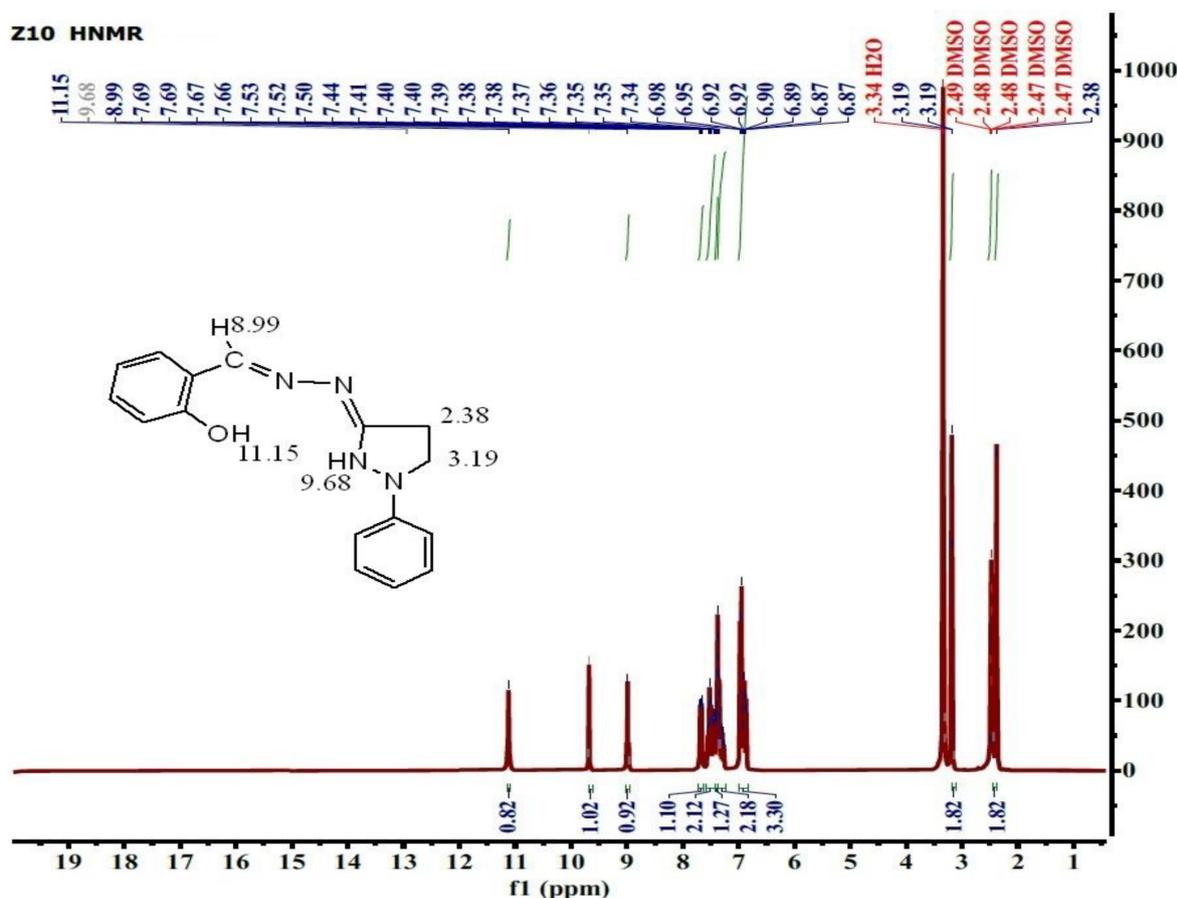
**Table 3.** C HN analysis of Compounds.

| Compound  | Analysis (calculated) |             |               |            |              |
|---|-----------------------|-------------|---------------|------------|--------------|
|   | C%                    | H%          | N%            | Cl         | M            |
| LH/[C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O] | 68.9 (68.55)          | 5.46 (5.75) | 19.45 (19.99) | -          | -            |
| [Co(LH) <sub>2</sub> ].H <sub>2</sub> O               | 59.66(60.47)          | 4.94(5.07)  | 16.89(17.63)  | -          | 10.13(9.27)  |
| [Ni(LH) <sub>2</sub> ].2H <sub>2</sub> O              | 58.53(58.83)          | 5.12(5.25)  | 16.27(17.15)  | -          | 9.69(8.98)   |
| [Cu(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]            | 45.81(46.38)          | 4.57(4.62)  | 12.36(13.52)  | 8.03(8.56) | 14.65(15.34) |
| [Zn(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]            | 46.72(46.18)          | 4.76(4.60)  | 12.52(13.46)  | 7.93(8.52) | 14.43(15.71) |

