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

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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 (L^1,L^2). (L^1) derived from 4-aminoantipyrine and *O*-phenylene dia mine then (L^2) derived from (L^1) and 2-benzoyl benzoic acid. Structural features are obtained from their elemental microanalyses, molar conductance, IR, UV–Vis ، ^{1}H, ^{13}CNMR spectra and magnetic susceptibility. The magnetic susceptibility and UV–Vis, IR spectral data of the ligand (L^1) complexes get square–planar and tetrahedral geometries and the complexes oflig and (L^2) 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-aminoantipyrineand 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 literatureex 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

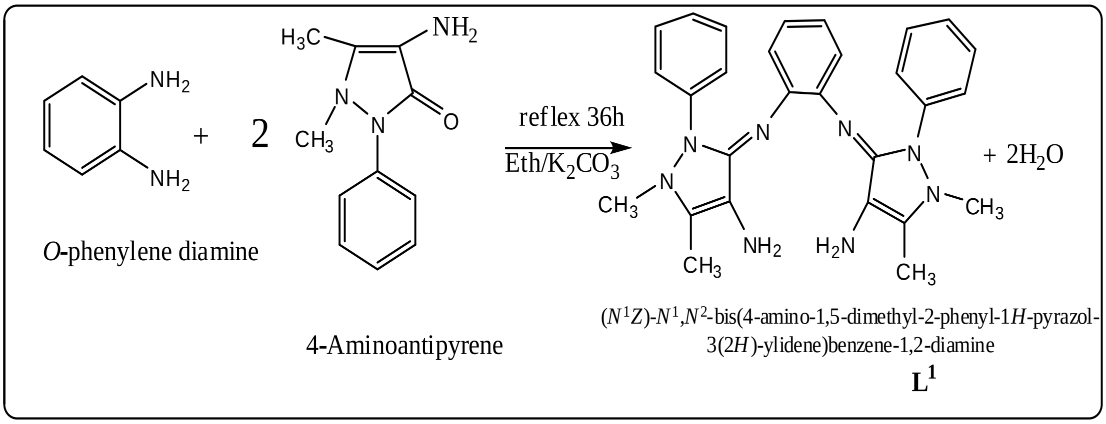
4-aminoantipyrine,*O*-Phenylenediamine and 2-benzoyl benzoic acid and several metal(II) chlorides are Merck compounds .Glacial acetic acid reagent and trade solvents are distilled and they are used for the synthesis of all compounds.

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 (^{1}H and^{13}C-)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^{-3}M 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 [(N^{1}Z, N^{2}Z)-N^1, N^2-bis (4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylide)benzene-1,2-diamine] (L^1)[10]

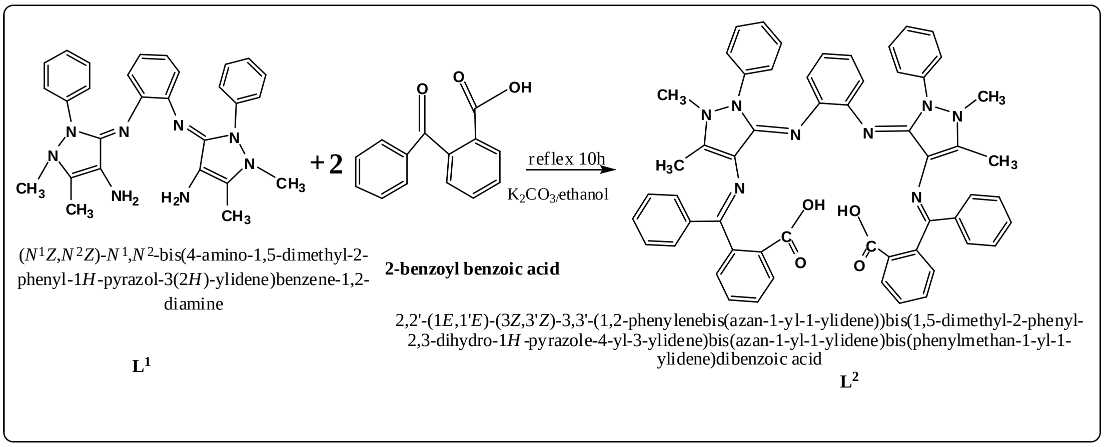
4-Aminoantipyrine (4.06g, 0.02 mmol) in 10 mL of hot ethanol is stirred with *O*-phenylenediamine (1·671g, 0.01 mmol) after adding [anhydrous potassium carbonate] in 30 ml of ethanol is refluxed for 36hrs.The potassium carbonate is filtered off from the mixture and the solvent is vaporised. The precipitate 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 L^1

