

Synthesis, characterization , evaluation of antibacterial activity of Co (II) , Ni(II), and Hg (II) Complexes with Mannich bases and Phosphine ligands.

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Abstract The new mannich bases 1-(((5-chloro-2,4-dimethoxyphenyl)amino)methyl)indoline-2,3-dione (L_1) and 3-(((5-chloro-2,4-dimethoxyphenyl)amino)methyl)pyrimidine-2,4(1H,3H)-dione (L_2) have been synthesized by condensation of isaten or thymine with formaldehyde and 5-chloro-2,4-dimethoxyaniline . The ligands have been characterized by various physical and spectral techniques such as Micro elemental analysis and spectroscopic methods ultraviolet-visible, infrared and nuclear magnetic resonance. Reaction of mannich bases (L_1, L_2) with one equivalents of metal salts ($CoCl_2 \cdot 6H_2O, NiCl_2 \cdot 6H_2O$ and $HgCl_2$) afforded the presumably tetrahedral complexes $[M(L)Cl_2]$; L is L_1 or L_2 . Reaction of $[M(L)Cl_2]$ with tertiary phosphines ligands ; $dppm$, PPh_3 in molar ratios 1:1 (complex : $dppm$ ligand) or 1:2 (complex : PPh_3 ligand) afforded mixed ligands complexes $[M(L)(phosphine)]Cl_2$ and $[M(L)(phosphine)_nCl_2]$, where is L is L_1, L_2 , phosphine is $dppm, PPh_3$ and $n=1$ or 2 . The synthesized complexes were characterized by the above mentioned techniques as well as the conductivity and magnetic measurements. The obtained results showed that the complexes have tetrahedral or octahedral geometry. The antibacterial activities of the ligands and some of prepared complexes against two types of bacteria are also reported.

The Key words: mannich bases, phosphines ligands, Mixed ligands, thymine & Isaten,

Introduction

Mannich reaction consists of amino alkylation of an acidic proton placed next to a carbonyl group with formaldehyde and ammonia or any primary or secondary amine. The final product is a β -amino carbonyl compound. Reactions between imides and aromatic aldehydes have also been considered as Mannich reactions. A review of the literature regarding Mannich reactions shows extensive volume on chemical, biological and toxicological feature of Mannich bases ^[1-6] with vast applications as polymers, dispersants in lubricating oil and pharmaceutical agents. It is well known that compounds containing amide moiety as functional group have been found to possess donor properties and exhibited a wide range of biological activities ^[7-13]. Transition metals are essential for normal functioning of living

organisms and are, therefore, of great interest as potential drugs ^[14]. The coordination chemistry of nitrogen donor ligands is an interesting area of research. A great deal of attention in this area has been focused on the complexes formed by metals with bidentate ligands using both the nitrogen atoms of the substrates. The study of structural and binding features of various Mannich base complexes can play an important role in better understanding of the complex biological processes. Several drugs showed increased activity as metal chelates rather than as organic compounds ^[15]. It has been reported in the literature survey that cobalt (II) complexes with octahedral geometry show remarkable intercalative binding affinity as well as DNA cleavage properties ^[16,17]. Furthermore cobalt is an element of biological interest which is present in the active center of vitamin B12, which regulates the synthesis of DNA indirectly. It is known that there are about eight cobalt dependent proteins ^[18]. Many cobalt complexes possess antitumor, anti-proliferative, antimicrobial and antifungal activity ^[19-26].

Materials

All chemicals and phosphine ligands were Commercially supplied and used without further Purification .

Physical measurements

Melting Points were obtained on Electro thermal 9300 and are uncorrected. Elemental analyses(C.H.N.S) were carried out on Elementar Vario ELIII. Conductivity measurements were made with DMSO solutions using digital Conductivity meter (Cond 7II0), Magnetic susceptibilities were determined at 25⁰C using susceptility balance (Sherwood scientific). IR spectra were recorded on FTIR 8400si Shimadzu spectrometer in the range 400- 4000 cm⁻¹ as KBr disc. Electronic spectra were measured between 250-1200 nm with 10⁻³M solutions in DMSO Solvent (spectroscopic grade) at 25⁰C using Shimadzu, UV 1650PC spectrophotometer. NMR spectra (¹H,¹³C and³¹P NMR) were Performed in DMSO-d⁶ solutions using a Bruker400 MHz spectrometers, ³¹P NMR spectra were recorded on origin Bruker Biospin spectrometer.