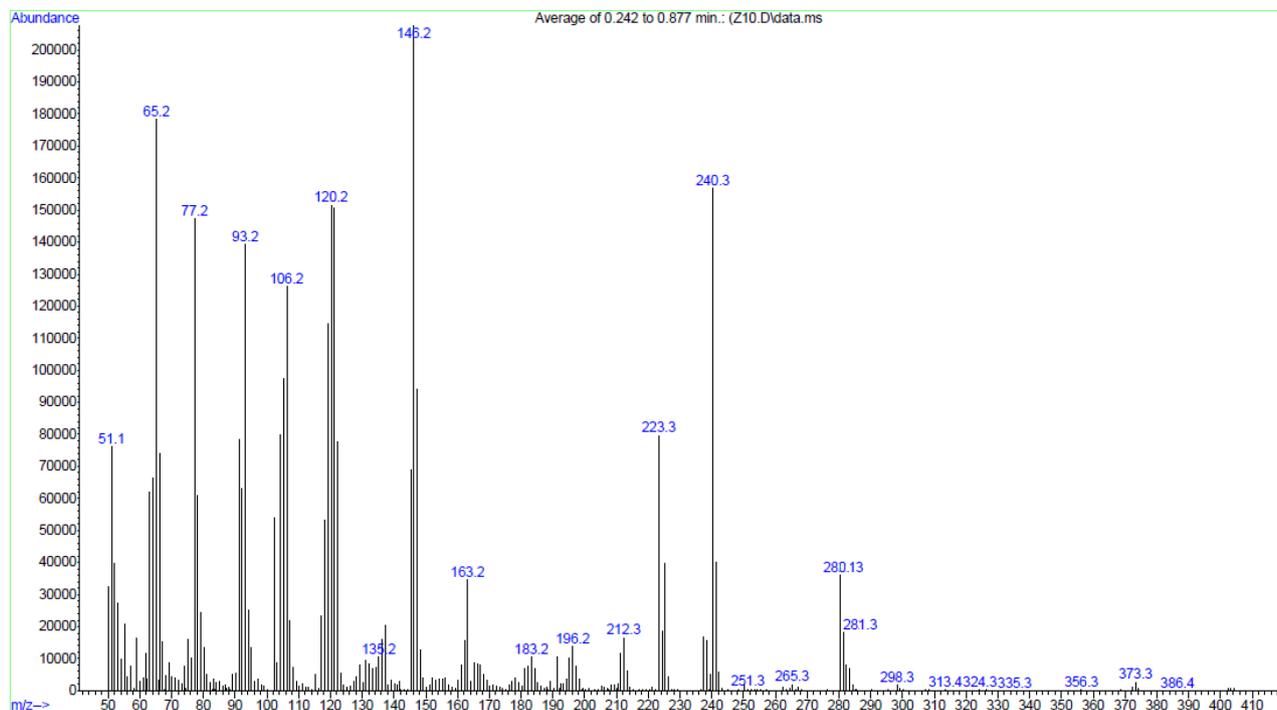
organic compounds. The <sup>1</sup>H-NMR spectra of the ligand (L) in dimethyl sulfoxide (DMSO-d<sup>6</sup>) Fig. 1. The <sup>1</sup>H-NMR spectrum revealed all of the peaks required to confirm the chemical structure of the ligand that was produced (L). A triplet peak observed at 2.38 & 3.19 ppm for 2CH<sub>2</sub> for pyrazolidine ring. The protons of the aromatic ring unit multiplate peaks appeared at regions between 6.87 ppm to 7.69 ppm.<sup>14</sup> The proton of azomethine group (HC=N) shows a singlet peak at 8.99 ppm.<sup>15</sup> A single peak can be observed at 9.68 ppm in (N-H) pyrazolidine ring, will the proton of hydroxyl group (O-H) show a singlet peak at a 11.15 ppm.<sup>16,17</sup>

