

**Synthesis, Characterization, Biological Activity and Antioxidant Studies of New Metal Ion Complexes Based on (E)-4-((benzo[d]thiazol-2-ylimino)methyl)-1,5-dimethyl-2-phenylpyrazolidin-3-ol**

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## RESEARCH ARTICLE

# Synthesis, Characterization, Biological Activity and Antioxidant Studies of New Metal Ion Complexes Based on (E)-4-((benzo[d]thiazol-2-ylimino)methyl)-1,5-dimethyl-2-phenylpyrazolidin-3-one

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## ABSTRACT

The study involved synthesis of four new complexes involving bidentate ligand [(E)-4-((benzo[d]thiazol-2-ylimino)methyl)-1,5-dimethyl-2-phenylpyrazolidin-3-one] with the general formula  $[M(L)_2Cl_2].xH_2O$  or  $[MLCl_2].xH_2O$ , where M represents  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$ . The ligand was synthesized by treating the 4-Antipyrinecarboxaldehyde and 2-aminobenzothiazoles in an alcoholic solution. The structural characteristics of ligand and complexes were characterized quantitatively and qualitatively by using various techniques including elemental analyses, magnetic susceptibility measurement, molar conductivity, infrared, ultraviolet absorption, Gc-Mass, and  $^1H$ -NMR spectroscopy studies. The physical measurements indicated that the prepared complexes are non-electrolyte and showed that the ligand is bidentate when coordinated with metal ions through the nitrogen of azomethine (-C=N-) and oxygen atom of carbonyl (-C=O) for antipyrine, octahedral geometry for  $Mn^{2+}$  and  $Ni^{2+}$  complexes but tetrahedral geometry of  $Co^{2+}$  and  $Cu^{2+}$  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, tetracyclin, 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:** Antioxidant effectiveness, 4-antipyrinecarboxaldehyde, 2-aminobenzothiazoles, Biological activity, Schiff base complexes

## Introduction

Schiff bases reaction was studied by Hugo Schiff in 1984. Due to their high coordination number and capacity to form complexes with a wide range of metal ions, including those from transition metals, Schiff's bases are frequently utilized in coordination chemistry. In this research. Condensation of primary

amines and active carbonyl groups can result in the formation of Schiff bases; there are two ways to produce an amine.<sup>1</sup>

The study of synthesizing and characterizing novel metal ion complexes with Schiff bases, including hetero atoms, holds potential practical uses due to their chelating capability and adaptability, making them ideal partners for stable complex formation.<sup>2</sup>

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The Schiff base compounds are formed by reacting a primary amine with the carbonyl group of aldehydes ( $\text{RHC=O}$ ) or ketone ( $\text{R}_2\text{C=O}$ ). The functional group carbon nitrogen double bond ( $\text{-C=N-}$ ) in Schiff bases is known as azomethine.<sup>3</sup> A wide range of heterocyclic Schiff bases have potential physical, chemical, and biological features.<sup>4</sup>

The remarkable Schiff base class of molecules has prospective applications in several areas of chemistry.<sup>5</sup> Schiff bases have the characteristic of a potential ligand because of the carbon double bond nitrogen group in their structures. For example, forming a complex with metals is a defining property of the carbon double bond nitrogen bond.<sup>6,7</sup> The thermal endurance, liquid crystal characteristic, conductivity, and chelate formation of Schiff bases are just a few of the numerous reasons why they are gaining more and more attention in scientific circles and becoming more critical in our daily lives. This interest has accelerated the synthesis of new Schiff base and metal complexes with diverse properties and expanded their application areas.<sup>8,9</sup> Research efforts have changed their emphasis from developing novel substances to finding new applications. Various sectors exploit the liquid crystal characteristic of some metal complexes. These include the aerospace industry, screens for televisions and computers, digital clock displays.<sup>10–12</sup> Surely, the discovery of new heteroaromatic azomethines has increased due to their demonstrated use as appealing leading structures for the production of catalysts, organic synthesis intermediates, and dyes.<sup>13</sup> Schiff bases may also be utilized as corrosion inhibitors in various metal electrolyte systems because their electron-rich centers, particularly the imine moiety, adsorb and create a corrosion mitigation surface coating. Because of its  $\pi$ -acceptor characteristics, this moiety may form strong bonds with metallic ions.<sup>14,15</sup> Schiff bases have been shown to exhibit a wide range of biological properties in biological chemistry,<sup>16</sup> including antimalarial, antiproliferative,<sup>17</sup> analgesic, anti-inflammatory, antiviral, antipyretic, antifungal, and antibacterial.<sup>18</sup> Many research was conducted on Schiff bases complexes that are used as antioxidants.<sup>19</sup> Due to their chelating capabilities, as well as the ease of separation and flexibility on the  $\text{C=N}$  group, Schiff bases are increasingly regarded intriguing ligands for coordination chemistry.<sup>20</sup> In comparison with free Schiff bases, complexation of Schiff bases with metals results in improved antibacterial and antifungal activities.<sup>21–23</sup> The research aims at describing the synthesis of novel Schiff base ligand and using it as a ligand to provide sites that are potential donors and form complexes with  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and

$\text{Cu}^{2+}$ . The ligand and its complexes have been fully characterized, and a biological activity study and antioxidants studies were conducted.