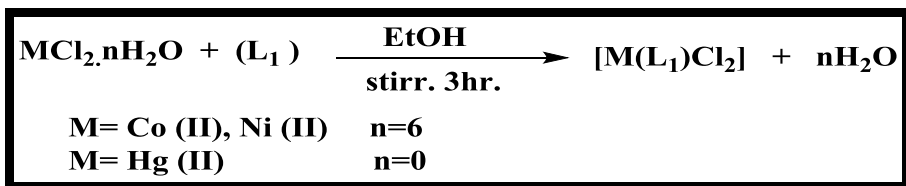
Synthesis:

Synthesis of ligands , (L₁), (L₂)were prepared by Previously described method ^[27] .

Synthesis of Metal Complexes

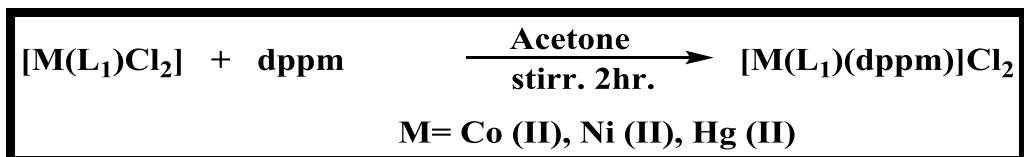
Synthesis of [M(L₁)Cl₂]

In a round bottom flask (100ml) (3.00 mmole, 1g) of ligand (L) were dissolved in (20ml) of absolute ethanol. Then (3.00 mmol, 0.68g) of CoCl₂.6H₂O dissolved in (20ml) of ethanol were added. The mixture was stirred for three hours until a light blue precipitate was formed. The precipitate was filtered off washed with cold distilled water and ethanol, then recrystallized with THF and dried for three hours in an electric oven at temperature of (50 ° C) .



Synthesis of [Co(L₁)(dppm)]Cl₂

A solution of (dppm) ligand (1.00 mmole, 0.38g) in acetone (15 ml) was added to a solution of [Co(L)Cl₂] (0.095mmole,0.054g) in acetone (15 ml) , The mixture was stirred for 2 h , blue precipitate was formed. The resulting Product was filtered off and washed with a small portion of distilled water then recrystallized in absolute ethanol and dried for 4h in an oven at 50 °C . The other Phosphine Complexes were Synthesized by the same procedure,(Table 1).by using the proper molar ratio 1:1(complex : dppm ligand) or 1:2 (complex : PPh₃ ligand)



Results And Discussion

Physical and spectral techniques were used for identification of synthesized Complexes. The solid Prepared Complexes are soluble in most Common solvents such as DMSO, DMF and THF but, Partially soluble in EtOH and unslouble in H₂O. All attempts to isolate crystals for x-ray single crystal diffraction analysis were unsuccessful . The analytical data agree well with the suggested structures. The molar conductivity values of the Complexes in DMSO Solutions^[28].is indicative of their non-electrolytic and electrolytic nature .This is consistent with the stoichiometry assumed for the complexes, micro elemental analysis measurements for the Complexes gave approximated values Compared with the theoritical values.

Table 1: Some physical properties, conductance data C.H.N.S and yield % of the complexes

No.	Compound	Colour	M.P/ °C	yiel d%	Molar Δ cond./ mole ⁻¹ , cm ⁻¹ hom	Micro elemental analysis calculated (found)			
						C%	H%	N%	S%
	L ₁	Brown	202-204	81	-	58.81 (58.88)	4.40 (4.36)	8.04 (8.08)
	L ₂	White	143- 145	77	-	51.50 (51.62)	4.97 (4.95)	12.82 (12.90)

