Synthesis, Characterization and Biological Activity of Schiff Bases Chelates with Mn(II), Co(II), Ni (II), Cu(II) and Hg(II)

Lecturer. Dr. Rehab K. al shemary
Assist. Prof. Dr. Lekaa K. Abdul Karim
Lecturer. Dr. Wurood A. Jaafar

Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Baghdad, Iraq.

E-mail: drrehabalshemary@gmail.com.

Received 27/1 /2016
Accepted 25/5 /2016

Abstract:
In this paper, some series of new complexes of Mn(II), Co(II), Ni (II) Cu(II) and Hg(II) are prepared from the Schiff bases (L¹, L²). (L¹) derived from 4-aminoantipyrine and O-phenylene dia mine then (L²) derived from (L¹) and 2-benzoyl benzoic acid. Structural features are obtained from their elemental microanalyses, molar conductance, IR, UV–Vis, ¹H, ¹³CNMR spectra and magnetic susceptibility. The magnetic susceptibility and UV–Vis, IR spectral data of the ligand (L¹) complexes get square–planar and tetrahedral geometries and the complexes of ligand (L²) get an octahedral geometry. Antimicrobial examinations show good results in the sharing complexes.

Key words: Schiff Base Complexes, Biological Activity and NMR.

Introduction:
Now there are new studies attracting the attention of biochemists around new types of Schiff bases derivative from 4-aminoantipyrine and its complexes, generally because of their use in the assortment of applications in analytical biological, pharmacological, clinical areas and especially chemotherapeutic applications [1-3]. The precedent literature ex plains increasing activity for organic compounds used drugs when they are treated as metal complexes [4-6]. In the 1980s some investigations show that the interaction of little molecules with DNA are very necessary for the styling of new kinds of molecules such as pharmaceutical [7] and their transition metal complexes which have chemical nuclease activity; it is studying the technicality of DNA with transition metal complexes and the interaction model [8]. The reconnoitring of metal complexes and their application in antineoplastic, bioengineering and molecular biology medication have become hotspots in recent years[9]. 4-aminoantipyrine ligand has become a flexible system by condensation with a set of reagents such as carbazides, aldehydes, thiosemicarbazides and ketones etc [10]. This paper reports synthesis and characterization of new Schiff bases ligands derived from 4-
aminoantipyrine and their complexes with Mn(II), Co(II), Ni (II) Cu(II) and Hg(II).

Materials and Methods:
Chemicals
4-aminoantipyrine, O-Phenylene diamine and 2-benzoyl benzoic acid and several metal(II) chlorides are Merck compounds. Glacial acetic acid reagent and trade solvents are distilled and they are used for the synthesis of all compounds.

Instrumentation
Electronic spectra are recorded using UV-Vis. spectrophotometer type CECIL, England, by using quartz cell has path length (1cm) in range (200-1000)nm in DMSO at room temperature. Then Melting point is measured by “Gallenkamp Melting point Apparatus”. Elemental microanalysis C.H.N. are carried out using Euro Vector EA 3000 A Elemental Analysis(Italy). FT-IR measurements are calculated on Shimadzu- 8300, Spectrophotometer in the range of (4000-400cm⁻¹) as KBr disc. In DMSO by using a Bruker 300 MHZ (Switzerland) are obtained on (¹H and¹³C-)NMR spectra, Chemical shift of are obtained in δ(ppm) unit downfield internal reference (TMS), Conductivity measurements are obtained from WTW conductivity meter by using ethanol as a solvent of 10⁻³M concentration at room temperature. Magnetic susceptibility measurements are obtained at room temperature on the solid state applying Faraday's Method using Bruker BM6 instrument. Metal analyses of complexes are determined by using a Shimadzu PR-5. ORAPHIC PRINTER atomic absorption spectrophotometer.

Synthesis of [(N¹Z, N²Z)-N¹, N²-bis (4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylidene)benzene-1,2-diamine] (L¹)[10]

4-Aminoantipyrine (4.06g, 0.02 mmol) in 10 mL of hot ethanol is stirred with O-phenylenediamine (1.671g, 0.01 mmol) after adding [anhydrous potassium carbonate] in 30 ml of ethanol is refluxed for 36hrs. The potassium carbonate is filtered off from the mixture and the solvent is evaporated. The precipitate separated is washed with diethyl ether. Recrystallization has been carried out in methanol. The yields (2.5g, 62%), m.p: 160-162 °C, Scheme (1).