### Mass spectral of schiff bases ligand

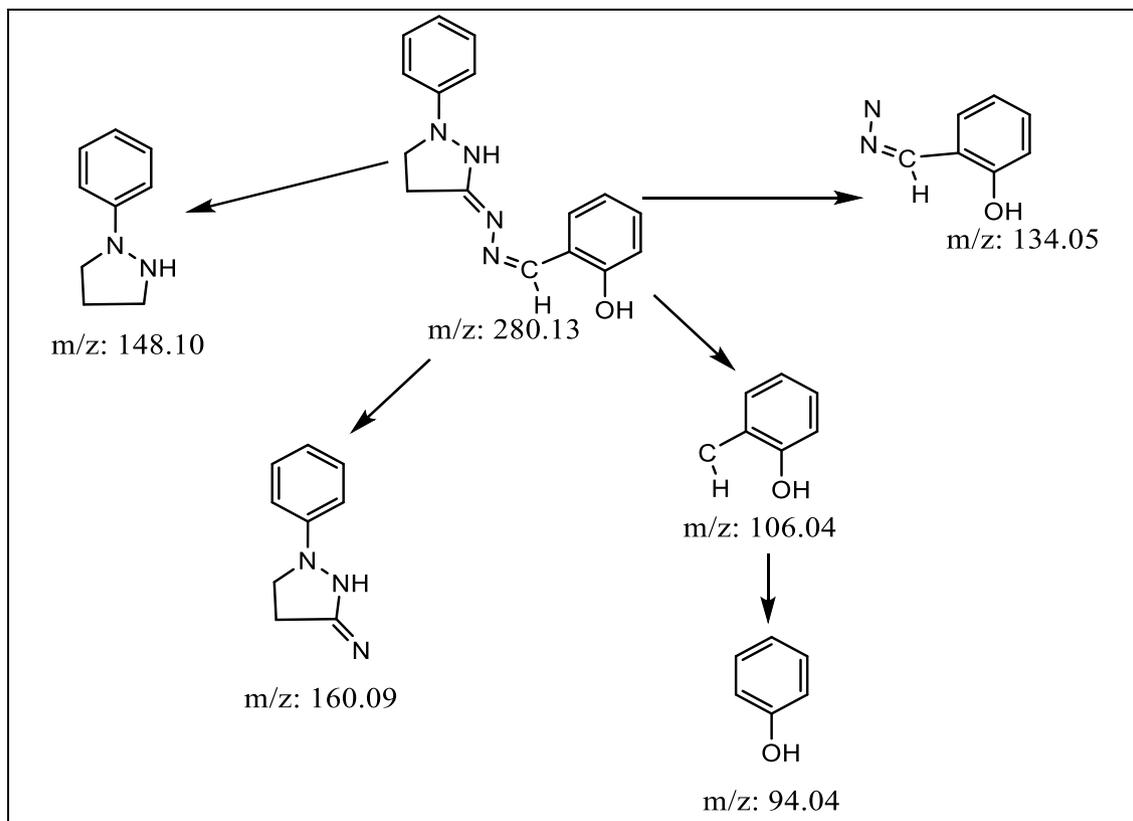
The mass spectrum is used in order to ascertain the molecular weight of the produced molecule. There is good agreement between the mass spectrum, of the ligand [C<sub>19</sub>O H<sub>16</sub>N<sub>4</sub>]and the proposed molecular structure shown in Fig. 2. The predicted m value (280.13) g mol<sup>-1</sup>, which was in very excellent agreement with the calculated values m/e (280.33), validating their formula weight for the ligand. The fragmentation pattern and the extract mass for each pattern are shown in Scheme 2 to provide mass information for the ligand.



**Fig. 1.** <sup>1</sup>H-NMR of Schiff bases(2-((Z)-((E)-1-phenylpyrazolidin-3-ylidene)hydrazineylidene)methyl)phenol).



**Fig. 2.** Mass spectrum of (2-((Z)-(((E)-1-phenylpyrazolidin-3-ylidene)hydrazineylidene)methyl)phenol).



**Scheme 2.** The proposed mass fragmentation pathways of ligand.

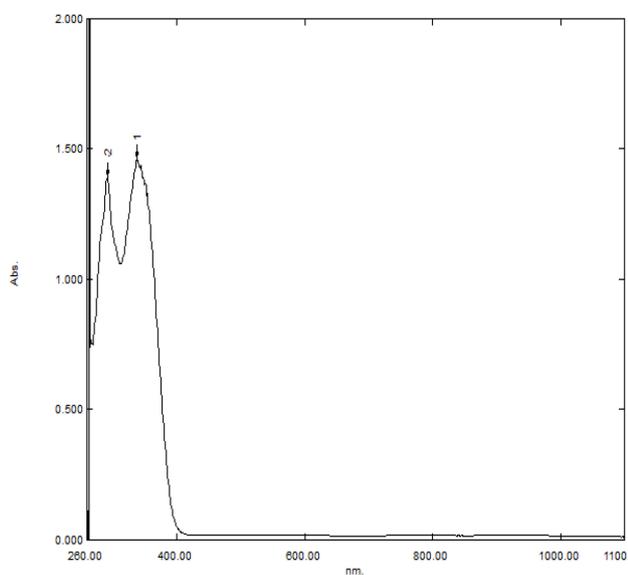
**Table 4.** Electronic spectra for Schiff base ligand and complexes.