Synthesis of (N^{1}Z,N^{2}Z)-N1,N2-bis(4-(diphenylmethyleneamino) -1,5-dimethyl -2- phenyl- 1H-pyrazol-3(2H) -ylidene) benzene-1, 2-diamine(L^2)

An ethanolic solution of (L^1) (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 vaporised. The pale orange solid discreteis filtered 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)



(N^1Z,N^2Z)-N^1,N^2-bis(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylidene)benzene-1,2-diamine

2-benzoyl benzoic acid

2,2'-(1E,1'E)-(3Z,3'Z)-3,3'-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazole-4-yl-3-ylidene)bis(azan-1-yl-1-ylidene)bis(phenylmethan-1-yl-1-ylidene)dibenzoic acid

L^1

L^2

Scheme (2): Synthesis Route of L^2

Synthesis of Complexes:

A solution of ($M(II)Cl_2$) metal (II) chloride(2.38 g $CoCl_2.6H_2O$, 2.37 g $NiCl_2.6H_2O$, 1.05 g $CuCl_2.2H_2O$, 1.98 g $MnCl_2.4H_2O$ and 2.71 g $HgCl_2$) in absolute ethanol (1 mmol) is refluxed with solution from ethanol of the Schiff base (1 mmol) ,(4.78g,L^1) 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(L^1&L^2) and its Complexes

Empirical Formula	Chemical Formula	Molecular Weight	M.P°C	Colour	Yield %	% (.Calc)Found				
						C	H	N	Cl	Metal
L^1	$C_{28}H_{30}N_8$	478.59	160-162	pale yellow	62	(70.27) 70.00	(6.32) 6.07	(23.41) 23.70	-	-
$[Co(L^1)]Cl_2$	$C_{28}H_{30}Cl_2CoN_8$	608.43	234-236	Greenish blue	77	(55.27) 55.11	(4.97) 4.65	(18.42) 18.42	(11.65) 11.72	(9.69) 10.23
$[Cu(L^1)]Cl_2$	$C_{28}H_{30}Cl_2CuN_8$	613.04	225-227	Olive	80	(54.86) 55.11	(4.93) 4.65	(18.28) 18.42	(11.57) 11.72	(10.37) 10.23
$[Ni(L^1)]Cl_2$	$C_{28}H_{30}Cl_2NiN_8$	608.19	246-248	pale yellow	75	(55.30) 55.21	(4.97) 4.74	(18.42) 18.13	(11.66) 11.54	(9.65) 10.23
$[Mn(L^1)]Cl_2$	$C_{28}H_{30}Cl_2MnN_8$	604.44	227-229	pale yellow	78	(55.64) 55.11	(5.00) 4.65	(18.42) 18.22	(11.73) 11.56	(10.30) 9.21ss
$[Hg(L^1)]Cl_2$	$C_{28}H_{30}Cl_2HgN_8$	750.09	247-249	pale yellow	69	(55.27) 55.10	(4.97) 4.77	(18.54) 18.31	(11.65) 11.43	(9.09) 9.15
L^2	$C_{56}H_{46}N_8O_4$	894.36	178-180	Pale-orange	71	(75.15) 75.45	(5.18) 5.23	(12.52) 11.78	-	-
$[Co(L^2)]$	$C_{57}H_{44}CoN_8O_4$	966.31	250-252	Dark brown	74	(70.15) 69.91	(4.90) 4.30	(11.59) 11.09	-	(6.09) 5.88
$[Cu(L^2)]$	$C_{56}H_{44}CuN_8O_4$	956.55	233-235	Reddish brown	84	(70.32) 70.10	(4.64) 4.55	(11.71) 11.22	-	(6.64) 6.68
$[Ni(L^2)]$	$C_{56}H_{44}N_8NiO_4$	951.69	252-254	Greenish brown	78	(70.67)70.41	(4.66) 4.24	(11.77) 12.00	-	(6.17)6.07
$[Mn(L^2)]$	$C_{56}H_{44}MnN_8O_4$	947.94	240-242	brown	70	(70.95) 70.88	(4.68) 4.32	(11.82) 11.65	-	(5.80) 5.55
$[Hg(L^2)]$	$C_{56}H_{44}HgN_8O_4$	10947. 94	229-231	brown	86	(61.50) 61.21	(4.06) 3.87	(10.25) 10.08	-	(18.34) 17.83