Scheme(1): synthesis route of L¹

Synthesis of (N¹Z,N²Z)-N1,N2-bis(4-(diphenylmethyleneamino) -1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H) -ylidene) benzene-1,2-diamine(L²)

An ethanolic solution of (L¹) (7.74 g, 0.01 mol) is added to the solution of ethanol of 2-benzoyl benzoic acid (4.06 g, 0.02 mol), and the product mixture is refluxed for 10 h after the supplement of
[anhydrous potassium carbonate]. The [potassium carbonate] is filtered off from the mixture then the solvent is vapourised. The pale orange solid discrete is then recrystallized from 5ml of [methanol, distilled water, acetone] and diethyl ether, yield: (3g, 71%): m.p: 178-180 °C., as shown in Scheme (2)

![Chemical structure](image)

**Scheme (2): Synthesis Route of L^2**

**Synthesis of Complexes:**
A solution of (M(II)Cl)₂ metal (II) chloride (2.38 g CoCl₂,6H₂O, 2.37 g NiCl₂,6H₂O, 1.05 g CuCl₂,2H₂O, 1.98 g MnCl₂,4H₂O and 2.71 g HgCl₂) in absolute ethanol (1 mmol) is refluxed with solution from ethanol of the Schiff base (1 mmol), (4.78g,L₁) or (8.95g,L^2) for 1 h. The solution is then minimised to (2/3) two-third on a water bath. The resultant precipitate is filtered, washed completely with hot ethanol then by vacuum it was dried.

**Table (1): Some Physical Properties of Prepared Ligands(L₁&L^2) and its Complexes**

| Empirical Formula | Chemical Formula | Molecular Weight (g/mol) | M.P °C | Colour       | Yield % | % (Calc)/Found C % | H % | N % | Cl % | Metal |
|-------------------|------------------|--------------------------|--------|--------------|---------|---------------------|-----|-----|------|-------|
| L₁                | C₃₃H₆₀N₄        | 478.59                   | 160-162 | pale yellow  | 62      | (70.27)             | 6.32 | 18.42 | 11.65 | 9.69  |
| [Co(L₁)]Cl₂      | C₃₃H₆₀CoN₄Cl₂   | 608.34                   | 234-236 | Greenish blue | 77      | (55.27)             | 6.45 | 18.42 | 11.72 | 10.23 |
| [Cu(L₁)]Cl₂      | C₃₃H₆₀CuN₄Cl₂   | 613.04                   | 225-227 | Olive        | 80      | (54.86)             | 6.45 | 18.42 | 11.72 | 10.23 |
| [Ni(L₁)]Cl₂      | C₃₃H₆₀NiCl₂     | 608.19                   | 246-248 | pale yellow  | 75      | (55.30)             | 6.45 | 18.42 | 11.65 | 9.65  |
| [Mn(L₁)]Cl₂      | C₃₃H₆₀MnN₄Cl₂   | 604.44                   | 227-229 | pale yellow  | 78      | (55.64)             | 6.45 | 18.42 | 11.73 | 10.30 |
| [Hg(L₁)]Cl₂      | C₃₃H₆₀HgN₄Cl₂   | 750.09                   | 247-249 | pale yellow  | 69      | (55.27)             | 6.45 | 18.31 | 11.43 | 9.15  |
| L²                | C₃₃H₆₀N₄        | 894.36                   | 178-180 | Pale-orange  | 71      | (75.15)             | 5.23 | 12.52 | 11.78 | -     |
| [Co(L²)]Cl₂      | C₃₃H₆₀CoN₄Cl₂   | 966.31                   | 250-252 | Dark brown   | 74      | (70.15)             | 6.45 | 11.59 | 11.09 | 6.09  |
| [Cu(L²)]Cl₂      | C₃₃H₆₀CuN₄Cl₂   | 956.55                   | 233-235 | Reddish brown | 84      | (70.32)             | 4.65 | 11.71 | 6.06  | 6.68  |
| [Ni(L²)]Cl₂      | C₃₃H₆₀NiCl₂     | 951.69                   | 252-254 | Greenish brown | 78      | (70.67)             | 4.64 | 12.00 | -     | 16.73 |
| [Mn(L²)]Cl₂      | C₃₃H₆₀MnN₄Cl₂   | 947.94                   | 240-242 | brown        | 70      | (70.95)             | 4.65 | 11.82 | -     | 5.80  |
| [Hg(L²)]Cl₂      | C₃₃H₆₀HgN₄Cl₂   | 10947.94                 | 229-231 | brown        | 86      | (61.50)             | 3.87 | 10.08 | -     | 17.83 |
Biological Activity
We studied effects of biological screening for the compounds by testing in vitro against the bacteria: (Escherichia coli), (Staphylococcus aureus), (Bacillus subtilis) and (Pseudomonas aeruginosa) by the well-diffusion method at 25°C [10]. The well is filled with the test solution (10^{-3}M) is prepared by dissolving the compounds in DMSO using a micropipette and the plate is incubated for 24hs. Using agar nutrient as the medium inoculated with microorganisms. During this time, the test solution spread and the evolution of the inoculated bacteria are affected.