## Materials and methods

### Materials and instrumentation

The study utilized reagents and chemicals provided by Sigma-Aldrich. absolute ethanol (99%), and 99%,  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$  99%,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  99%,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  99%,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  99%, 4-Antipyrinecarboxaldehyde (97%) and 2-Aminobenzothiazoles (97%). The melting point of the prepared compounds was measured by a Stuart (SMP10) electrothermal melting point apparatus. Using infrared spectra device of type (Shimadzu-8000S) and disc (KBr) for ligand and (CsI) for complexes, in the range ( $200\text{--}4000\text{ cm}^{-1}$ ). 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  $^1\text{H-NMR}$ , 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  $190.00\text{--}1100\text{ nm}$ .

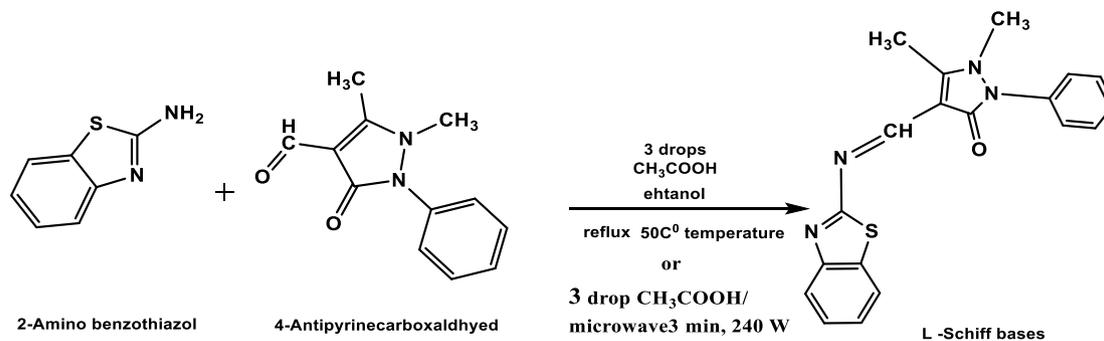
### Synthesis schiff base ligand (L)

#### First Method:<sup>24</sup>

In a 100 ml round-bottom flask, 1.389 g (0.009248 mol) of 2-aminobenzothiazol was dissolved in 20 ml of ethanol to create a Schiff's bases ligand. After adding 2 g (0.009248 mol) of 4-antipyrinecarboxaldehyde to 20 ml of ethanol at room temperature, (3 drops) of glacial acetic acid were added with continuous stirring until the components were homogeneous, the mixture was boiled and refluxed at  $80\text{ }^\circ\text{C}$  for 4 hours, it yielded a pure form of (L). The yellow crystals were precipitated, recovered by filtering, washed with absolute ethanol, dried for 24 hours, and then recrystallized from Mix (40:60) methanol: ethanol. After being filtered and dried for 24 hours, the re-crystallized powder had a melting point (M.P) of  $207\text{--}209\text{ }^\circ\text{C}$  and a yield of 69%, Scheme 1.

#### Second Method:<sup>25</sup>

Preparing of Schiff base was conducted by mixing in the crucible a stoichiometric 1.389 g (0.009248 mol)



**Scheme 1.** Synthesis of L-schiff bases.

of 2-aminobenzothiazol with 2 g (0.009248 mol) of 4-antipyrine-careboxaldehyde and adding 3 drops of glacial acetic acid. The mixture was put in microwave irradiation at 240 W for (3) minutes. The yellow powder was collected, and then dried before being recrystallized from Mix (40:60) methanol: ethanol. After filtering the yellow crystal, it was collected and allowed to dry for 24 hours. Melting point (M.P) of 207–209 °C and a yield of 85%, [Scheme 1](#).