| Compound  | Molar Cond.<br>Ohm <sup>-1</sup><br>cm <sup>2</sup> .mol <sup>-1</sup> | $\mu_{\text{eff}}$ B.M | Electronic<br>arrangement | $\lambda$ max<br>(nm)           | Assignments   | Geometry   |
|---|--|------------------------|---------------------------|---------------------------------|---|------------|
| LH\C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O | 2.5  |                        |                           | 292<br>338                      | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$  |            |
| [Co(LH) <sub>2</sub> ].H <sub>2</sub> O             | 12.9   | 4.88                   | d <sup>7</sup>            | 293<br>355<br>556<br>712<br>889 | $\pi \rightarrow \pi^*$<br>C.T<br>$^4T_{1g} \rightarrow ^4T_{1g}(p)$<br>$^4A_{2g}(F) \rightarrow ^4T_{1g}$<br>$^4T_{1g} \rightarrow ^4T_{2g}(F)$          | Octahedral |
| [Ni(LH) <sub>2</sub> ].2H <sub>2</sub> O            | 33.4   | 3.22                   | d <sup>8</sup>            | 293<br>351<br>471<br>784<br>912 | $\pi \rightarrow \pi^*$<br>C.T<br>$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$<br>$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$<br>$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ | Octahedral |
| [Cu(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]          | 8.2  | 1.75                   | d <sup>9</sup>            | 294<br>412<br>695               | $\pi \rightarrow \pi^*$<br>C.T<br>$^2E_g \rightarrow ^2T_{2g}$  | Octahedral |
| [Zn(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]          | 18.1   | 0.00                   | d <sup>10</sup>           | 300<br>356<br>424               | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$<br>C.T(M→L)  | Octahedral |

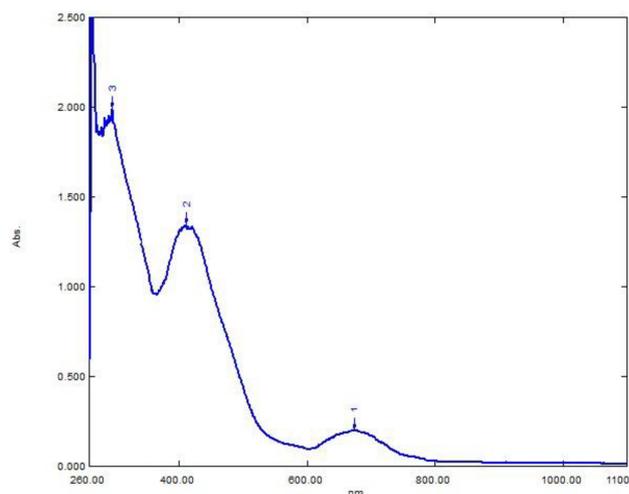
0.00 = Dia = diamagnetic.

### UV-visible ligand and complexes

In Fig. 3, absorption spectra appeared at 292 nm to be due to the transfer of electrons from  $\pi \rightarrow \pi^*$  and transition  $n \rightarrow \pi^*$  peaks around 338 nm. Complexes have revealed changes in the absorption bands that indicate a coordination with metal ions through the functional set azomethine nitrogen and charge transfer peaks also appeared, as do d-d transition peaks.<sup>18</sup> Peaks appeared in the cobalt complex in

**Fig. 3.** UV/Vis spectra of ligand.

the d-d region transition at (556, 712 and 889) nm, which are related to the electronic shift ( $^4T_{1g} \rightarrow ^4T_{1g}(p)$ ,  $^4T_{1g} \rightarrow ^4A_{2g}(F)$  and  $^4T_{1g} \rightarrow ^4T_{2g}(F)$ ). The nickel complex spectrum appeared in the d-d region in three bands (471, 784 and 912) nm, which are related to the electronic transition  $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ ,  $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ ,  $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ . The copper complex, Fig. 4, appeared in spectrum bands (412 and 695) nm that are related to the electronic transition (C.T,  $^2E_g \rightarrow ^2T_{2g}$ ). As for zinc complexes,<sup>19</sup> no transitions occur because the outer shell is stable and saturated.<sup>20</sup> And they're all explained in Table 4.

**Fig. 4.** UV/Vis spectra of Cu(II) complex.

**Table 5.** FT-IR Spectra analysis of ligand and Complexes.

| Compound  | $\nu(\text{OH})$ | $\nu(\text{H}_2\text{O})$ | $\nu(\text{N-H})$ | $\nu(\text{C=N})$ | Twisting $\nu(\text{H}_2\text{O})$ | Wagging $\nu(\text{H}_2\text{O})$ | $\nu(\text{M-O})$ | $\nu(\text{M-N})$ | $\nu(\text{M-Cl})$ |
|---|------------------|---------------------------|-------------------|-------------------|------------------------------------|-----------------------------------|-------------------|-------------------|--------------------|
| LH\C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O | 3423             | -                         | 3207              | 1600              | -                                  | -                                 | -                 | -                 | -                  |
| [Co(LH) <sub>2</sub> ].H <sub>2</sub> O             | -                | 3456                      | 3257              | 1623              | 752                                | 682                               | 563               | 460               | -                  |
| [Ni(LH) <sub>2</sub> ].2H <sub>2</sub> O            | -                | 3440                      | 3227              | 1612              | 754                                | 694                               | 590               | 466               | -                  |
| [Cu(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]          | -                | 3433                      | 3272              | 1609              | 757                                | 694                               | 595               | 445               | 221                |
| [Zn(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]          | -                | 3431                      | 3193              | 1610              | 756                                | 696                               | 590               | 447               | 306                |