Results and Discussion:
The synthesised ligands (L^1 and L^2) have been characterised by [(C.H.N), FT-IR, ^1H, ^13CNMR, UV-Vis] spectroscopic method. The molar conductance of (10^{-3} M) in DMSO solutions of prepared complexes indicate the(1:2 electrolytes) for (L^1) and non-electrolytic for (L^2) complexes, data are presented in Table (5).

FT-IR Spectra
The value of the IR spectra of two ligands and their complexes are listed in Table (2). The bands in spectra of the ligands and complexes are compared and considered. The IR spectra of ligand (L^1) displays a strong peak at 1622 cm^{-1} refers to ν(C=N) azo methane group. This peak shifts to lower energy region by (13-9) cm^{-1} in the complexes [11]. It suggests bonding through (C=N) nitrogen. The sharp peaks around 3427 and 3342 cm^{-1} in the spectra of (L^1) has been assigned to amine groups. In the complexes Table (3) the IR spectra show characteristic peaks in the region 3390-3360 and 3286 -3257 cm^{-1} which are lower in comparison with free NH_2. Hence, it can be concluded that the nitrogen atoms of the amino groups are involved in metal coordination [12]. In all complexes, new band in there gion (565-545) cm^{-1} are due to the formation of ν(M-N) band.

The IR spectrum of Schiff base(L^2) shows two strong bands at 1647 and 1624 cm^{-1} referring to ν(C=N) groups. In
IR spectra of metal complexes; they shift down (7-36 cm⁻¹) due to chelating coordination of the (C=N) nitrogen's to the central metal ion. The appearance of broad peak at 3446 cm⁻¹ in the ligand (L²) has been given to ν(OH) carboxylic group. In the complexes spectra this band disappeared, supporting the idea that the ligand chelated during deprotonated oxygen of (COOH) [13]. The νasymmetric(COO⁻) and νsymmetric(COO⁻) stretching vibrations of the (carboxylate O) are observed at (1436,1319) cm⁻¹ for the free ligand (L²), these stretching vibrations are shifted to higher or lower frequencies at (1450-1471) cm⁻¹ and (1327-1392) cm⁻¹ for all the complexes, (Δνasym-Δνsym)= (123-79) cm⁻¹, supporting the notion that the ligand coordinate during deprotonated O of carboxylate [14]. In all complexes, new peaks in range (565-545) cm⁻¹ and (486-447) cm⁻¹ referred to the fashioning of ν(M-N) and ν(M-O) bands respectively [15].

Table 2: Characteristic Infrared Absorption Frequencies in (cm⁻¹) of Ligand and Complexes

| Compound | ν(OH) | νasymmetric(NH₂) | νsymmetric(NH₂) | ν(C-H) | ν(C=O) | ν(C≡N) | νasymmetric(COO⁻) | νsymmetric(COO⁻) | Δν | M-N | M-O |
|----------|-------|------------------|-----------------|--------|--------|--------|-------------------|------------------|-----|-----|-----|
| L¹       | -     | 3427             | 3343            | 3068   | 2920   | 1622   | 1572             | -                | -   | -   | -   |
| [Co(L¹)₂]Cl₂ | 3367 | 3274            | 3087            | 2944   | 1612   | 1574   | -                | -                | -   | -   | 459 |
| [Cu(L¹)₂]Cl₂ | 3337 | 3267            | 3062            | 2991   | 1610   | 158    | -                | -                | -   | -   | 459 |
| [Ni(L¹)₂]Cl₂ | 3367 | 3286            | 3078            | 2967   | 1619   | 1560   | -                | -                | -   | -   | 459 |
| [Mn(L¹)₂]Cl₂ | 3390 | 3278            | 3062            | 2991   | 1610   | 1567   | -                | -                | -   | -   | 459 |
| [Hg(L¹)₂]Cl₂ | 3360 | 3257            | 3010            | 2959   | 1617   | 1567   | -                | -                | -   | -   | 459 |
| L²       | 3446  | -                | 3021            | 2991   | 1647   | 1624   | 1563             | 1440             | 1321| 119| -   |
| [Co(L²)₂] | -     | -                | 3084            | 2967   | 1655   | 1598   | 1571             | 1460             | 1339| 121| 574|
| [Cu(L²)₂] | -     | -                | 3062            | 2944   | 1603   | 1597   | 1561             | 1466             | 1342| 124| 574|
| [Ni(L²)₂] | -     | -                | 3022            | 2991   | 1629   | 1599   | 1567             | 1459             | 1332| 127| 594|
| [Mn(L²)₂] | -     | -                | 3032            | 2991   | 1630   | 1599   | 1567             | 1457             | 1356| 101| 582|
| [Hg(L²)₂] | -     | -                | 3030            | 2991   | 1640   | 1614   | 1567             | 1455             | 1351| 104| 587|

