Synthesis, Characterization and Antibacterial Activity of 1,4-di [aminomethylene carboxyl] phenylene (H$_2$L) and its Complexes Co(II), Cu (II), Zn(II) and Cd (II)

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Abstract. A binucleating tetradentate Schiff base ligand, 1,4- di[aminomethylene carboxylic] phenylene (H$_2$L) and its forth new binuclear complexes [Co(II), Cu(II), Zn(II) and Cd(II)] were prepared via reaction metal (II) chloride with ligand (H$_2$L) using 2:1 (M:L) in ethanol solvent. The new ligand (H$_2$L) and its complexes were characterized by elemental microanalysis (C,H,N), atomic absorption, chloride content, molar conductance's magnetic susceptibility, FTIR UV- Vis spectral and, $^1$H, $^{13}$C- NMR (for H$_2$L). The antibacterial activity with bacteria, *Staphylococcus aureus*, *Bacillus* and *Esccherichia Coli* were studied.

1. Introduction

Schiff base and their metal complexes play an important role in the development of coordination chemistry, resulting in an enormous number of publication. Mohalakshmi and Rajavel have been synthesized [M$_2$(L)]X type (M(II) = Cu, Ni, VO) X= ClO$_4$, SO$_4^{2-}$, L = Schiff base derived from 2-Carboxybenzalddehyde and 3,3’,4,4’-teraaminobiphenyl. They found to be higher antibacterial activity than the free ligand [1]. Bis (O-vaniline) benzidine and its complexes (M$^{(II)}$= Cu, Co, Mn, Zn) and Sm (III), VO$_2$(VI) have been synthesized with 3D molecular modeling and analysis for bond lengths and bond angles have also been carried out on Ni- complex [2]. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated because of their applicability. Chelating ligands contaning O and N donor atoms show broad biological activity and are special interest because of the variety of ways in which they are bonded metal ions [2, 3-8]. It is well known Schiff bases complexes have numerous applications, such as in the treatment cancer [9], as antibactericide agents and as antifungicide agents [10,11]. Recently one of our group research has studied mixed ligand (1,5- Dimethyl-3-oxo-2- phenyl- 2,3-dihydro- $^1$H-pyrazol-4-ylimino) and azide ion forming complexes with Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) ion [12].

Mononuclear complexes [L.M.XH$_2$O], L=[-2-Carboxy methane amino]phenylimino] acetic acid and, [LM.XH$_2$O]Cl L= pyrimidine-2-ylimino acetic acid with M(II) = Co, Ni, Cu, Cd, Hg and Pb were prepared too [13,14]. This paper described the synthesis spectral and magnetic studies of Schiff base 1,4- di-[aminomethylene carboxy] phenylene (H$_2$L) and its binuclear M(II) = Cu, Co, Zn, and Cd complexes. Indeed, the biological activity of the ligand (H$_2$L) and its complexes are screened against selected kinds of bacteria *Bacillus cereus*, *Staphylococcus aureus* and *E.Coli*. 
2. Experimental Part

2.1. Chemicals
All chemicals were purchased from BDH, and used without further purifications.

2.2. Instruments
- FTIR spectra were recorded in KBr on Shimadzu- 8300 Spectrophotometer in the range of (4000-400 cm\(^{-1}\)).
- The electronic spectra in DMSO were recorded using the UV-Visible spectrophotometer type (spectra 190-900 nm) CECEL, England, with quartz cell of (1 cm) path length.
- The melting point was recorded on "Gallen kamp Melting Point Apparatus".
- The Conductance Measurements were recorded on W. T. W. conductivity Meter.
- Metal analysis. The metal contents of the complexes were determined by atomic absorption (A. A.) technique. Using a shimadzu PR-5. ORAPHIC PRINTER atomic absorption spectrophotometer.
- Balance Magnetic Susceptibility model MSB-MLI Al-Nahrain University
- The characterize of new ligand (H\(_2\)L) is achieved by:
  A: \(^1\text{H}\) and \(^{13}\text{C}\)-NMR spectra were recorded by using a Bruker 300 MHZ (Switzerland). Chemical Shift of all \(^1\text{H}\) and \(^{13}\text{C}\)-NMR spectra were (ppm) unit\(e\)recorded in downfield from internal reference tetramethylsilane (TMS), using DMSO-d\(_6\) as a solvent, were done at AL-al-Bayt University, AlMafrag, Jordan
  B: Elemental analysis for carbon, hydrogen and nitrogen was using a Euro Vector EA 3000 A Elemental Analyses (Italy), analysis (A and B) were done at AL-al-Bayt University, AlMafrag, Jordan.