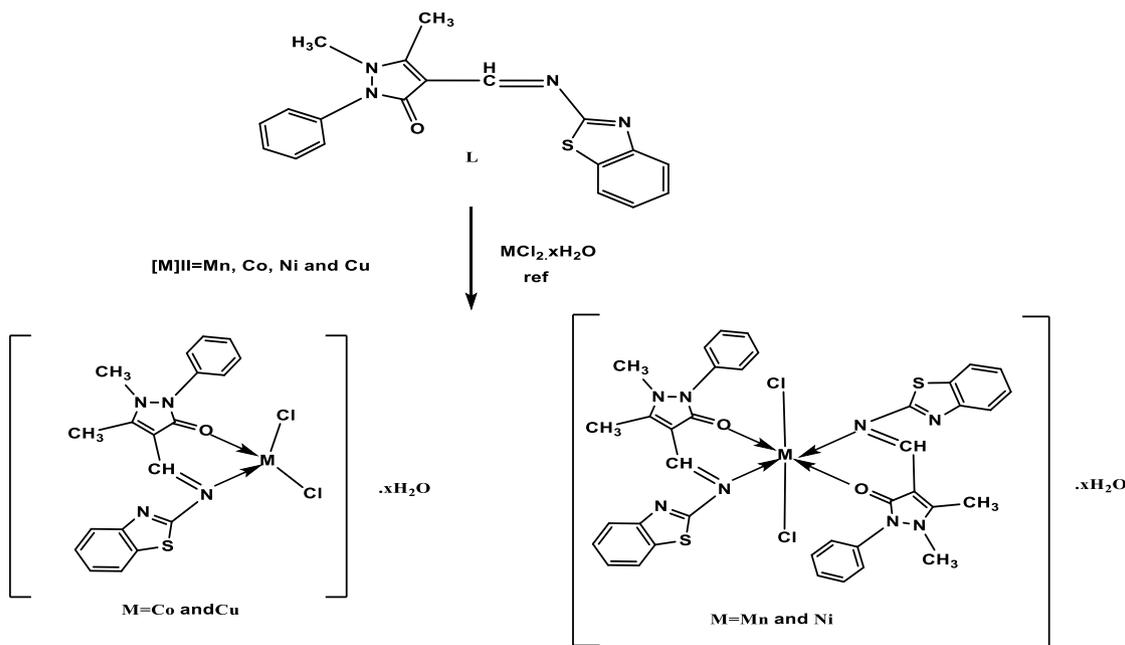
#### Preparations of complexes

In a 50 ml circular glass vial with a flat bottom, the prepared ligand (L) (0.15 g, 0.00042 mol) was dissolved with agitation in 10 ml of ethanol. Metal chloride hydrate according to the (0.00021 mol) was dissolved in 10 ml of ethanol and added to the ligand solution, and vigorous agitation until complete

dissolution. The mixture was subjected to the reflux procedure for 10 hours, until a colorful precipitate indicated the formation of a complex. The reaction was then halted, and the product was allowed to settle at room temperature before being filtered, rinsed with clean cold water, and desiccated using ether. The product was filtered and desiccated at 50 degrees Celsius, providing exceptional to excellent yields of 59–73%, [Scheme 2](#).

#### Antibacterial activity

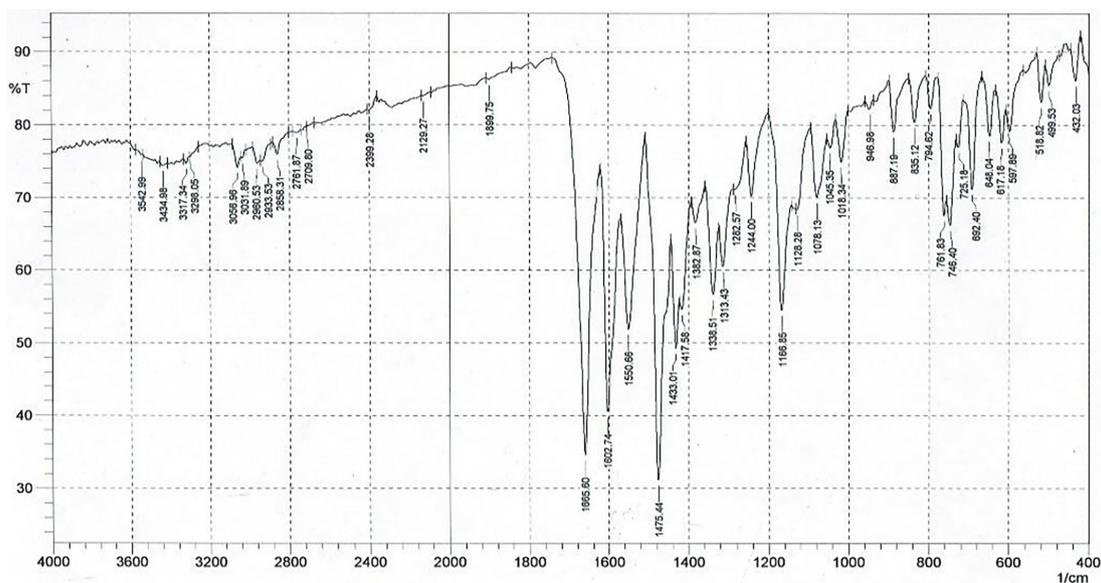
The drilling method experiment was carried out, and four types of pathogenic bacteria namely: *Pseudomonas*, *E. coli*, *strepto* and *staph* were developed under aerobic conditions at (37°C°) for (24 hours). The compound is effective against four bacteria kinds (two kinds positive for Gram, and two kinds negative



**Scheme 2.** Preparation of complexes.

**Table 1.** Physical properties and analytical percentages data of ligand and complexes.

Compound	Color	Dec. Point °C	Yield%	Analysis (calculated)				
				C%	H%	N%	Cl	M
L/[C <sub>19</sub> H <sub>16</sub> ON <sub>4</sub> S]	Yellow	207–209	69% 85%	65.58 (65.50)	4.91 (4.63)	16.05 (16.08)		
[Mn(L) <sub>2</sub> Cl <sub>2</sub> ].5H <sub>2</sub> O	Light yellow	300 Dec	73%	50.32 (50.00)	3.98 (4.64)	12.56 (12.28)	7.07 (7.77)	5.73 (6.02)
C <sub>38</sub> H <sub>42</sub> Cl <sub>2</sub> MnN <sub>8</sub> O <sub>7</sub> S <sub>2</sub>	Light orange	260 Dec	69%	41.89 (41.47)	3.79 (4.40)	10.36 (10.18)	13.55 (12.88)	12.11 (10.71)
[Co(L) Cl <sub>2</sub> ].5H <sub>2</sub> O	Gold	160	59%	48.36 (48.84)	4.05 (4.75)	11.35 (11.99)	7.07 (7.59)	6.49 (6.28)
C <sub>19</sub> H <sub>24</sub> N <sub>4</sub> O <sub>5</sub> SCoCl <sub>2</sub>	Light yellow	260 Dec	74%	41.72 (41.12)	3.93 (4.36)	10.67 (10.10)	13.35 (12.78)	11.11 (11.45)
[Ni(L) <sub>2</sub> Cl <sub>2</sub> ].6H <sub>2</sub> O								
C <sub>38</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>8</sub> NiO <sub>8</sub> S <sub>2</sub>								
[Cu(L) Cl <sub>2</sub> ].2H <sub>2</sub> O								
C <sub>19</sub> H <sub>24</sub> N <sub>4</sub> O <sub>5</sub> SCuCl <sub>2</sub>								