NMR Spectra

¹H NMR spectrum of (L¹) in DMSO-d₆ Figure(2), Table(3a) solution shows the following signals: =C-CH₃ at δH 2.15, DMSO at δH 2.5, N-CH₂ at δH 3.33, NH₃ at δH 6.25, C₆H₅ as multiplet at δH 6.67 ~7.07, Ph-NH- at δH 7.41[15,16,7]. The ¹³C NMR spectrum of L¹ in DMSO-d₆, Figure(3), Table (3b) solution shows the signals at: (8.83 for =C-CH₃ group); (34.95 for N-CH₃ group); (40.59 for DMSO); (109.54 for =C-N); (123.09~135.89) to 4 benzene rings) and (140.48 for C=C in antipyrine). The peak observed at 164.57 is due to the C=N imine groups[16, 8].

¹H NMR spectrum of (L²) Figure (4), Table (4a) in DMSO-d₆, solution shows the following signals: DMSO-d₆ at δH 2.5, N-CH₃ at δH 2.15, OH-CH at δH 3.34, C₆H₅ as multiplet at δH 6.67 ~7.14, Ph-NH- at δH 7.84. The peaks observed at δH 13.14 is attributable to the acidic OH group present in the 2-benzoyle benzoic acid, shown Table(2b) [16,9]. The ¹³C NMR spectrum of L² in DMSO-d₆, Figure(5), Table(4b) solution
shows the signals at: (9.13 for –C–CH$_3$ group); (34.70 for N–C$_3$H$_7$ group); (40.59 for DMSO); (110.18 for –C–N); (123.90–135.89) to 4 benzene rings) and (140.48 for C=C in antipyrine). The peak observed at 167.17 is due to the acidic COOH group present in the 2-benzoyle benzoic acid. The peak observed at (164.89) was attributable to the C=N imine group [15,10].
Fig. (4): $^{13}$C- NMR Spectrum of Ligand (L$^1$)

Table (3a): $^1$H-NMR Chemical Shifts for Ligand (L$^1$) (ppm in DMSO)

|   | CH$_3$-N | DMSO | CH$_3$-C= | NH$_2$ | C$_6$H$_5$-Ph-NH$_2$- |
|---|----------|------|----------|-------|---------------------|
|   | 2.16     | 2.5  | 3.33     | 4.79  | 6.67-7.07           | 7.84   |

Table (3b): $^{13}$C-NMR Chemical Shifts for Ligand (L$^1$) (ppm in DMSO)

|   | CH$_3$-C= | CH$_3$-N | DMSO | =C-N$_{pyridine}$ | C=C$_{aromatic}$ | C=C$_{pyridine}$ | HC=N |
|---|----------|----------|------|------------------|----------------|----------------|------|
|   | 8.83     | 34.95    | 40.50| 110.18           | 123.90-135.98  | 140.48         | 164.57|

Table (4a): $^1$H-NMR Chemical Shifts for Ligand (L$^2$) (ppm in DMSO)

|   | DMSO | CH$_3$-N | CH$_3$-C= | C$_6$H$_5$ | Ph-NH$_2$- | OH |
|---|------|----------|----------|-----------|------------|----|
|   | 2.5  | 2.15     | 3.34     | 6.67-7.14 | 7.84       | 13.14 |
Electronic Spectra