### Molar conductivity measurements

The measured molar conductivity ( $m$ ) of  $M(\text{II}) = \text{Co}, \text{Ni}, \text{Cu}$  and  $\text{Zn}$  complexes in DMF solutions at a temperature of  $25^\circ\text{C}$  are listed in Table 4. All complexes have ( $\text{Cl}^-$ ) in the internal coordination domain, indicating that all of the complexes were nonelectrolytes.<sup>21</sup>

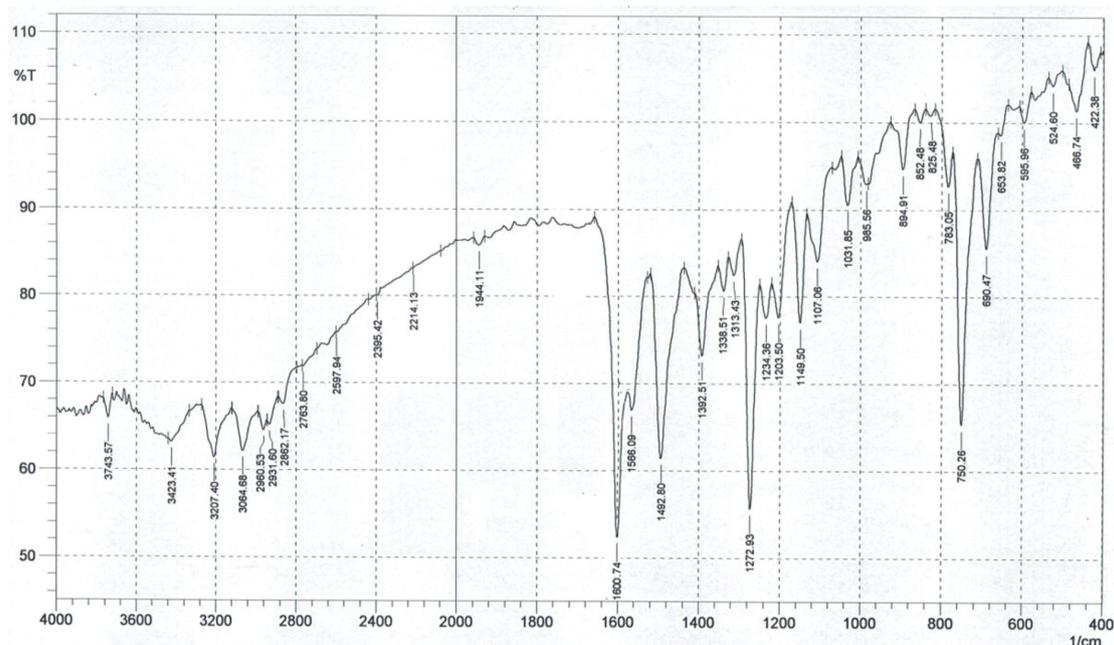
### FT-IR spectra analysis of ligand and complexes

FTIR spectra analysis of the prepared ligand and complex are summarized in Table 5. We note in Fig. 5 the appearance of a strong absorbent band at  $1600\text{ cm}^{-1}$  that belongs to the group of azomethine (imine), and this is a sign of the formation of a Schiff base.<sup>22</sup> There is a package at  $3207\text{ cm}^{-1}$  that goes back to  $\text{NH}$  and there was a clear difference between the complex spectrum and the ligand. Where it appeared of new bands is a result of the coordination between the ligand and the ions of transitional metals.<sup>23</sup> A set of  $\nu(\text{C=N})$  is shifted in the complexes ( $1623, 1612, 1609, 1610\text{ cm}^{-1}$ , respectively).<sup>24</sup> The disappearance

of the  $\text{OH-phenol}$  package and, in addition, the appearance of new absorbent bands back to  $\nu(\text{M-O}), \nu(\text{M-N})$  and  $\nu(\text{M-Cl})$  at  $563\text{--}595\text{ cm}^{-1}, 445\text{--}466\text{ cm}^{-1}$  and  $221, 306$ . Complexes have absorption packages in the range of  $3456\text{ cm}^{-1}, 752\text{ cm}^{-1}$ , and  $682\text{ cm}^{-1}$ , indicating that the water molecules are within the coordination field.<sup>25</sup>