**Fig. 1.** FT-IR spectrum for ligand (L).

for Gram). The test was conducted at the University of Baghdad's environmental laboratory.<sup>26</sup>

## Results and discussion

### 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 1. 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>27</sup>

### FT-IR spectroscopy

Regarding the FT-IR spectrum analysis Fig. 1, Schiff bases compound [L] all these spectra share a common characteristic: absorption peaks in the medium range, specifically at (1650, 1602 and 1550) cm<sup>-1</sup>. These

peaks are attributed to C=O (carbonyl group),<sup>28</sup> C=N (azomethine group),<sup>29</sup> and C=C, bonds respectively.

### <sup>1</sup>H-NMR spectral of schiff bases ligand

Nuclear magnetic resonance spectroscopy is a method for determining the chemical surroundings of organic compounds. The <sup>1</sup>H-NMR spectra of the ligand (L) in dimethyl sulfoxide (DMSO-d<sub>6</sub>) with tetramethyl silane (TMS) as the internal reference standard is shown in Fig. 2. 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 single peak observed at 2.77 ppm for CH<sub>3</sub>. A single peak can be observed at 3.46 ppm in N-CH<sub>3</sub>, The protons of the 4-aminobenzothiazole ring unit show multiplet peaks at regions between 7.80 ppm to 7.98 ppm. Will the 4-aminopyrine ring unit show peaks at regions between 7.29–7.59 ppm. The proton of azomethine group (HC=N) shows a singlet peak at an 8.81 ppm.<sup>30</sup>