The (UV-Vis) spectrum for the (L¹), exhibits two high intense absorption peaks at (243 nm) and (289 nm), assigned to ($\pi \rightarrow \pi^*$) transition respectively [17], Table (5). The (UV-Vis) spectrum of [Co(L¹)Cl₂] complex exhibits three peaks, the first high broad peak at (261 nm) is due to the (L.F), while the second weak peak at (347 nm) is due to the (C.T). The third peak at (467 nm) is assigned to $^5A_2$ ($P$) $\rightarrow T_1$ ($P$) transition and magnetic moment $\mu_{eff} = 2.41$ B.M at room temperature, the low value of the magnetic moments suggest low spin [12, 18] a coordination number of four for the central Co (II) ion and obtaining a square planar geometry. [Cu(L¹)]Cl₂ complex exhibits three peaks, the first high broad peak at (251 nm) is due to the L.F, while the second band at (357 nm) is due to the (C.T). The third weak peak at (633 nm), which assigned to $^3T_2 \rightarrow ^2E$, transition. Cu (II) complex shows a value of $\mu_{eff} =1.73$ $\mu_B$. The observed magnetic moments of Cu (II) showing 1 unpaired electron with paramagnetic kind and propose a square plane geometry in terms of Jahn-Teller effects[13].[Ni(L¹)]Cl₂ complex, exhibits four peaks, the first high peak at (271 nm) is due to the ligand field, while the second middle broad peak at (354 nm) is due to (C.T). The third and fourth weak peaks at (514 nm) and at (630 nm) can be assigned to the $^1A_g \rightarrow ^1A_2g$ ($\nu_2$) and $^1A_g \rightarrow ^1B_1g$ ($\nu_1$) transitions respectively. Magnetic susceptibility of Ni(II) complex diamagnetic, a coordination number of four for the central Ni(II) ion and attaining square planar geometry [14]. [Mn(L¹)]Cl₂ complex, exhibits three peaks, the first high band at (258 nm) is due to (L.F) and the second peak at (304 nm) is due to the (C.T) transition, the three weak peak at (514 nm) can be assigned to the $^6A_1 \rightarrow ^4T_1$ ($\nu_3$). Magnetic moment $\mu_{eff} = 4.58$ B.M at room temperature, this low value the magnetic moments suggest high spin [15] a coordination number of four for the central manganese (II) ion and attaining a tetrahedral geometry. [Hg(L¹)]Cl₂ complex does not appear any band in the visible region, shows a peak at (269 nm) is due to (L.F) absorption, and therefore the bands appear at (310 and 385) nm in the spectrum of the complex could be attributed to the (C.T) transition. Magnetic susceptibility measurements for Hg (II) (d⁰⁰) show diamagnetic as perspective from their electronic arranging [16].

The (UV-Vis) spectrum for the (L²), exhibits two small absorption peaks at (264 nm) and, and high intense absorption peak at (297 nm) assigned to (π→π*) transition respectively [17].[Co(L²)] complex, exhibits three peaks, the first high intense peak at (277 nm) is due to the (L.F), while the second peak at (365 nm) is due to the (C.T). The third weak peak at $\nu_1 = (410$ nm) assigned to $^4T_{1g(P)} \rightarrow ^4T_{1g(P)}$. The room temperature magnetic moment ($\mu_{eff} = 5.42$ B.M) corresponded to a high spin octahedral symmetry [12, 17].[Cu(L²)] complex, exhibits three peaks, the first and second high intense peaks at (272 nm) and (323 nm) are due to the (L.F) and (C.T) transitions. The third and fourth weak peaks at (417 nm) and (937 nm) are assigned to ($^2B_1g \rightarrow ^2B_2g$) and ($^2B_1g \rightarrow ^2A_1g$) transitions. Hence the Cu (II) complex showed distorted octahedral geometry. Cu (II) complex displays value of ($\mu_{eff} = 1.81$ B.M) [18, 19].

[Nil²] complex, exhibits five peaks.
the first and second high intense peak at (276 nm) and (356 nm) is due to the (L.F), while the third peak at (408 nm). The fourth and fifth peaks at (734 nm) and (887 nm) which assigned to \( (^3A_2g \rightarrow ^3T_1g(F) \rightarrow ^3T_2g)(v_2) \) (d-d), and \( (^3A_2g(F) \rightarrow ^3T_2g(F)(v_1)) \) (d-d), transitions, respectively in an octahedral geometry. The complex exhibit a value of \( \mu_{\text{eff}} = 2.82 \) B.M, which suggests an octahedral geometry around the central Ni ion [19]. [Mn(L$_2^2$)] complex exhibits four peaks, the first and second high peaks at (275nm) and (331nm) are due to (L.F) and (C.T) transition. The fourth-week peak at (396nm) and (957 nm) can be assigned to the \( 6^1A_1g(F) \rightarrow ^4T_2g \quad (G(v_3)) \) and \( 6^1A_1g(F) \rightarrow ^4T_2g \quad (G(v_2)) \) transitions. Magnetic moment \( \mu_{\text{eff}} = 4.72 \) B.M at room temperature, this low data of the magnetic moments suggest high spin [20] a coordination number of 6 for the central manganese (II) ion and attaining an octahedral geometry. [Hg(L$_2^2$)] complex exhibits two high peak at (212 nm) is due to the (L.F), while the second peak at (350 nm) is due to the, in an octahedral geometry. There is no ligand field stabilisation activity Hg (II) ions because of its completed (d$^{10}$) shell. This metal ion is diamagnetic and does not possess any d-d transition [21]