1.	$[\text{Co}(\text{L}_1)\text{Cl}_2]$	Light blue	93-95	70	7
2.	$[\text{Co}(\text{L}_1)(\text{pph}_3)_2]\text{Cl}_2$	Dark blue	73-75	78	79	61.5 8 (61.4 1)	4.39 (4.38)	2.74 (2.70)
3.	$[\text{Co}(\text{L}_1)(\text{dppm})]\text{Cl}_2$	Blue	102-104	75	76
4.	$[\text{Ni}(\text{L}_1)\text{Cl}_2]$	Light green	162- 164	79	5	42.9 0 (42.8 2)	3.22 (3.17)	5.65 (5.88)
5.	$[\text{Ni}(\text{L}_1)(\text{pph}_3)_2]\text{Cl}_2$	Green	53-54	74	75	58.4 1 (58.2 8)	4.38 (4.31)	3.20 (3.24)
6.	$[\text{Ni}(\text{L}_1)(\text{dppm})]\text{Cl}_2$	Light green	108-109	80	78	55.8 1 (55.7 8)	4.40 (4.56)	5.05 (5.00)
7.	$[\text{Hg}(\text{L}_1)\text{Cl}_2]$	Black	113- 115	74	14	13.2 5 (13.3 0)	1.85 (1.91)	4.36 (4.43)
8.	$[\text{Hg}(\text{L}_1)(\text{pph}_3)_2]\text{Cl}_2$	Brown	61-62	81	10
9.	$[\text{Hg}(\text{L}_1)(\text{dppm})]\text{Cl}_2$	Light brown	100-102	73	13	60.0 4 (60.1 3)	4.04 (4.09)	1.74 (1.78)
10.	$[\text{Co}(\text{L}_2)\text{Cl}_2]$	Blue	113- 115	78	8
11.	$[\text{Co}(\text{L}_2)(\text{pph}_3)_2]\text{Cl}_2$	Blue	208-210	77	83
12.	$[\text{Co}(\text{L}_2)(\text{dppm})]\text{Cl}_2$	Light blue	114-116	73	71	55.7 3 (55.8 3)	4.40 (4.45)	4.92 (5.01)
13.	$[\text{Ni}(\text{L}_2)\text{Cl}_2]$	Light green	228- 230	71	11	13.7 0 (13.7 9)	1.97 (1.93)	5.41 (5.36)
14.	$[\text{Ni}(\text{L}_2)(\text{pph}_3)_2]\text{Cl}_2$	Red	97-99	75	77
15.	$[\text{Ni}(\text{L}_2)(\text{dppm})]\text{Cl}_2$	Green	130-132	79	68

16.	[Hg(L ₂)Cl ₂]	White	105- 106	68	4	53.4 9 (28.1 6)	2.63 (2.70)	7.10 (7.04)
17.	[Hg(L ₂)(pph ₃) ₂ Cl ₂ 1]	White	147-149	76	10	53.4 8 (53.5 3)	4.19 (4.13)	3.75 (4.74)
18.	[Hg(L ₂)(dppm)Cl 2]	White	165-167	69	3

Electronic spectra magnetic Susceptibility results

The electronic spectra of the Mannich bases ligands (L₁ and L₂) and Co(II), Ni (II) and Hg(II) Complexes as well as the magnetic result are listed in (Table2) , L₁ and L₂ has an absorption band at(248 ,258)nm assigned to, $\pi \rightarrow \pi^*$ transitions, the second band that appears at (310,364) nm is due to $n \rightarrow \pi^*$ transition . The Cobalt Complexes display bands in d-d region at(608 , 632 , 639 , 678 ,694 , 699) nm, related to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ characteristic for tetrahedral geometry around cobalt atom ^[29-31]. The magnetic moments of the Complexes is typical for tetrahedral structure ^[31].The Spectra of Ni(II) Complexes also display bands in the visible region which are Characteristic for tetrahedral Complexes. The magnetic moment values of the Ni (II) complexes as well as, the other analytical data are in agreement with their tetrahedral structures ^[31,32], The prepared mercury Hg (II) complexes display charge transfer bands in the range (406 - 459) nm. The Hg (II) complexes do not have any (d-d) transitions due to their filled (d) orbital . Transitions appeared in the range (300-312)and(207-246) cm^{-1} They are related to the ligand transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. According to the results obtained the prepared complexes may have a tetrahedral shape and for some of them might be an octahedral geometry. ^[33-35]