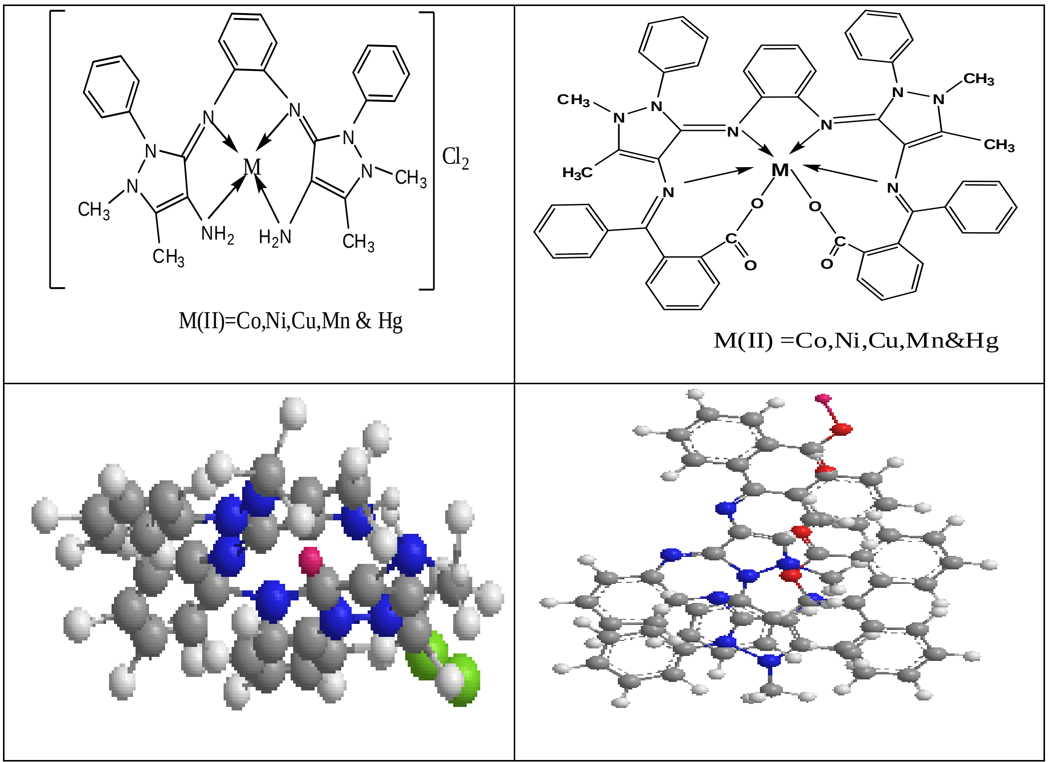


Fig.(1) : The Molecular and (3D) Structures of ComplexesL^1 and L^2

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, ^{1}H, ^{13}CNMR, 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 (L^2) 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 $\upsilon_{asym.}(COO^-)$ and $\upsilon_{sym.}(COO^-)$ stretching vibrations of the (carboxylate O) are observed at (1436,1319) cm^{-1} for the free ligand (L^2), these stretching vibrations are shifted to higher or lower frequencies at (1450-1471) cm^{-1} and (1327-1392) cm^{-1} for all the complexes, ($\Delta\upsilon_{asym.}$- $\Delta\upsilon_{sym.}$)= (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	υ(OH)	$\upsilon_{asy}(NH_2)$ $\upsilon_{sy}(NH_2)$	υ(C- H) aromatic	υ(C- H) aliphatic	$\upsilon(C=N)_{azomethine}$	υ(C=C)	$\upsilon_{assm.}$ COO^-	$\upsilon_{symm.}$ COO^-	Δυ cm^{-1}	M–N M–O
L^1	-	3427 3342	3068	2920	1622	1572	-	-	-	-
$[Co(L^1)]Cl_2$	-	3367 3272	3047	2945	1615	1567	-	-	-	549 486
$[Cu(L^1)]Cl_2$	-	3379 3267	3062	2991	1610	158	-	-	-	548 457
$[Ni(L^1)]Cl_2$	-	3367 3286	3037	2967	1619	1560	-	-	-	560 459
$[Mn(L^1)]Cl_2$	-	3390 3278	3087	2944	1612	1574	-	-	-	565 447
$[Hg(L^1)]Cl_2$	-	3360 3257	3010	2959	1617	1568	-	-	-	565 447
L^2	3446	-	3021	2991	1647 1624	1563	1440	1321	119	-
$[Co(L^2)]$	-	-	3084	2967	1635 1598	1571	1460	1339	121	574 460
$[Cu(L^2)]$	-	-	3064	2944	1633 1597	1563	1466	1342	124	574 461
$[Ni(L^2)]$	-	-	3098	2959	1629 1608	1567	1459	1332	127	594 488
$[Mn(L^2)]$	-	-	3032	2991	1630 1599	1561	1457	1356	101	582 480
$[Hg(L^2)]$	-	-	3048	2991	1640 1614	1567	1455	1351	104	587 459