### Table (5): Electronic Spectral Data of the Ligands (L$^1$ & L$^2$) and their Metal Complexes.

| Compound          | $\mu_{\text{eff}}$ | $\lambda_m$ | $\lambda nm$ | wave number (0/cm$^{-1}$) | $\varepsilon_{\text{max}}$ molar$^{-1}$ | Assignments | Geometries |
|-------------------|---------------------|-------------|--------------|---------------------------|----------------------------------------|-------------|------------|
| L$^1$             | -                   | -           | 243          | 41152                     | 2113                                  | x→2A$^*$    | -          |
| L$^1$             | -                   | -           | 289          | 34602                     | 1546                                  | -           | -          |
| [Co(L$^1$)]Cl$_2$ | 2.41                | 73          | 261          | 38314                     | 21541                                 | LF          | Tetrahedral|
| [Cu(L$^1$)]Cl$_2$ | 1.73                | 78          | 251          | 39840                     | 2149                                  | LF          | Tetrahedral|
| [Ni(L$^1$)]Cl$_2$ | 4.48                | 75          | 258          | 38759                     | 2149                                  | LF          | Tetrahedral|
| [Mn(L$^1$)]Cl$_2$ | 5.42                | 10          | 277          | 36101                     | 1956                                  | LF          | Octahedral |
| [Cu(L$^2$)]Cl$_2$ | 1.81                | 15          | 272          | 36764                     | 2351                                  | LF          | Octahedral |
| [Ni(L$^2$)]Cl$_2$ | 3.23                | 13          | 276          | 36231                     | 1963                                  | LF          | Octahedral |
| [Mn(L$^2$)]Cl$_2$ | 4.72                | 18          | 277          | 36363                     | 1977                                  | LF          | Octahedral |
| [Hg(L$^2$)]Dia   | 16                  | 212         | 30211        | 34920                     | 1546                                  | C.T         | Octahedral |
|                  |                     |             | 28571        | 34920                     | 1546                                  | C.T         | Octahedral |

Baghdad Science Journal

Vol.14(2)2017

398
Diamagnetic

**Antibacterial Activities:**

Tetradentate and hexadentate Schiff base ligands ($L_1, L_2$) and the Mn(II), Cu(II), Ni(II), Co(II), and Hg(II) complexes showed biological activities against the four types of bacterial Figure (6&7), Table(6). On the comparing the antimicrobial activities of the Schiff base ligands and their complexes with those of normal bacteria, it was shown that the complexes had reasonable activity as compared to the normal but all the metal complexes were larger active than their free ligands. The maximum inhibition zone of the metal complexes than the free ligand can be expounded based on the chelation theory and the overtone concept. The overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with given groups are on account of reduced the polarity of the metal ion in upon chelation [22]. Furthermore, this enhances the blocking of the metal binding sites and the penetration of the complexes into lipid membranes in the enzymes of bacteria that rises the delocalization of the π-electrons above the full chelating ring [23].

![Fig. (6): The Variance between the Antimicrobial Activity of (L₁) and their Complexes](image)

![Fig. (7): The Variance between the Antimicrobial Activity of (L₂) and their Complexes](image)

**Table (6): Diameter of Zone of Inhibition (mm) for Ligands (L₁, L₂) and their Complexes.**

| Comp.      | Escherichia. Coli | Staphylococcus aureus | Bacillus | Pseudomonas |
|------------|-------------------|-----------------------|----------|-------------|
| $L_1$      | 2                 | 2                     | 1        | 3           |
| [Co(L₁)Cl₂]| 16                | 12                    | 15       | 17          |
| [Cu(L₁)Cl₂]| 8                 | 10                    | 15       | 12          |
| [Mn(L₁)Cl₂]| 18                | 23                    | 10       | 16          |
| [Ni(L₁)Cl₂]| 16                | 20                    | 14       | 20          |
| [Hg(L₁)Cl₂]| 19                | 23                    | 25       | 18          |
| $L_2$      | 6                 | 5                     | 4        | 7           |
| [Co(L₂)]  | 14                | 13                    | 16       | 18          |
| [Cu(L₂)]  | 17                | 19                    | 20       | 17          |
| [Mn(L₂)]  | 16                | 15                    | 22       | 18          |
| [Ni(L₂)]  | 19                | 20                    | 24       | 11          |
| [Hg(L₂)]  | 21                | 24                    | 21       | 16          |
Conclusion:
A tetradeinate Schiff base ligand (L\(^1\)) formed from the condensation of 4-aminopridine and O-phenylenediamine and a hexadentate Schiff base ligand (L\(^2\)) formed from the condensation of (L\(^1\)) and 2-benzoyl benzoic acid are synthesised and characterised. The metal complexes with Ni\((II)\), Hg\((II)\), Co\((II)\), Cu\((II)\) and Mn\((II)\) ions with the ligands(L\(^1\))and(L\(^2\)) are synthesised and characterised . The bonding of the ligand in the metal complexes and the thorough geometry has been concluded on the basis of various spectroscopic mechanics. The relative in vitro antimicrobial results suggest that all complexes display a significant antimicrobial activity as compared to the ligand, L\(^1\), L\(^2\) and their Ni\((II)\), Hg\((II)\), Co\((II)\), Mn\((II)\) and Cu\((II)\) complexes.