Table 2: Electronic and magnetic measurements of the complexes

No.	Compounds	wave length (nm)	Wave number (cm^{-1})	Transitions	μ_{eff} B.M	Geometrical shape
-	L ₁	310 248	32252 40322	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-	-
-	L ₂	364 258	27472 38759	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-	-
1.	[Co(L ₁)Cl ₂]	694 297 232	14398 33670 43010	${}^4A_2(F) \rightarrow {}^4T_1(P)$ $n \rightarrow \pi^*$	4.180	Tetrahedral

				$\pi \rightarrow \pi^*$		
2.	$[\text{Co}(\text{L}_1)(\text{pph}_3)_2]\text{Cl}_2$	632 301 241	15873 33222 41493	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1$ (P) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--	Tetrahedral
3.	$[\text{Co}(\text{L}_1)(\text{dppm})]\text{Cl}_2$	678 312 225	14524 32051 44345	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1$ (P) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--	Tetrahedral
4.	$[\text{Ni}(\text{L}_1)\text{Cl}_2]$	1112 695 337 220	8992 14388 29629 45454	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$ (F) ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1$ (P) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	3.192	Tetrahedral
5.	$[\text{Ni}(\text{L}_1)(\text{pph}_3)_2]\text{Cl}_2$	1190 748 358 213	8403 13368 27932 46838	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$ (F) ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1$ (P) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--	Tetrahedral
6.	$[\text{Ni}(\text{L}_1)(\text{dppm})]\text{Cl}_2$	1126 789 304 236	8880 12674 32894 42372	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$ (F) ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1$ (P) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	3.6948	Tetrahedral
7.	$[\text{Hg}(\text{L}_1)\text{Cl}_2]$	464 311 246	21512 32154 40650	${}^{(\text{C.I})}$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Diamagnetic	Tetrahedral
8.	$[\text{Hg}(\text{L}_1)(\text{pph}_3)_2]\text{Cl}_2$	406 306 230	21696 32626 43478	${}^{(\text{C.I})}$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Diamagnetic	octahedral
9.	$[\text{Hg}(\text{L}_1)(\text{dppm})]\text{Cl}_2$	453 312 221	22062 32051 45248	${}^{(\text{C.I})}$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Diamagnetic	octahedral
10.	$[\text{Co}(\text{L}_2)\text{Cl}_2]$	639 317 240	15649 31496 41666	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1$ (P) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--	Tetrahedral
11.	$[\text{Co}(\text{L}_2)(\text{pph}_3)_2]\text{Cl}_2$	608 305 238	16447 32786 41928	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1$ (P) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	4.707	Tetrahedral
12.	$[\text{Co}(\text{L}_2)(\text{dppm})]\text{Cl}_2$	699 293 221	14295 34129 45248	${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1$ (P) $n \rightarrow \pi^*$	--	Tetrahedral

				$\pi \rightarrow \pi^*$		
13.	$[\text{Ni}(\text{L}_2)\text{Cl}_2]$	1152 818 361 216	8676 12224 27700 46189	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--	Tetrahedral
14.	$[\text{Ni}(\text{L}_2)(\text{pph}_3)_2]\text{Cl}_2$	1177 779 344 250	8492 12836 29069 40000	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--	Tetrahedral
15.	$[\text{Ni}(\text{L}_2)(\text{dppm})]\text{Cl}_2$	1196 699 345 231	8357 14306 28985 43290	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	4.022	Tetrahedral
16.	$[\text{Hg}(\text{L}_2)\text{Cl}_2]$	475 306 242	21011 32679 41322	(C.T) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Diamagnetic	Tetrahedral
17.	$[\text{Hg}(\text{L}_2)(\text{pph}_3)_2]\text{Cl}_2$	483 300 233	20691 33333 42826	(C.T) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Diamagnetic	octahedral
18.	$[\text{Hg}(\text{L}_2)(\text{dppm})]\text{Cl}_2$	489 305 207	20041 32733 48309	(C.T) $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Diamagnetic	octahedral