NMR Spectra

^{1}HNMR spectrum of (L^1) in DMSO-d_6 Figure(2),Table(3a) solution shows the following signals: =C-C$\underline{H}_3$ at δ_H 2.15, DMSO at δ_H 2.5, N-C$\underline{H}_3$ at δ_H 3.33, N$\underline{H}_2$at δ_H 6.25, $C_6\underline{H}_5$ as multiplet at δ_H6.67 ~7.07, Ph-NH- at δ_H 7.84[15,16,7].The ^{13}CNMR spectrum of L^1 in DMSO-d_6 Figure(3),Table (3b) solution shows the signals at: (8.83 for =C-$\underline{C}H_3$ group);(34.95 for N-$\underline{C}H_3$ 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].

^{1}HNMR spectrum of (L^2) Figure (4), Table (4a)in DMSO-d_6 solution shows the following signals: DMSO-d_6 at δ_H 2.5, N-C$\underline{H}_3$ at δ_H 2.15, OH-C$\underline{H}$ at δ_H 3.34, $C_6\underline{H}_5$ as multiplet at δ_H6.67 ~7.14, Ph-NH- at δ_H 7.84. The peaks observed at δ_H 13.14 is attributable to the acidic OH group present in the 2-benzoyle benzoic acid, shown Table(2b) [16,9]**.**The ^{13}C NMR spectrum of L^2 in DMSO-d_6 Figure(5),Table(4b) solution shows the signals at: (9.13 for =C-$\underline{C}H_3$ group);(34.70 for N-$\underline{C}H_3$ 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 $\underline{C}$OOH group present in the 2-benzoyle benzoic acid. The peak observed at (164.89) was attributable to the C=N imine group [15,10].

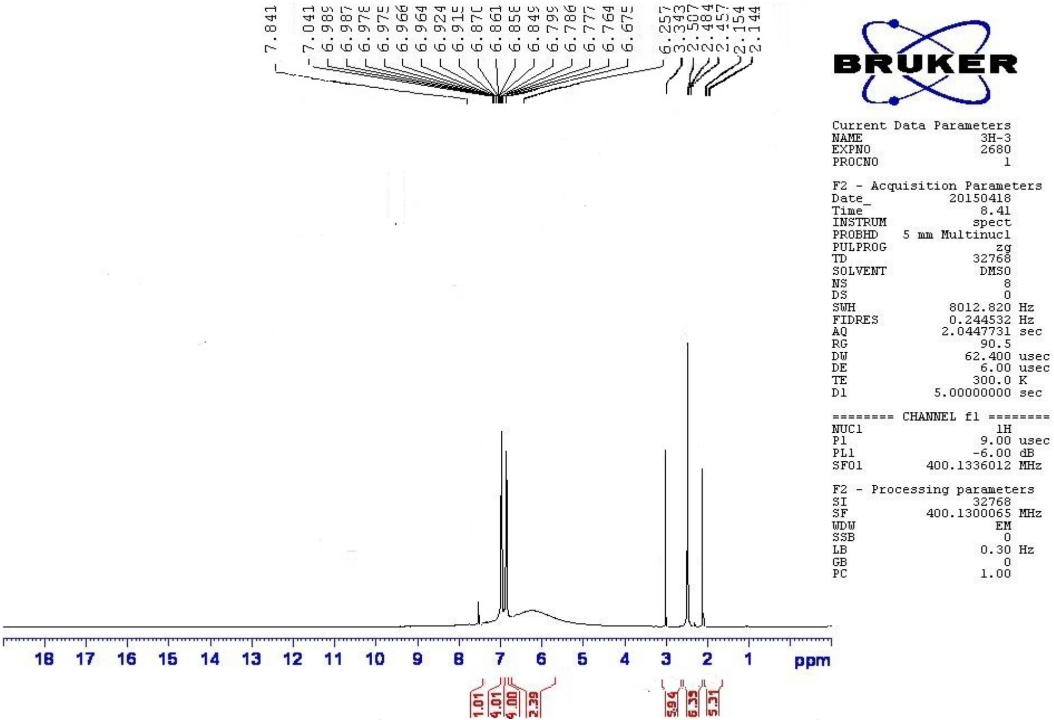


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Fig.(2):^{1}*H- NMR Spectrum of Ligand* (L^1)