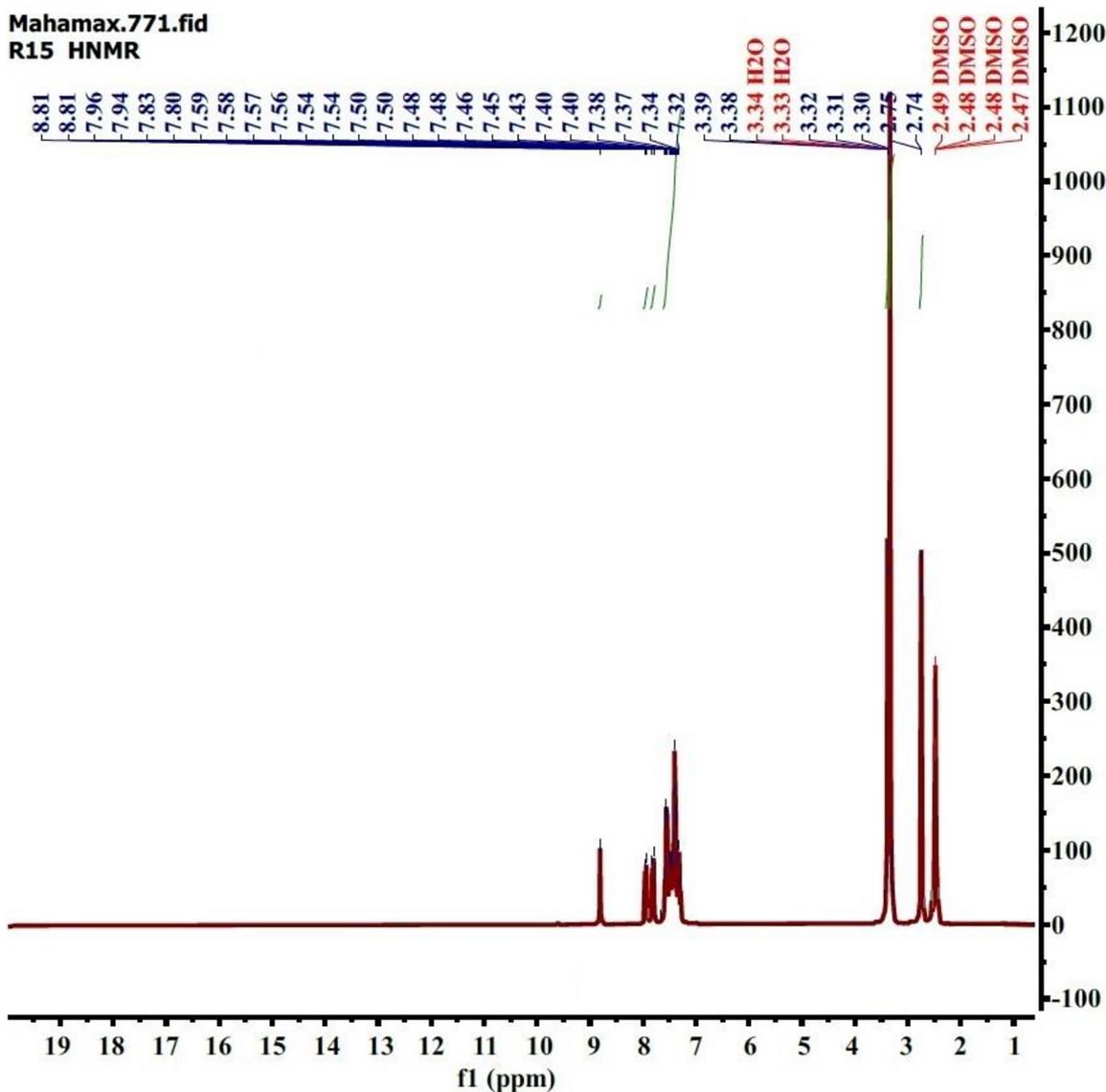


Fig. 2. <sup>1</sup>H-NMR of Schiff bases ligand.

#### 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>S] and the proposed molecular structure shown in Fig. 3. The predicted m value (348.84) g.mol<sup>-1</sup>, which were in very excellent agreement with the calculated values m/e (348.3), validating their formula weight for the ligand. The fragmentation pattern and the extract mass for each pattern are shown in Scheme 3. to provide mass information for the ligand.

#### UV-visible ligands and complexes

At room temperature, show that electronic spectrum of the electronic spectra of L and their complexes were measured in DMF (1 × 10<sup>-3</sup> M) solution in the range 190–1100 nm. The Schiff base ligand UV-Vis spectra exhibited one significant intensity absorption peaks at (385) nm, which was attributed to intra-ligand interactions [n → π] transitions of azomethine, respectively.<sup>31</sup> Changes in the placement of absorption bands in the complex spectra were detected, indicating metal ion coordination via the azomethine and carbonyl group (C=O).<sup>32,33</sup> The cobalt compound

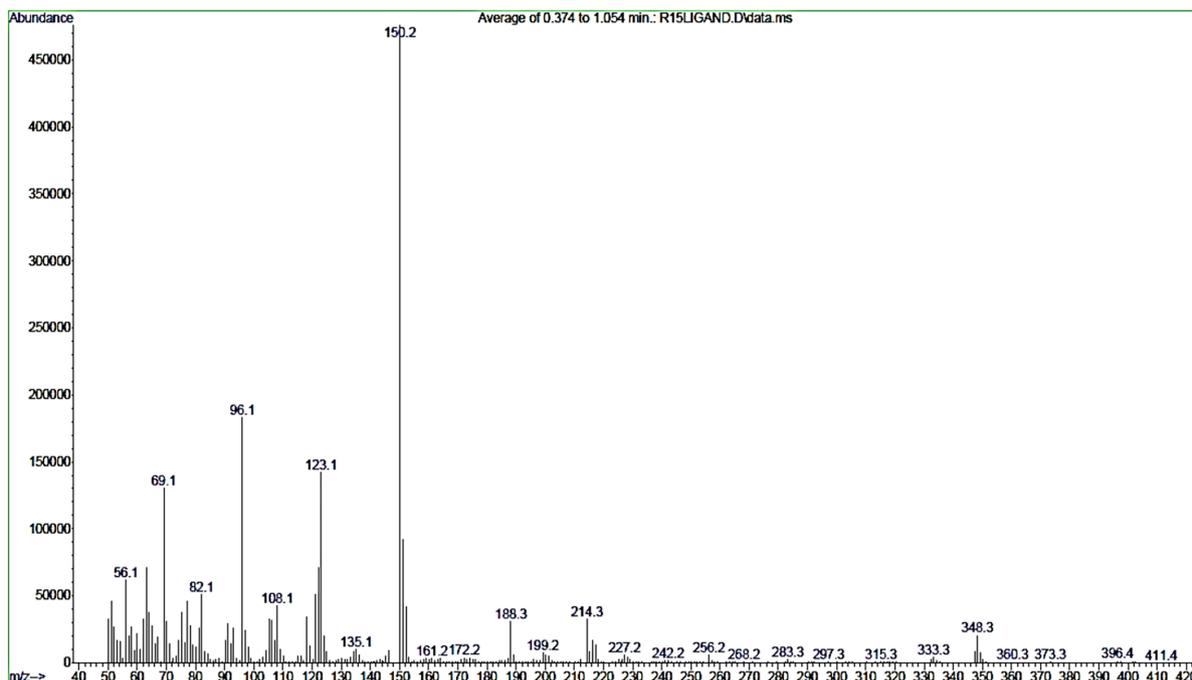
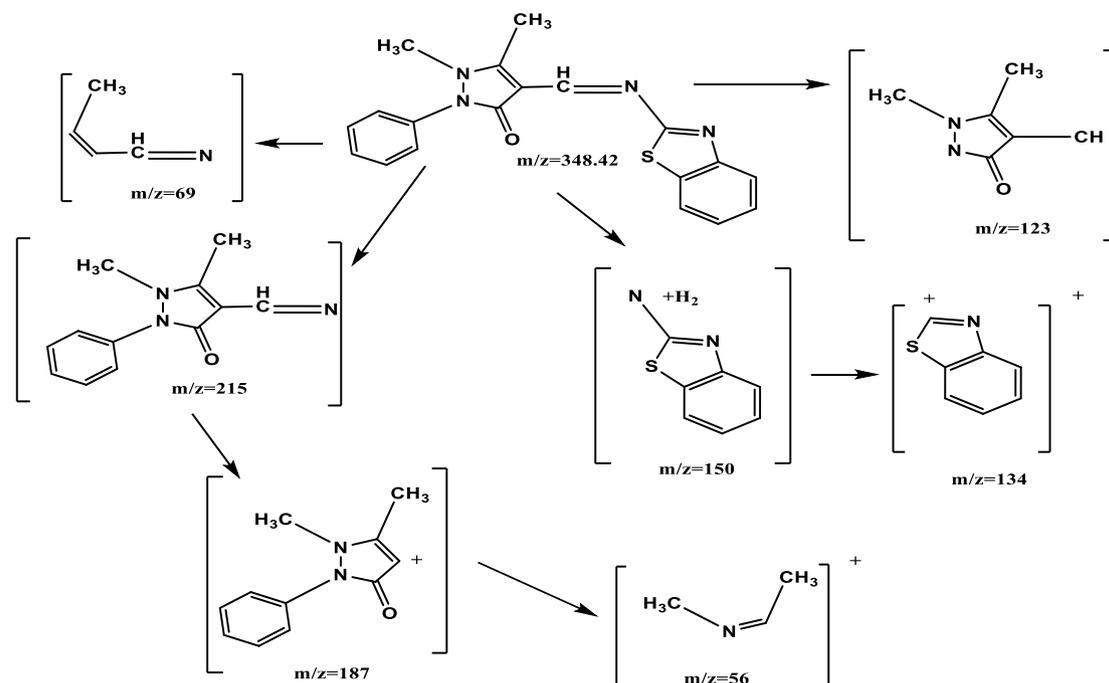