2.3. Synthesis of ligand (H\(_2\)L)
A solution of glyoxylic acid (0.15 g, 2 mmol.) in ethanol (15 ml) was added to a solution of p-phenylene diamine (0.11 g, 1 mmol.) in ethanol (5 ml). The resulting mixture was stirred and refluxed for (4 hrs) Brown powder precipitate was filtered off and recrystallization to the precipitate with hot mixture of methanol: acetone: distilled water (5:5:2) ml to give brown crystals, m.p. (170-172°C), yield 88%

2.4. Synthesis of Co-Complex
A solution of (H\(_2\)L) (0.22 g, 1mmol) in ethanol (20 ml) and a solution of CoCl\(_2\).6H\(_2\)O (0.48 g, 2.4 mol.) in ethanol (5 ml). The mixture was refluxed and stirred for 30 min. the mixture was filtered and dried. The product was recrystallized from hot methanol, dried over anhydrous calcium chloride the pale brown product obtained, M.p. 110 °C, and yield 78%. A similar method was used to prepare of Cu (II) (0.34 g, 2 mmol, m.p. 115°C, and yield 76%, Zn (II) (0.24 g, 2 mmol, m.p. 210°C, and yield 80% and Cd(II) (0.40 g, 2 mmol, m.p. 220°C, and yield 81% complexes. The physical properties for synthesized ligand (H\(_2\)L) and its complexes are shown in table (1).
Table 1. The physical properties for synthesizes ligand (H$_2$L) and its complexes.

| Empirical Formula | Yield % | M.P °C | Colour | Found | Calc. % | Solubility |
|-------------------|---------|--------|--------|--------|---------|------------|
| H$_2$L= C$_{10}$H$_8$O$_4$N$_2$ | 82 | 170-172 | Brown | 54.54 | 3.63 | 12.72 | Methanol, Ethanol, Acetone, DMF |
| [(Co)$_2$(L)(H$_2$O)$_7$Cl].9H$_2$O | 78 | 110 | Pale brown | 15.66 | 4.96 | 3.65 | 18.53 | 15.40 | DMF |
| [(Cu)$_2$(L)(H$_2$O)$_7$Cl].Cl | 76 | 115 | Pale brown | 15.88 | 4.91 | 3.84 | 19.08 | 16.08 | DMF |
| [(Zn)$_2$(L)(H$_2$O)$_7$Cl].3H$_2$O | 80 | 210 | Dark brown | 20.01 | 3.80 | 5.11 | 22.80 | 21.06 | DMSO |
| [(Cd)$_2$(L)(H$_2$O)$_7$Cl].8H$_2$O | 81 | 220 | Dark brown | 15.70 | 3.40 | 3.66 | 18.58 | 29.31 | = |

3. Results and Discussion

3.1. Characterization of ligand (H$_2$L)

In this study, new Schiff base ligand (H$_2$L) type NO / donor atoms was synthesized according to the used method shown in Scheme (1).

![Scheme 1: Synthesis route of ligand (H$_2$L)](image)

Spectroscopic methods [FT-IR, UV-Vis, $^1$H-$^{13}$C-NMR] along with melting point and element microanalysis (C.H.N) were used to characterized new ligand (H$_2$L).

3.1.1. NMR Spectral Data

The $^1$H-NMR spectrum of ligand H$_2$L, Figure 1, multiple chemical shifts range $\delta$ (6.44-7.40) ppm. May assign to aromatic protons. The proton of carboxylic group appeared as slightly multiple broad $\delta$ (9.70, 10.20) ppm. The imine proton (HC=N) is showed as a doublet at $\delta$ (8.1, 8.3) ppm. The signal at $\delta$ (2.5) ppm, refer to deurated DMSO $d_6$ [15-17].

$^{13}$C-NMR spectrum of ligand (H$_2$L). Figure 2, and shows chemical shift for carbonyl group of carboxylic group appeared as expected downfield at (175) ppm. The chemical shifts at (159) ppm was attributed to azomethine group (HC=N). Signals related to aromatic carbon were detected at range (110-130) ppm. Finally, the chemical shift at (40-45) ppm was as due to DMSO-$d_6$ [18].
3.2. Characterization of \((H_2L)\) complexes

The complexes of ligand \((H_2L)\) with \(\text{Co(II)}\), \(\text{Cu(II)}\), \(\text{Zn(II)}\), and \(\text{Cd(II)}\), were prepared via reaction metal (II) chloride salt with ligand \((H_2L)\) using 2:1 \((M:L)\) mole ratio in ethanol solvent respectively. The method of this synthesis shows in scheme 2).