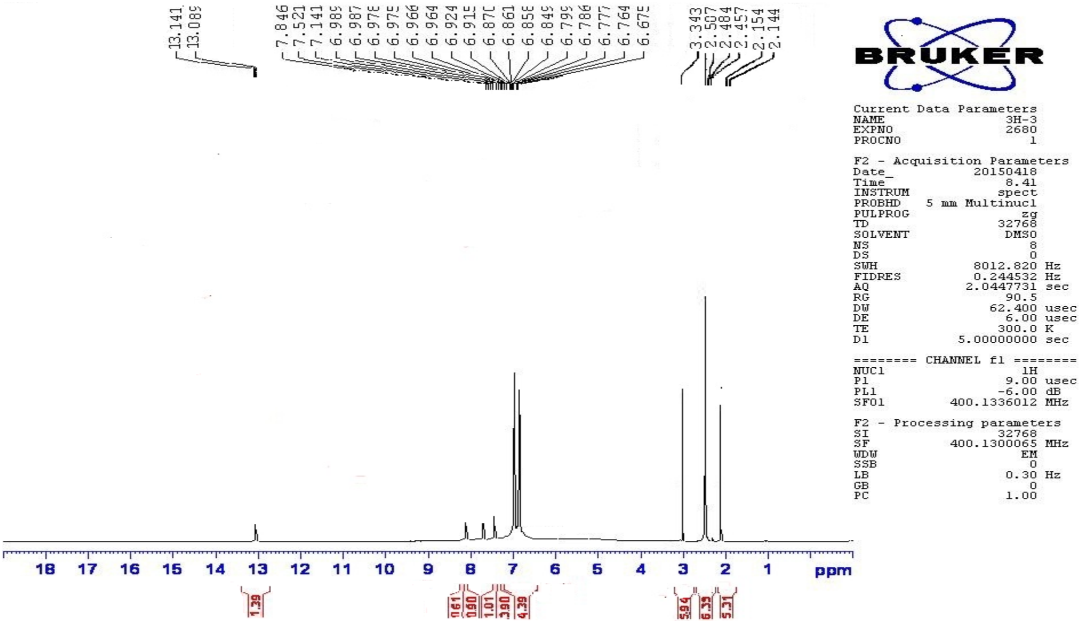

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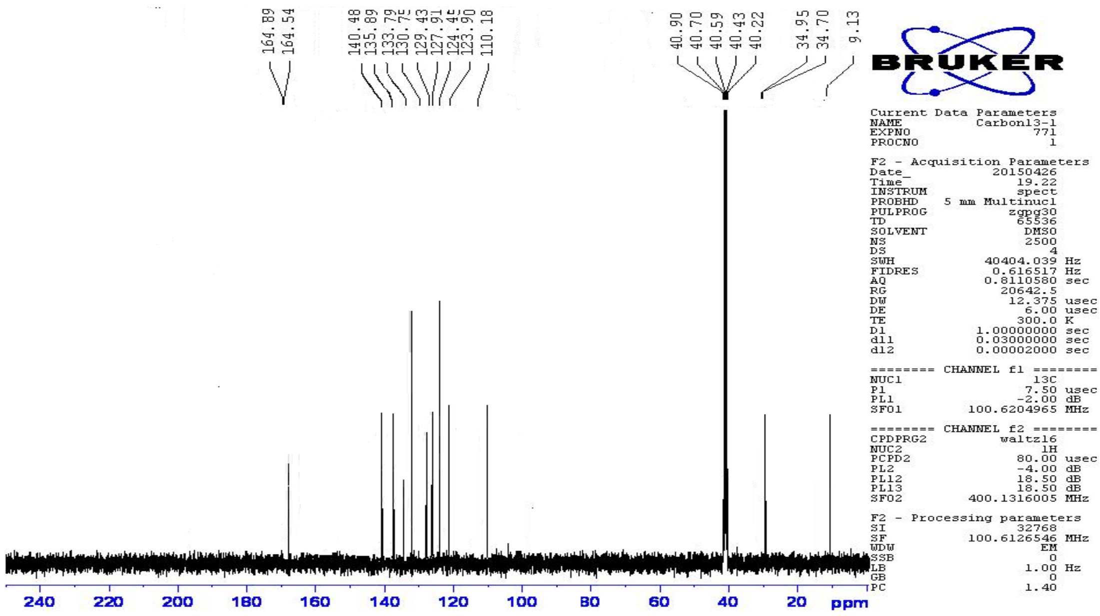
Fig.(3): ^{1}*H- NMR Spectrum of Ligand* (L^2)