References
[1] Torayama, H.; Hitoshi, M.; 1997, Preparation and characterization of novel cyclic tetranuclear manganese (III) complexes: Mn(III) 4 (X-salmphen) 6 (X-salmphenH 2= N, N'-di-substituted-salicylidene-1,3-diaminobenzene(X=H,5Br). Polyhedron 16(21): 3787-3794.
[2] Vivekan, D.; Biradar, B.; Mruthyunjayswamy, H. M. 2013, Synthesis Characterization and Antimicrobial Activity Studies of Some Transition Metal Complexes Derived from 3-Chloro-N'-[(1E)-(2-hydroxyphenyl)methylene]-6methoxy-1-benzothiophene-2-carboxyhydrazide, the Sci. World J., 13: 451629.
[3] Kiranmai, K.; Prashanthi, Y.; Subhashini, N. J. P. and Shivaraj, H.; 2010, Synthesis, characterization and biological activity of metal complexes of 3-amino-5-methyl isoxazole Schiff bases. J. of Chem. and Pharma. Research 2(1): 375-384.
[4] Raaman, N.; Dhaveethu, J. R. and Saktthivel, A.; 2007, Synthesis, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies Synthesis, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies, J. of Chem. Sci., 119(4): 303–310.
[5] Vaira, D.; Peruzzini, M. M., and StopponiP, 1986, Reactivity of arsenic selenides and telluride: Cobalt complexes containing the Selena-or tellura-diarsirene cyclic units trihapto-bonded to the metal atom-crystal and molecular structures of [(triphos) Co (As \(_2\) Se)](BF \(_4\))(C\(_2\) H\(_5\)OH) and [(trips) Co (As2Te)] (BF\(_4\)(C\(_6\)H\(_5\)O\(_6\)) 0.5, Polyhedron,5(4) :945-950.
[6] Suresh, M. S. and Prakash V., 2011, Preparation Characterization and Antibacterial Studies of Chelates of Schiff Base Derived from 4-Aminoantipyrrine, Furfural and o-Phenylenediamine, E-J. of Chemi., 8(3):1408-1416.
[7] Fernandez-Torres, M. J. 2013, Synthesis, Characterization and Biological Studies on some Derivatives of N-(4-Aminobenzene sulphonyl) Morpholine Carrying Amino Acid, Alkoxyand Triazole Moieties, Inter. J. of Chem.; 9(2): 33-40.
[8] Raman, N.; Thalamuthu, S.; Dhaveethuraja, J. N. and Sharmila, B., 2008, DNA Cleavageand Antimicrobial Activity Studies on Transition Metal (II)Complexes of 4-Aminotipyrine derivative, J. of the Chilean Chem. Soci. 53(1):1450.
[9] Al-Hamdani, A. A. S. 2010, Synthesis and Characterization of Some New Transition Metal Complexes with 2,5-di(4-amino
phenazonyl) Hexane, J. of Al-Nahrain University 13 (4), 15-22
[10] Ergene, E.; Sivas, H. and Benkli, K.; 2010, Biological activities of Cu(II) and Hg(II) complexes of a hexadentate Schiff base ligand, Turkish J. of Bio.; 34(4): 379-387.
[11] Nakamoto, K.; 1997,"Infrared and Raman Spectra of Inorganic and Coordination Compounds", 5th Edit., Part B; Wiley; New York.
[12] Lateef, S. M.; Sarhan, B. M.; Al-Saeedi, W. A. J., 2015, Synthesis, Characterization and Biological Activity For Complexes Vo(II), Mn(II), Co(II) And Ni(II) With New Multidentate Ligand [2-(E)-(4-(Z)-2-Hydroxy-1,2-Diphenyl ethylened amino)-1,5-Dimethyl-2-Phenyl-1h-Pyrazol-3(2h)-Ylideneamino) Propanoic Acid][H2L]Type (N2O2), Inter. J. of Eng. Sci.& Research Techn.;4(2), 606-620.
[13] Waleed, K. M; Haider, D.J, Kwalha, M. S and Lateef, S. M., 2015, Synthesis and Spectroscopic Study of New Bidentate Schiff Base type (NN) and it’s Complexes with MnIl, FeIl, CoII, NiII, CuII and CdII Ions",Diyala J. for pure sci.;11(1):19-30.
[14] Lin-Vien, D., N.B. Colthup, W.G. Fately & J.C. Grasselli, 1991. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules Academic Press; San Diego.
[15] Ebtihal K. K.; Lateef, S. M. and Abbas A.A, 2015, Synthesis and Characterization of Some Transition Metal Complexes with New Schiff Base Ligand Derivative from Isatin. J. of Kufa for Chem. Sci.;1(10): 74–85.
[16] Dudley, H. W. and Fleming, I.; 1980, Spectroscopic methods in organic chemistry, 5th Edit Part A; England.
[17] Lever, A.B.P.;(1984) "Inorganic spectroscopy" Elsevier publishing company, 3th Edit; Wiley; New York.
[18] Muna, A. H., 2013, Coordination behaviour of N/O donor ligand with some transition metals, Acta. Chim. Pharm. Indica: 3(2), 127-134.
[19] Sharma, R.; Samadhiya, P.; Srivastava, S. D. and Srivastava, S. K., 2011, Synthesis and biological activity of 2-oxo-azetidine derivatives of phenothiazine, Org. Commun. 4(2):42-51.
[20] Raman, N.; Sakthivel, A. and Rajasekaran K. 2007, Synthesisand Spectral Characterization of Antifungal Sensitive Schiff Base Transition Metal Complexes, Microbiology,35(3),150–153.
[21] Al-Ansary, A. L.; Abdel-Fattah, H. M. and Abdel-Kader, N. S.; 2008. Synthesis and characterization of tetradentatetis-Schiff base complexes of di- and tri-valent transition metals, J.of Coord. Chem., 61(18), 2950–2960.
[22] Reham, H.; Hassan, A.;Manal, M. and Nehad, A. L., 2013,Synthesis of New Schiff Base from Natural Products for Remediation of Water Pollution with Heavy Metals in Industrial Areas, J .of Chem. 20(13),10.
[23] Al-Noor, T. H.; Abdul Karim, L. K.;2016, Synthetic, Spectroscopic And Antibacterial Studies Of Co(II), Ni(II), Cu(II), Zn(II), Cd(II)And Hg (II),Mixed Ligand Complexes Of Trimethoprim Antibiotic And Anthranilic Acid, tofiq J. of Med. Sci.;3(2):64-75.
تحضير، تشخيص والفعالية البايولوجية لمخلبيات قواعد شيف مع المنغنيز (II)، الكوبالت (II)، النحاس (II) والزنبق (II).