### Biological efficacy against positive and negative bacteria

The experiment was carried out in aerobic circumstances at a temperature of  $37^\circ\text{C}$ . Drilling was utilized to expose each Agar active chemical, Agar bacterium to two kinds of bacteria, both negative bacteria and positive bacteria. Results from tests on the aforementioned bacteria at  $1 \times 10^{-3}\text{M}$  concentrations of the DMF solvent.<sup>26,27</sup> In this study, *Pseudomonas*, *E. coli*, *strepto* and *staph* were used as bacterial strains to determine their antibacterial properties. According to the results, metal complexes exhibited greater antibacterial activity than synthesized Schiff bases ligand. The *strepto* were less active than the standard

**Fig. 5.** FT-IR of ligand

**Table 6.** Anti-bacterial activity of ligand and complexes prepared.

| Sample | Compound  | <i>Pseudomonas</i> | <i>Escherichia coli</i> | Streptococcus | <i>Staphylococcus aureus</i> |
|--------|---|--------------------|-------------------------|---------------|------------------------------|
| 17     | LH\C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O | 20 mm              | -                       | -             | 13 mm                        |
| 20     | [Co(LH) <sub>2</sub> ].H <sub>2</sub> O             | -                  | 14 mm                   | 14 mm         | 17 mm                        |
| 19     | [Ni(LH) <sub>2</sub> ].2H <sub>2</sub> O            | 21 mm              | 15 mm                   | -             | 16 mm                        |
| 18     | [Cu(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]          | -                  | -                       | -             | 17 mm                        |
| 21     | [Zn(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]          | 17 mm              | 15 mm                   | 14 mm         | 18 mm                        |

**Table 7.** Pharmacological resistance to positive and negative bacteria.

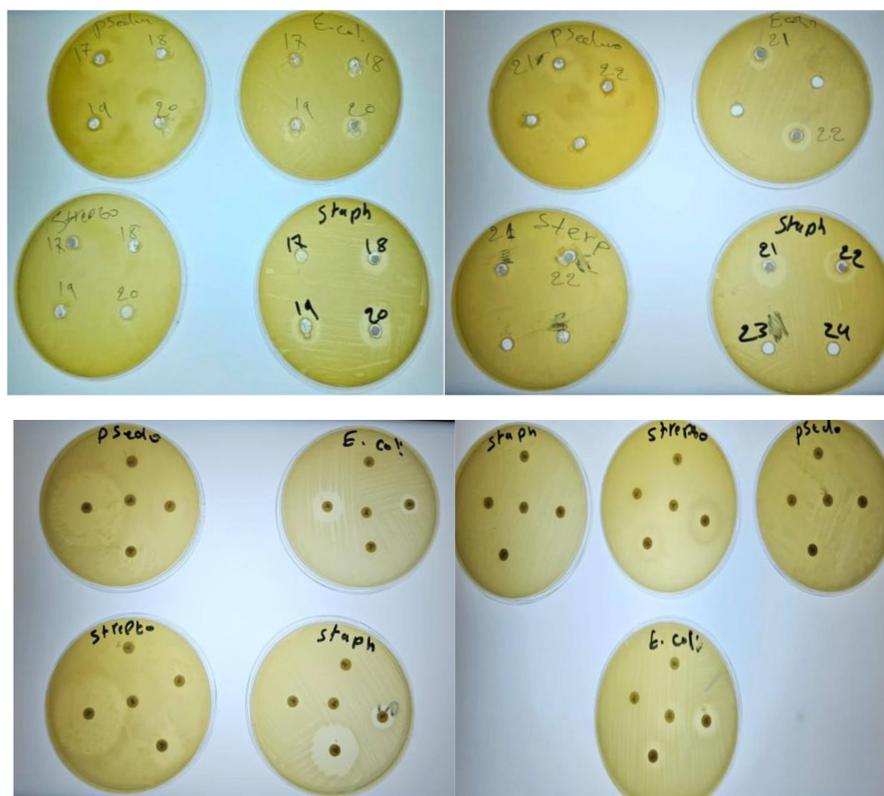
| Name of bacteria   | DO    | TE    | DA | RA | CLR | LEV   | AMK   | CRO   | VA    | AM |
|--------------------|-------|-------|----|----|-----|-------|-------|-------|-------|----|
| <i>Staph</i>       | -     | -     | -  | -  | -   | -     | -     | 13 mm | 24 mm | -  |
| <i>E. coli</i>     | 15 mm | 10 mm | -  | -  | -   | 16 mm | 11 mm | -     | -     | -  |
| Streptococcus      | 15 mm | 13 mm | -  | -  | -   | 37 mm | -     | 18 mm | -     | -  |
| <i>Pseudomonas</i> | -     | -     | -  | -  | -   | 22 mm | -     | 11 mm | -     | -  |