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======== CHANNEL f2 ========
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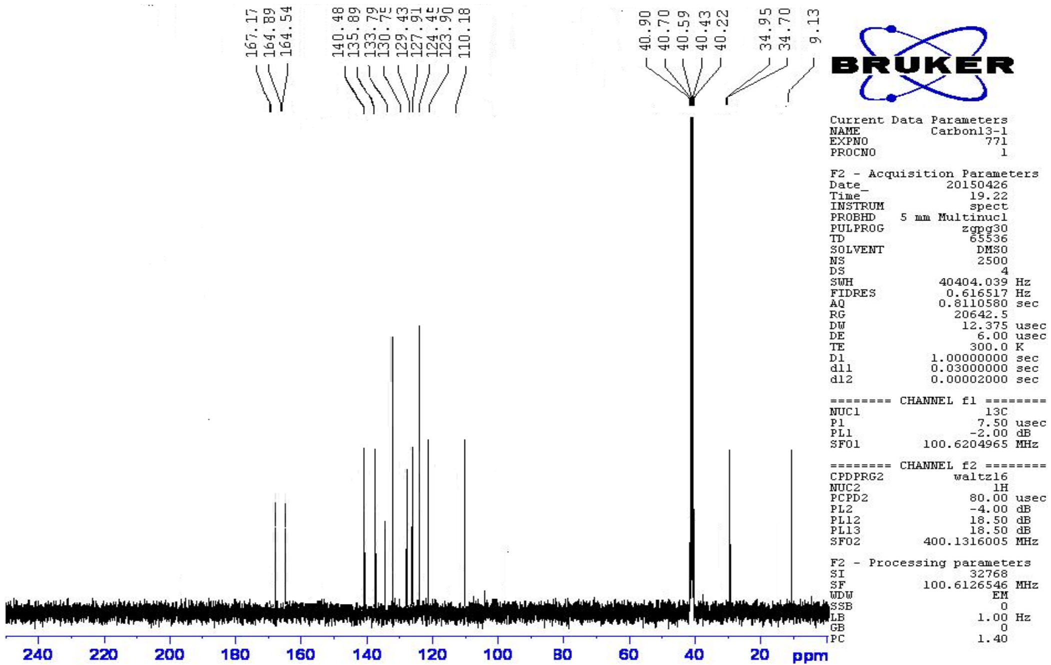
Fig.(4): ^{13}*C- NMRSpectrum of* Ligand(L^1)



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PL13               18.50 dB
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F2 - Processing parameters
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Fig.(5): ^{13}*C- NMR Spectrum of Ligand*(L^2)

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

CH_3-N	DMSO	CH_3-C=	NH_2	$C_6\underline{H}_5$	Ph-N$\underline{H}$-
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=	$C_6\underline{H}_5$	Ph-N$\underline{H}$-	O$\underline{H}$
2.5	2.15	3.34	6.67-7.14	7.84	13.14

Table (4b): ^{13}C-NMR Chemical Shifts for Ligand (L^2) (ppm in DMSO)

CH_3-C=	CH_3-N	DMSO	=C-$N_{pyridine}$	C=$C_{aromatic}$	C=$C_{pyridine}$	HC=N	COOH
9.13	34.70	40.59	110.18	123.90-135.89	140.48	164.54	167.17

Electronic Spectra

The (UV- Vis) spectrum for the (L^1), exhibits two high intense absorption peaks at (243 nm) and (289 nm), assigned to (π→π*) transition respectively [17], Table (5).

The (UV- Vis) spectrum of [Co(L^1)] Cl_2complexexhibits three peaks, the first high broad peak at (261 nm) is due to the (L.F), while the second weak peak at (347nm) is due to the (C.T). The third peak at (467 nm) is assigned to $^4A_{2\ (F)} \rightarrow {}^4T_{1\ (F)}$ transition and magnetic moment μ_{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(L^1)]Cl_2 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 peaks at (633 nm), which assigned to $^2T_2 \rightarrow {}^2E$, transition. Cu (II) complex shows a value of μ_{eff} =1.73 μ_B. The observed magnetic moments of Cu (II) showing 1 unpaired electron with paramagnetic kind and propos a square plane geometry in terms of Jahn-Teller effect[13].[Ni(L^1)]Cl_2 complex, exhibits four peaks, the first high peak at (271nm) 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 (514nm) and at (630nm) can be assigned to the$^1A_1g \rightarrow {}^1A_2g$ (υ_2) and $^1A_1g \rightarrow {}^1B_1g$ (υ_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(L^1)]Cl_2 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$^6A_1 \rightarrow {}^4T_1$ (υ_3), transition. Magnetic moment μ_{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(L^1)]Cl_2complex does not appear any band in the visible region, shows apeak at (269nm) is due to (L.F) absorption, and therefore the bands appear at (310and 385) nm in the spectrum of the complex could be attributed to the (C.T) transition. Magnetic susceptibility measurements for Hg (II) (d^{10}) show diamagnetic as perspective from their electronic arranging [16].