Fig. 3. Mass spectrum of Ligand.



Scheme 3. The proposed mass fragmentation pathways of ligand.

spectrum showed two bands (312, 606 and 673) nm, which represented the permitted transitions and had a magnetic moment of (4.51) MB. This is equivalent to the magnetic moment of quaternary complexes within the tetrahedral [C.T,  ${}^4A_2(F) \rightarrow {}^4T_1(P)$ ]. Nickel complex demonstrated Four bands (355, 672, 773,

and 901) nm bands, which represent Four transitions [C.T,  ${}^3A_2g(F) \rightarrow {}^3T_1g(P)$ ,  ${}^3A_2g(F) \rightarrow {}^3T_2g(F)$  and  ${}^3A_2g(F) \rightarrow {}^3T_2g(F)$ ], while the value of the magnetic moment was equal (3.15) BM. The spectrum of copper complex showed two bands in the (345 and 910) nm, resulting from the combined two transitions of

**Table 2.** The Electronic spectra, magnetic susceptibility measurements, and some physical properties of ligand and its complexes in a solvent (DMF) concentration ( $1 \times 10^{-3}\text{M}$ ) are displayed.

Compound	Molar Cond. $\text{Ohm}^{-1}\text{cm}^2.\text{mol}^{-1}$	electronic arrangement	$\mu_{\text{eff}}$ B.M	$\lambda$ max (nm)	Assignments
L/[C <sub>19</sub> H <sub>16</sub> ON <sub>4</sub> S]	-	-		265 385	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[Mn(L) <sub>2</sub> Cl <sub>2</sub> ].5H <sub>2</sub> O	25	d <sup>5</sup>	5.85	288 365 431	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T
[Co(L)Cl <sub>2</sub> ].5H <sub>2</sub> O	16	d <sup>7</sup>	4.51	312 602 673	C.T $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$
[Ni(L) <sub>2</sub> Cl <sub>2</sub> ].6H <sub>2</sub> O	38	d <sup>8</sup>	3.15	355 672 773 901	C.T $^3\text{A}_2\text{g}(\text{F}) \rightarrow ^3\text{T}_1\text{g}(\text{F})$ $^3\text{A}_2\text{g}(\text{F}) \rightarrow ^3\text{T}_2\text{g}(\text{F})$ $^3\text{A}_2\text{g}(\text{F}) \rightarrow ^3\text{T}_2\text{g}(\text{F})$
[Cu(L)Cl <sub>2</sub> ].2H <sub>2</sub> O	11	d <sup>9</sup>	1.69	345 910	C.T $^2\text{T}_2 \rightarrow ^2\text{E}$

**Table 3.** The infrared spectrum of the L – Schiff bases and its complexes.

Symbol of M (II) complexes	V(O-H) water/ $\text{Cm}^{-1}$	v(C=O) $\text{Cm}^{-1}$	v(C=N) $\text{Cm}^{-1}$	v(M-O) $\text{Cm}^{-1}$	v(M-N) $\text{Cm}^{-1}$	v(M-Cl) $\text{Cm}^{-1}$
L/[C <sub>19</sub> H <sub>16</sub> ON <sub>4</sub> S]	3434	1665	1602	—	—	—
[Mn(L) <sub>2</sub> Cl <sub>2</sub> ].5H <sub>2</sub> O	3431	1656	1623	531	428	345
[Co(L)Cl <sub>2</sub> ].5H <sub>2</sub> O	3456	1652	1622	520	443	385
[Ni(L) <sub>2</sub> Cl <sub>2</sub> ].6H <sub>2</sub> O	3425	1654	1622	500	441	364
[Cu(L)Cl <sub>2</sub> ].2H <sub>2</sub> O	3433	1658	1625	528	418	366

[C.T and  $^2\text{T}_2 \rightarrow ^2\text{E}$ ], It has a magnetic moment of (1.69) BM within the tetrahedral complex. We do not expect transitions to occur in Mn complex since their outer shells are stable during saturation or semi-saturation, respectively, and the observed bands are mentioned in Table 2.