Do: doxycycline, TE: tetracycline, DA: clindamycin, RA: rifampin, CLR: clarithromycin, LEV: levofloxacin, AMK: amikacin, CRO: ceftriaxone, VA: vancomycin, AM: ampicillin

*E. coli*, *staph* and *Pseudomonas*. The *Pseudomonas* and *staph* showed the highest action towards Schiff bases ligand and complexes, with a maximum activity of 21 mm. It came to light that the findings of ligand efficacy and its complexes were very effective against bacteria compared with antibiotic (doxycycline, tetracycline, clindamycin, rifampin, clarithromycin, levofloxacin, amikacin, ceftriaxone, vancomycin, ampicillin) Tables 6 and 7 and Fig. 6.

#### Determination of DPPH radical scavenging efficiency

The inhibitory effect of ligand L and its minerals, including M(II) = Co, Ni, Cu and Zn, on reactive oxygen species was evaluated using DPPH. The combination of the ligand and its mineral causes a change in color of DPPH from purple to yellow due to the transfer of hydrogen from the ligand to the DPPH

**Fig. 6.** Biological activity of Schiff base and complexes.

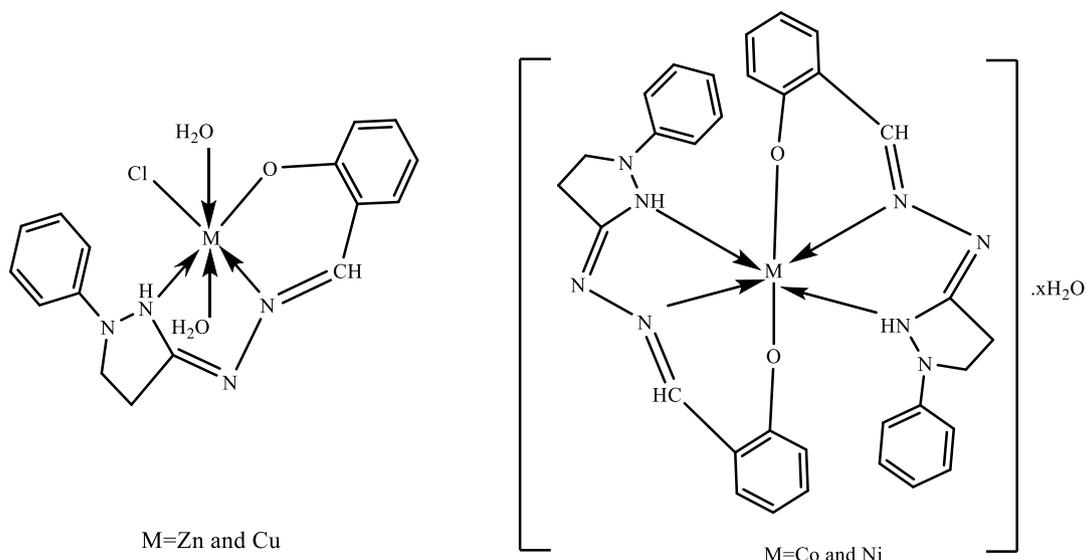


Fig. 7. Suggested structure for complexes.

Table 8. Radical scavenging activities, Percentage Inhibition and IC<sub>50</sub> values.

| Compound   | Abs. 517 nm | DPPH% |
|--|-------------|-------|
| Blank LH   | 1.536 dill  |       |
| C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O | 0.763       | 50.33 |
| [Co(LH) <sub>2</sub> ].H <sub>2</sub> O          | 0.584       | 61.98 |
| [Ni(LH) <sub>2</sub> ].2H <sub>2</sub> O         | 0.799       | 47.98 |
| [Cu(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]       | 0.931       | 39.38 |
| [Zn(LH)(H <sub>2</sub> O) <sub>2</sub> Cl]       | 0.577       | 62.43 |

molecule. The color conversion was detected using a UV-Vis spectrophotometer at 517 nm. The inhibitory activity of the ligand L and its complexes on reactive oxygen species was ranked complex based on the higher DPPH value indicating lower antioxidant effectiveness. The highest antioxidant activity for Zn(II) and Co(II) complex was 62.43% and 61.98% respectively. This included the higher antioxidant activity of the synthesized Schiff bases due to the presence of hydroxyl-group. The free radical scavenging effects of all the compounds with the DPPH radical were evaluated using the following equation: The value of antioxidant efficacy was extracted from the equation and presented in Table 8.<sup>28,29</sup>