Spectroscopic methods \([\text{FT-IR, U \textendash Vis, A.A.}]\) along with molar conductivity, elemental microanalysis \(C, H, N,\) chloride content, magnetic susceptibility and melting point were used to characterize the prepared ligand complexes. The complexes are stable and soluble in DMSO, DMF

3.2.1. Molar conductance

The molar conductance of the complexes \((\text{Co (II), Cu(II)})\) in DMSO solvent lie in the \((52.8, 33.1)\) S.cm\(^2\) molar\(^{-1}\), indicating its electronic nature \((1:1)\) ratio, the molar conductance of the complexes \([\text{Zn(II)}, \text{Cd(II)}]\) in DMSO solvent \((12.23, 13.37)\) S.cm\(^2\) molar\(^{-1}\) refer to non-electrolytic nature \([19]\).

3.2.2. Magnetic Susceptibility

The magnetic susceptibility for all complexes were measured at room temperature and the effective magnetic moment \((\mu_{\text{eff}})\) values were listed in table (2). The magnetic susceptibility measurement for the dinuclear complexes \(\text{Co (II)}\) and \(\text{Cu (II)}\) are \((6.79)\) and \((2.54)\) B.M which suggests the presence of
unpaired electron. Large and permanent magnetizations may be established within the ferromagnetic metals [Co (II) and Cu (II)] [20,21].

Table (2) The molar conductance and magnetic susceptibility of the complexes

| Empirical Formula | Λ M S. cm⁻² molar⁻¹ | ratio | μ effect BM |
|-------------------|---------------------|-------|-------------|
| [(Co₂)(L)(H₂O)₂Cl]Cl9H₂O | 52.8 | 1:1 | 6.79 |
| [(Cu₂)(L)(H₂O)₂Cl]Cl | 33.1 | 1:1 | 2.54 |
| [(Zn₂(L)(H₂O)₂Cl]3(H₂O) | 12.23 | Neutral | - |
| [(Cd₂(L)(H₂O)₂Cl]8(H₂O) | 13.37 | Neutral | - |

3.2.3. FT-IR Spectral data

IR spectral at the ligand (H₂L) figure 3 shows disappearance of ν(C=O) (1795) cm⁻¹ and ν(NH₂) (3381, 3373) cm⁻¹ in starting material, and appeared new strong bands at (1690 and 1650 cm⁻¹) are due to ν(C=O) of carboxylic group and (HC=N) imines [22, 23]. The stretching band of middle intensity at [3350-3294] cm⁻¹ attributed to ν(OH) of carboxylic group compared with precursors which indicates the ligand (H₂L) has been obtained. Bands corresponding to (C—H) aromatic stretching at (3140-3043) cm⁻¹. Band at 829 is due to para disubstuted phenyl [24].

The IR spectra of ligand (H₂L) complexes Cu(II), Zn(II), Cd(II) and Co(II) 'figure 4', table (3) exhibited band at (3396-3363) cm⁻¹ and (987-720) cm⁻¹ refer to water coordinate [25]. The bands (835-827) cm⁻¹ attributed to p-substituted aromatic [26]. The detected bands of (620) cm⁻¹, (1625) cm⁻¹, and (1650) cm⁻¹ in the IR spectra of all ligand complexes refer to stretching frequency of imine group (HC=N) which were shifted to lower frequency when if compared with that of free ligand (H₂L) (1650) cm⁻¹ showing that coordination with the metal ions was occurred via nitrogen atom of imine group (HC=N) [23,24]. The ν(C=O), νas (COO) and νs (COO) stretching vibrations of the carboxylate group are observed at (1665-1650) cm⁻¹ and (1398-1350) cm⁻¹. For all complexes (Δas − Δs) equal (313-252) cm⁻¹, supporting, the idea the ligand coordinate through deprotonated oxygen of mono dentate carboxylate [26,27]. New bands are found in the spectra of all complexes in the regions (597-532) cm⁻¹ which are attributed to ν (M—N) mode [16]. The bands at (459-412) cm⁻¹ refer to ν (M—O) mode [19]. Therefore, from IR spectra, its concluded that the ligand behave an anion tetradentate and bind to the two metals; two imines and two carboxylates, forming octahedral for Co(II), Cu (II) and tetrahydral for Zn(II) and Cd(II) structures.
Figure. 3 FT-IR spectrum of ligand H$_2$L

Figure. 4 FT-IR spectrum of Co-complex
3.2.4. \textit{U.V–Vis} Spectral Data

The electronic spectral data for ligand (H$_2$L) and its complexes are summarized in table (4). The electronic spectra for ligand displayed absorption at (266,345) nm (37594-28985) cm$^{-1}$ were attributed to intraligand $\pi \to \pi^*$, $n \to \pi^*$, respectively [28]. The UV-Vis spectrum of Co (II) complex fig. (5). Displayed broad centered band at (656) nm (15244) cm$^{-1}$ was attributed to (d—d) spin allowed electronic transition type $4T_{1g} \to 4A_{2g}$ characteristic octahedral geometry around Co(II) [29]. The UV-Vis spectrum of Cu (II) complex showed broad peak centered at (580) nm (17241) cm$^{-1}$ was assigned to $2E_g \to 2T_{2g}$ transition, conforming octahedral geometry around Cu(II) [30]. The electronic spectrum of Zn (II), Cd (II) complexes exhibited charge transfer peaks compared with free ligand in UV.spectrum which are common phenomenon for metal complexes where (d—d) transitions are excluded [31].