The (UV- Vis) spectrum for the (L^2), exhibits two small absorption peaks at (264nm) and, and high intense absorption peak at ((297 nm) assigned to (π→ π*)transition respectively [17].**[Co(L^2)]**complex, exhibits three peaks, the first high intense peak at (277nm) is due to the (L.F), while the second peak at(365nm) is due to the (C.T).The third weak peak at υ_1= (410nm) assigned to$^4T_{1g(F)} \rightarrow {}^4T_1g_{(P)}$.The room temperature magnetic moment (μ_{eff} =5.42B.M) corresponded to a high spin octahedral symmetry [12, 17].**[Cu(L^2)]** 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 (417nm) and (937nm)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 (μ_{eff}=1.81B.M)[18,19].

[Ni(L^2)]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 $_{(F)}$$\rightarrow$$^3T_1g_{(F)}$ (ν_2)) (d–d), and ($^3A_2g_{(F)}$$\rightarrow$ $^3T_2g_{(F)}$ (ν_1)) (d–d), transitions, respectively in an octahedral geometry. The complex exhibit a value of μ_{eff} = 2.82 B.M, which suggests an octahedral geometry around the central Ni ion [19]. [Mn(L^2)]complex, exhibits four peaks, the first and second high peaks at (275nm) and (331nm) are due to (L.F) and (C.T)transition. The fourth-week peak at (396nm) and (957 nm) can be assigned to the $^6A_1g_{(F)}$$\rightarrow$$^4T_2g$ $_{(G)}$(υ_3) and^6A_1g $_{(F)}$$\rightarrow$$^4T_2g$ $_{(G)}$(υ_2)transitions. Magnetic moment μ_{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)] 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 activtiy 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	μ_{eff}	Λ_m S.Cm^2 molar^{-1}	λnm	wave number (ύ)cm^{-1}	ε_{max}molar^{-1}	Assignments	Geometries
L^1	-	-	243	41152	2131	$\pi\rightarrow\pi^*$	-
			289	34602	1546		
[Co(L^1)]Cl_2	2.41	73	261	38314	21541	L.F	Tetrahedral
			347	28746	278	C.T	
			467	21373	198	$^4A_{2(F)}\rightarrow{}^4T_{1(F)}$	
[Cu(L^1)]Cl_2	1.73	78	251	39840	2149	L.F	Tetrahedral
			357	27939	2361	C.T	
			633	15789	53	$^2T_2\rightarrow{}^2E$	
[Ni(L^1)]Cl_2	Dia.	71	271	36900	2137	L.F	Square planar
			354	28172	2341	C.T	
			514	19426	36	$^1A_1g\rightarrow{}^1A_2g$	
			630	15867	27	$^3A_1g\rightarrow{}^1B_1g$	
[Mn(L^1)]Cl_2	4.48	75	258	38759	2149	L.F	Tetrahedral
			304	32894	282	C.T	
			685	14598	96	$^6A_1\rightarrow{}^4T_1$	
[Hg(L^1)]Cl_2	Dia	76	269	37174	2141	L.F	Tetrahedral
			310	32258	152	C.T	
			385	25974	215	C.T	
L^2	-	-	264	3787	2131	$\pi\rightarrow\pi^*$	-
			297	33670	1546		
[Co(L^2)]	5.42	10	277	36101	1956	L.F	Octahedral
			365	27397	81	C.T	
			410	24390	142	$^4T_1g_{(F)}\rightarrow{}^4T_1g_{(P)}$	
[Cu(L^2)]	1.81	15	272	36764	2351	L.F	Octahedral
			323	30959	2111	C.T	
			417	23980	1832	$^2B_1g\rightarrow{}^2B_2g$	
			937	10672	24	$^2B_1g\rightarrow{}^2A_1g$	
[Ni(L^2)]	3.23	13	276	36231	1963	L.F	Octahedral
			356	28089	1907	C.T	
			408	24509	945	$^3A_2g_{(F)}\rightarrow{}^3T_1g_{(P)}$	
			734	13623	27	$^3A_2g_{(F)}\rightarrow{}^3T_1g_{(F)}$	
			887	11273	19	$^3A_2g_{(F)}\rightarrow{}^3T_2g_{(F)}$	
[Mn(L^2)]	4.72	18	275	36363	1977	L.F	Octahedral
			331	30211	1794	C.T	
			396	25252	784	$^6A_1g\rightarrow{}^4T_2g_{(D)}$	
			957	10449	12	$^6A_1g_{(F)}\rightarrow{}^4T_2g_{(G)}$	
[Hg(L^2)]	Dia	16	212	47169	1888	L.F	Octahedral
			350	28571	242	C.T	

Dia: diamagnetic

Antibacterial Activities:

Tetradent 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 bacteriathat rises the delocalization of the π-electrons above the full chelating ring [23].