The value of antioxidant efficacy was extracted from the equation

Dpph% =

$$\frac{\text{Blank Absorbance} - \text{sample Absorbance}}{\text{Blank Absorbance}} \times 100\%$$

PI = Percentage Inhibition

RSA = 100 - PI RSA = Radical Scavenging Activit

## Conclusion

The synthesis and characterization of M(II) = Co, Ni, Cu and Zn, complexes of the Schiff base ligand produced via the condensation reaction of (Z)-3-hydrazineylidene-1-phenylpyrazolidine and Salicylaldehyde are reported in this study. Various analytical and spectroscopic techniques, the data clearly indicate that the complexes have a composition of a certain type (M: L is 1:1) or (M: 2L is 1:2) All complexes are coordinated to oxygen atoms from the ligand and nitrogen atoms of azomethineand (N-H) Pyrazolidinone, and the octahedral geometry all complexes. The biological activities of azomethine (Schiff base), and its complexes have been summarized, these compounds exhibited significant activity against all the tested microorganisms. Then the potential of these prepared compounds as antioxidants was determined by inhibiting free radicals using DPPH as a free radical.

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## Authors' declaration

- Conflicts of Interest: None.
- We hereby confirm that all the figures and tables in the manuscript are ours. Furthermore, figures and images, that are not ours, have been included

with the necessary permission for re-publication, which is attached to the manuscript.

- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

## Authors' contribution statement

N. S. conceived the idea of the research and supervised the project. Z. M.A. performed the experiment, wrote the manuscript, and made the analysis. The findings were discussed by both authors, and they both contributed to the final version of the manuscript.

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# تحضير وتشخيص ودراسة النشاط البيولوجي لمعقدات فلزية جديدة مع قاعدة شف المشتقة من تفاعل 3-(Z)- هيدرازينيلدين-1-فينيل بيرازوليددين وتقييمه كمضادات للأكسدة

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## الخلاصة

يتضمن البحث تحضير عدة معقدات من العناصر الانتقالية والزنك (II) Zn, (II) Cu, (II) Ni, (II) Co تحتوي على الغلاف 3d، مع قواعد شف الناتجة عن تفاعل بين 3-(Z) -هيدرازيميليددين-1-فينيلبيرازوليددين وساليسيلالدهيد. تم التعرف على قاعدة شف باستخدام أطياف FT-IR، والتحليل الطيفي للأشعة فوق البنفسجية، والتحليل الدقيق للعناصر CHN، ومطياف الرنين المغناطيسي النووي ومطياف الكتلة. تمت دراسة المعقدات وتحديد استخدامها باستخدام التحليل الدقيق للعناصر CHN، ومطيافية FT-IR، ومطيافية الأشعة فوق البنفسجية المرئية (UV-Vis)، وقياس التوصيلية الكهربائية، والحساسية المغناطيسية. أظهرت النتائج أنه تم تصنيف هذه الليكاندات ثلاثية السن مانحة للمعادن وكانت صيغة المعقدات  $[M(LH)(H_2O)_2Cl]$  أو  $[M(LH)_2] \cdot xH_2O$ . أشارت القياسات الفيزيائية إلى أن المعقدات المحضرة غير الإلكترونية وأظهرت أن الليكاند ثلاثي السن عند تنسيقه مع أيونات المعادن عن طريق نيتروجين الأزوميثين (-C-N-) وذرة الأكسجين (OH) للسلسلديهايد والنيتروجين (N-H) للبيرازوليددينون. هندسة ثماني السطوح لجميع المعقدات وكانت نسبة الناتج جيدة. أكدت هذه الدراسة على أهمية استخدام طريقة التعقيد المعدني لتثبيت الروابط وزيادة نشاطها الحيوي. أظهر الفحص البيولوجي للمعقدات أن معقدات شف المعدنية الأساسية تظهر فعالية ملحوظة في مكافحة الكائنات الحية الدقيقة، وذلك باستخدام الإشريكية القولونية والزائفة والعقدية والمكورات العنقودية كسلالات بكتيرية باستخدام الدوكسيسيكليين والنتراسيكليين. الكلينداميسين، الريفامبين، كلاريثروميسين، ليفوفلوكساسين، أميكاسين، سيفتراكسون، فانكوميسين، أمبيسيلين كمرجع لتحديد المقاومة الدوائية للبكتيريا السلبية والإيجابية. ومن ثم جاءت نتائجهم جيدة في التثبيط. بعد ذلك ، تم تحديد قدرة هذه المركبات المحضرة كمضادات للأكسدة عن طريق تثبيط الجذور الحرة باستخدام DPPH كجذور حرة.

**الكلمات المفتاحية:** النشاط البيولوجي ، 1-فينيل-3-بيرازوليددينون ، التقييم كمضادات للأكسدة ، الساليسيلديهايد ، معقدات قواعد شف.