\begin{table}[h]
\centering
\begin{tabular}{lcccccc}
\hline
\textbf{Compound} & \textbf{$\nu$OH} & \textbf{$\nu$ (NH$_2$)} & \textbf{$\nu$ (C=N)} & \textbf{$\nu$ (C=O)} & \textbf{$\Delta$ cm$^{-1}$} & \textbf{P. subs.} \\
\hline
\textit{L}=&C$_{10}$H$_8$O$_4$N$_2$ & &  & 1745 &  & \\
\textit{p}-phenylene & 3361 & 3381 & 3008 & & & \\
diamine & 3371 & & &  &  & \\
Co-complex & 1650 & 3140 & 1690 & 1420 & 1380 & 829 \\
Cu-complex & 1630 & 3120 & 1650 & 1398 & 252 & 827 & 987 & 597 & 441 \\
Zn-complex & 1622 & 3130 & 1662 & 1350 & 312 & 829 & 735 & 534 & 417 \\
Cd-complex & 1625 & 3125 & 1665 & 1352 & 313 & 835 & 720 & 532 & 459 \\
\hline
\end{tabular}
\caption{Electronic spectral data of the ligand (H$_2$L) and its complexes}
\end{table}

Figure 5. Electronic spectrum of Co-complex

\begin{table}[h]
\centering
\begin{tabular}{lcccccc}
\hline
\textbf{Compound} & \textbf{$\lambda$ nm} & \textbf{$\nu$ wave number} & \textbf{E$_{max}$ molar$^{-1}$} & \textbf{Assignment} & \textbf{Proposed Structure} \\
\hline
\textit{L}=&C$_{10}$H$_8$O$_4$N$_2$ & 266 & 37594 & 785 & $\pi \to \pi^*$ \\
& & 345 & 28985 & 1135 & $n \to \pi^*$ \\
Co-complex & 656 & 15244 & 185 & $4T_{1g} \to 4A_{2g}$ & Distorted octahedral \\
\hline
\end{tabular}
\caption{Electronic spectral data of the precursor, ligand and its complexes}
\end{table}
4. Biological activity of the ligand (H₂L) and its Complexes.
Indicating the new ligand (H₂L) and its complexes, exhibited antibacterial activity against four kinds of bacterial *E. Coli*, *Staphylococcus aureus* and *Bacillus cereus* respectively. Table (5) and Table (6) shows the various activities of the ligand and its complexes can be explained on the bases of overtones' concept and Tweeds chelating theory [32-33].

Table (5) the inhibition circle diameter in millimetre for the bacteria after 24 hours in cubation paid and 37°C

| Compounds      | Bacillus cereus | Staphylococcus Aureus | E.Coli |
|----------------|-----------------|-----------------------|-------|
| Ligand H₂L     | 0               | 10                    | 13    |
| Co-complex     | 0               | 14                    | 15    |
| Cu-complex     | 0               | 8                     | 0     |
| Zn-complex     | 0               | 10                    | 8     |
| Cd-complex     | 0               | 10                    | 0     |

E.Coli  = Escherichia coli

Figure (6) Antibacterial activity of the ligand and its complexes (inhibition zone diameter, mm)
5. Conclusions
The new ligand (H₂L) and its complexes behave tetradentate ligand through its two azomethene nitrogen and two oxygen atom of \( \text{O} \stackrel{\text{C}}{\longrightarrow} \text{O} \) group of two five member ring with central metal ions, Co (II), Cu (II), Cd (II) and Zn(II) forming complexes with molecular formula.

\[
\begin{align*}
[M_2L_2Cl_2](OH_2)_2Cl. XH_2O \quad (M = \text{Co} \quad X = 0) \\
[M_2L_2Cl_2](OH_2)_2Cl. XH_2O \quad (M = \text{Zn} \quad X = 3) \\
[M_2L_2Cl_2](OH_2)_2Cl. XH_2O \quad (M = \text{Cd} \quad X = 8)
\end{align*}
\]

The distorted octahedral geometrical structure was suggested for Co(II) and Cu(II) complexes and tetrahedral for Zn(II) and Cd(II) complexes based on the characterization data for all technique.

The antibacterial study showed that the ligand H₂L and its complexes showed various activities to the strain of bacteria taken under study.

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