#### Molar conductivity measurements

Table 2 lists the measured molar conductivity (m) of M(II)=Mn, Co, Ni and Cu complexes in DMF solutions at a temperature of 25 °C. All complexes have (Cl<sup>-</sup>) in the internal coordination domain, indicating that all of the complexes were nonelectrolytes.<sup>34</sup>

#### FT-IR spectra of complexes

There is a distinct band seen in the tridentate Schiff base L the lengthening of the azomethine group is responsible for the development of a strong band at  $1602\text{ cm}^{-1}$ , respectively,<sup>35</sup> as can be seen in Table 3. The coordination of metal ions to nitrogen azomethine causes an increase in the frequency of  $\nu(\text{C}=\text{N})$  due to the decrease in electron density on the azomethine as a result of the donation of nitrogen electrons to the partially filled d-orbitals of the metal ions

(II).<sup>36,37</sup> The IR spectra of the complexes exhibit characteristic lines at  $1622\text{--}1625\text{ cm}^{-1}$ , which indicates that the metal ions coordinate to the Ligand through the azomethine nitrogen atom.<sup>38</sup> Furthermore, the absorption bands between  $1652$ , and  $1658\text{ cm}^{-1}$  can be attributed to the stretching of the carbonyl group (C=O). At  $418\text{--}449\text{ cm}^{-1}$ ,  $331\text{--}385\text{ cm}^{-1}$ , and  $507\text{--}588\text{ cm}^{-1}$ . In the spectra of the complexes measured in the far-infrared range, it was possible to make out new stretching modes that had not been seen in the L spectrum. As an evidence of creating bonds between the metal ions (II) and the nitrogen azomethine, chloride, and oxygen, these modes are assigned to (M-N), (M-Cl), and (M-O), respectively.<sup>39–41</sup> The broad band  $3446\text{ to }3342\text{ cm}^{-1}$  of the spectrum of FT-IR spectrum of all produced complexes can be attributed to (O-H) hydrated water molecules in molecular complex formulas but complex spectra.<sup>42</sup>

#### Antibacterial action of ligand and complexes

The experiment was carried out in aerobic circumstances at a temperature of 37 °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

**Table 4.** Antibacterial activity of preparation of schiff bases ligand and complexes.

Sample	<i>Pseudomonas</i>	<i>E. coli</i>	<i>strepto</i>	<i>Staph</i>
C <sub>19</sub> H <sub>16</sub> ON <sub>4</sub> S (L)	-	13 mm	-	13 mm
[Mn(L) <sub>2</sub> Cl <sub>2</sub> ].5H <sub>2</sub> O	-	14 mm	-	14 mm
[Co(L) Cl <sub>2</sub> ].5H <sub>2</sub> O	-	18 mm	-	16 mm
[Ni(L) <sub>2</sub> Cl <sub>2</sub> ].6H <sub>2</sub> O	-	16 mm	-	16 mm
[Cu(L) Cl <sub>2</sub> ].2H <sub>2</sub> O	-	16 mm	14 mm	14 mm

**Table 5.** Pharmacological resistance to negative and positive bacteria.

Name of bacteria	DO	TE	DA	RA	CLR	LEV	AMK	CRO	VA	AM
staph	-	-	-	-	-	-	-	13 mm	24 mm	-
E.coli	15 mm	10 mm	-	-	-	16 mm	11 mm	-	-	-
strepto	15 mm	13 mm	-	-	-	37 mm	-	18 mm	-	-
psedo	-	-	-	-	-	22 mm	-	11 mm	-	-

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

aforementioned bacteria at  $1 \times 10^{-3}$ M concentrations of the DMF solvent. 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 *Pseudomonas* were less active than the standard *E. coli*, *strepto* and *staph*. The *E. coli* and *staph* showed the highest action towards Schiff bases ligand and complexes, with a maximum activity of 18 nm. It came to light that the findings of ligand efficacy and its complexes were very effective against bacteria compared with antibiotic (doxycycline, tetracyclin, clindamycin, rifampin, clarithromycin, levofloxacin, amikacin, ceftriaxone, vancomycin, and ampicillin) Tables 4 and 5.