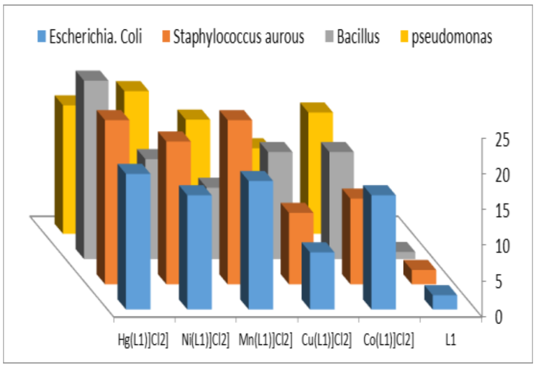

Fig.(6):The Variance between the Antimicrobial Activity of (L^1) and their Complexes

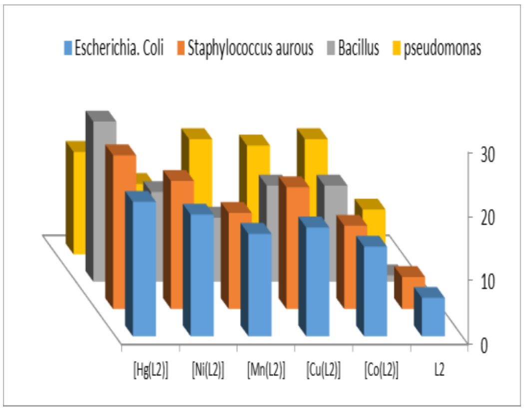

Fig. (7): The Variance between the Antimicrobial Activity of (L^2) and their Complexes

Table (6): Diameter of Zone of Inhibition (mm) for Ligands (L^1,L^2) and their Complexes.

Comp.	*Escherichia. Coli*	*Staphylococcus aureus*	*Bacillus*	*Pseudomonas*
L^1	2	2	1	3
$[Co(L^1)]Cl_2$	16	12	15	17
$[Cu(L^1)]Cl_2$	8	10	15	12
$[Mn(L^1)]Cl_2$	18	23	10	16
$[Ni(L^1)]Cl_2$	16	20	14	20
$[Hg(L^1)]Cl_2$	19	23	25	18
L^2	6	5	4	7
$[Co(L^2)]$	14	13	16	18
$[Cu(L^2)]$	17	19	20	17
$[Mn(L^2)]$	16	15	22	18
$[Ni(L^2)]$	19	20	24	11
$[Hg(L^2)]$	21	24	21	16

Conclusion:

A tetradentate 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.

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تحضير، تشخيص والفعالية البايولوجية لمخلبيات قواعد شيف مع المنغنيز (II) الكوبلت (II)، النيكل (II)، النحاس (II)، والزئبق (II)

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الخلاصة:

في هذا البحث تم تحضيرسلسلةجديدة من معقدات الفلزات الانتقالية من منغنيز ونيكل ونحاس وزئبق بتكافؤهم الثنائي من قواعد شيف (L^1 وL^2). اشتق الليكاندL^1 من 4- امينوانتي بريدين واورثو- فنيليندااي امين، واشتق الليكاند(L^2) من(L^1)و2- بنزويل حامض البنزويك. وتم لحصول على الصيغة التركيبية من التحليل الدقيق للعناصر، التوصيلية المولارية، الحساسية المغناطيسية، الأشعة تحت الحمراءوالدراسات الطيفية للأشعة فوق البنفسجية والمرئية، طيف الرنين النووي المغناطيسي البروتوني والكاربوني13. الحساسية المغناطيسية والبيانات ا لطيفية لأشعة فوق البنفسجية والمرئية والأشعة تحتالحمراء اقترحت ان معقدات الليكاند (L^1) ذات شكل مربع مستوي ورباعي السطوح بينما معقدات الليكاند (L^2) ذات شكل ثماني السطوح. أعطت فحوصات ضديد المايكروبات نتائج جيدة في المعقدات.

الكلمات المفتاحية: معقدات، قواعد شف، الفعالية البايولوجية، المخلبيات والرنين النووي المغناطيسي.