م.د. رحاب كاظم الشمري
أ.م.د. لقاء خالد عبد الكريم
م.د. ورود علي جعفر
قسم الكيمياء، كلية التربية ابن الهيثم للعلوم الصرفة، جامعة بغداد، بغداد، العراق

الخلاصة:
في هذا البحث تم تحضير سلسلة جديدة من معقدات الفلزات الانتقالية من منغنيز ونيكل ونحاس وزئبق بتكافؤهم الثنائي من قواعد شيف (L1² و L2²) الاصبع الكبدي (L1² و L2²) من 4- أمينوانتي بريدين ووريثو- فنيلينداي أمين، واقتح المكاد L1 من بنزويل حامض البنزويك. وتم الحصول على الصيغة التركيبية من التحليل الدقيق للعناصر، التوصيلية المولارية، الحساسية المغناطيسية، الأشعة تحت الحمراء، والدراسات الطيفية لأشعة فوق البنفسجية والمرئية، طيف الرنين النووي المغناطيسي البروتوني والكاربوني 13. الحساسية المغناطيسية والبيانات الطيفية لأشعة فوق البنفسجية والمرئية، حانة الاعتداء أقترح أن معقدات الكبدي (L1²) ذات نمط مربع مستوي ورباعي السطوح بينما معقدات الكبدي (L2²) ذات نمط ثماني السطوح. أعطت فحوصات مضارب المايكروبات نتائج جيدة في المعقدات.

الكلمات المفتاحية: معقدات، قواعد شيف، البايولوجية، المخلبيات، الرنين النووي المغناطيسي.

Baghdad Science Journal
Vol.14(2)2017

402