#### Determination of DPPH radical scavenging efficiency

The inhibitory effect of ligand L and its minerals, including Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> on reactive oxygen species was evaluated using DPPH methods. 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 molecule. The color conversion was detected using a UV-Vis spectrophotometer Selecta Spain/Barcelona 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 Ni<sup>2+</sup> and Mn<sup>2+</sup> complex were 54.30% and 45, 27% respectively.<sup>43–45</sup> The free radical scavenging effects of all the compounds with the DPPH radical were evaluated using the following equation: The value of

**Table 6.** Radical scavenging activities, percentage inhibition and IC<sub>50</sub> values.

Sample	Abs. 517 nm	DPPH%
Blank	1.536	
L	1.135	26.11
[Mn(L) <sub>2</sub> Cl <sub>2</sub> ].5H <sub>2</sub> O	0.842	45.27
[Co(L) Cl <sub>2</sub> ].5H <sub>2</sub> O	1.005	34.57
[Ni(L) <sub>2</sub> Cl <sub>2</sub> ].6H <sub>2</sub> O	0.980	54.30
[Cu(L) Cl <sub>2</sub> ].2H <sub>2</sub> O	0.997	35.18

antioxidant efficacy was extracted from the following Equation:

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

PI = Percentage Inhibition

RSA = 100 – PI

RSA = Radical Scavenging Activity and presented in Table 6, under the same conditions.<sup>46</sup>

## Conclusion

The synthesis and characterization of M(II)=Mn, Co, Ni and Cu complexes of the Schiff base ligand produced via the condensation reaction of 4-antipyrinecarboxaldehyde with 2-aminobenzothiazole are reported in this study. Various analytical and spectroscopic techniques, including the <sup>1</sup>H-, <sup>13</sup>C-NMR, FTIR, UV-vis, mass, and C.H.N elemental analysis techniques, were used to completely elucidate the synthesized ligand and complexes. Metal complexes' molar conductance value demonstrates their non-electrolytic nature. At room temperature, the complexes were shown to be stable. Based on the

spectroscopic results like Magnetic Susceptibility, Chloride-containing, and atomic absorption, 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 antipyrine ligand and it is considered one of the strongest electrons donor atoms, forming covalent bonds with the metal atom and azomethine nitrogen atoms from the 2-aminobenzothiazole ligand the octahedral geometry for  $Mn^{2+}$  and  $Ni^{2+}$  complexes but tetrahedral geometry of  $Co^{2+}$  and  $Cu^{2+}$  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.

### 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 presented in manuscript.
- No human studies are presented in 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. R. S.T. 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, تشخيص ودراسة الفعالية الحيوية ومضادات الاكسدة لمعقدات ايونات المعادن الجديدة مع ليكند [4-E (- بنزو [d] ثيازول-2-يليمينو) ميثيل]-5، 1-ثنائي ميثيل-2-فينيلبيرازوليدين-3-اون]

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## المستخلص

تم تحضير أربعة معقدات جديدة مع ليكند ثنائي السن: [4-E (- بنزو [d] ثيازول-2-يليمينو) ميثيل]-5، 1-ثنائي ميثيل-2-فينيلبيرازوليدين-3-واحد] بالصيغة العامة  $M(L)2Cl2 \cdot xH_2O$  أو  $M(L)2Cl2 \cdot xH_2O$ ، حيث يمثل  $M, Mn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}$  حيث تم تحضير قاعدة شف من تفاعل تكثيف 4-انتي بايرين كاربوكسالدهيد و-2-أمينوبنزوثيازول في محلول كحولي. تم تشخيص اليكند والمعقدات التي تم الحصول عليها كيميا ونوعيا باستخدام تقنيات مختلفة بما في ذلك التحليل الدقيق للعناصر، وقياس الحساسية المغناطيسية، والتوصيل المولي، والأشعة تحت الحمراء، الأشعة المرئية و فوق البنفسجية، وطيف الكتلة، طيف الرنين النووي المغناطيسي للبروتون. أشارت القياسات الفيزيائية إلى أن المعقدات المحضرة غير إلكتروليتيه وأظهرت أن اليكند تكون ثنائي السن عند تنسيقها مع أيونات المعادن من خلال ذرة النيتروجين أزوميثين ( $C = N$ ) وذرة الأكسجين من الكربونيل ( $C = O$ ) لجزيئة امينواتي بايرين، وكان الشكل الهندسي ثماني السطوح لمعقدات النيكل والمنغنيز ولكن شكل رباعي السطوح لمعقدات ايونات الكوبلت والنحاس ونسبة الناتج كانت جيدة. أكدت هذه الدراسة على أهمية استخدام طريقة التعقيد المعدني لاستقرار الليكند وزيادة نشاطها الحيوي. يوضح الفحص البيولوجي للمعقدات أن معقدات شيف للمعادن الأساسية تظهر فعالية ملحوظة في مكافحة الكائنات الحية الدقيقة، من خلال استخدام *Pseudomonas* و *E. Coli* و *strepto* و *staph* كسلالات بكتيرية وتم استخدام مرجع مثل الدوكسيسيكليين، التتراسيكلين، الكليندامايسين، ريفامبين، كلاريثروميسين، ليفوفلوكساسين، أميكاسين، سيفترياكسون، فانكوميسين، أمبيسلين لمقارنة المقاومة الدوائية للبكتيريا السلبية والإيجابية. وبالتالي كانت نتائجهم جيدة في التنشيط. بعد ذلك، تم استخدام المركبات المحضرة كمضادات للأكسدة عن طريق تثبيط الجذور الحرة باستخدام DPPH كجذر حر.

**الكلمات المفتاحية:** مضادات الاكسدة، 4-انتي بايرين كاربوكسالدهيد، 2-أمينوبنزوثيازول، النشاط البيولوجي، معقدات قواعد شف.