FTIR Results

The important infrared bands of the ligands and their complexes are collected in (Table3). The FTIR spectra of the complexes were interpreted by the free ligands. Absorption at $(3309\text{-}3369)\text{cm}^{-1}$ due to the presence of $\nu(\text{NH})$, these stretching are shifted toward a lower frequencies compared to free ligands and indicate the involvement of NH group in the bonding^[32]. The complexes exhibited the most characteristic bands occur at $(3010\text{-}3055)\text{cm}^{-1}$, $(2916\text{-}2991)\text{cm}^{-1}$, $(1671\text{-}1687)\text{cm}^{-1}$, $(1602\text{-}1618)\text{cm}^{-1}$, $(1560\text{-}1596)\text{cm}^{-1}$ and $(1452\text{-}1492)\text{cm}^{-1}$ due to the stretching vibrations of $\nu(\text{C}=\text{H})$ Ar, $\nu(\text{C}-\text{H})$ Alph, $\nu(\text{C}=\text{O})$ Amid, $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{C})_{\text{sym}}$ and $\nu(\text{C}-\text{N})$ respectively^[33,34]. The bands due to $\nu(\text{C}-\text{O}-\text{C})$ stretching vibration of the O-methoxy group of the phenyl ring (L_1, L_2) appeared at $(1350, 1379)\text{cm}^{-1}$ respectively. These bands are shifted to $(1332\text{-}1344)\text{cm}^{-1}$ in the metal complexes. Suggesting the involvement of the oxygen atom of the O-methoxy group in coordination with the metal ion. The infrared of the complexes showed bands at $(1429\text{-}1433)$, $(619\text{-}742)\text{cm}^{-1}$ $(420\text{-}486)\text{cm}^{-1}$ and $(570\text{-}590)\text{cm}^{-1}$ which are assigned to $\nu(\text{C}-\text{P})_{\text{Asym. \& sym.}}$, $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively^[35,36] Fig[1,2].

Table 3: IR data of synthesized complexes and ligands (cm⁻¹)

المعقد	v(N-H) Ani.	v(N-H) Thy.	v(C-H) Ar.	v(C-H)Alph.		v(C=O) Keton.	v(C=O) Imid	v(C=O) Amid	v(C=C)		v (C-N)	v (C-O-C)	v(C-P)		v(C-Cl)	v(M-N)	v(M-P)	v(M-O)
				Asym.	Sym.				Asym.	Sym.			Asym.	Sym.				
L1	3411(s)	-	3031(w)	2950(w)	2873(w)	1735(s)	-	1691(s)	1608(m)	1521(s)	1461(m)	1330(m)	-	-	860(m)	-	-	-
L2	3363(m)	3191(m)	3043(w)	2914(w)	2879(w)	-	1720(s)	1677(m)	1606(m)	1552(s)	1498(m)	1339(m)	-	-	860(m)	-	-	-
1.	3344(s)	-	3037(m)	2991(m)	2891(m)	1724(s)	-	1666(m)	1612(m)	1566(m)	1473(s)	1346(m)	-	-	810(m)	430(m)	-	573(w)
2.	3335(s)	-	3054(m)	2916(m)	2830(m)	1722(s)	-	1672(s)	1616(s)	1576(m)	1452(m)	1334(m)	1430(m)	690(w)	861(m)	432(m)	569(w)	577(w)
3.	3322(m)	-	3043(w)	2985(m)	2889(m)	1721(s)	-	1674(s)	1612(m)	1583(m)	1454(m)	1344(m)	1431(m)	669(w)	845(m)	420(m)	542(w)	577(w)
4.	3309(m)	-	3028(w)	2968(m)	2843(m)	1724(s)	-	1687(s)	1618(w)	1595(w)	1465(m)	1340(m)	-	-	839(m)	440(m)	-	571(w)
5.	3345(s)	-	3035(w)	2965(w)	2849(w)	1722(s)	-	1672(s)	1611(s)	1588(m)	1492(s)	1339(m)	1429(w)	619(w)	850(m)	452(m)	561(w)	570(w)
6.	3387(m)	-	3055(m)	2920(m)	2882(m)	1708(m)	-	1674(s)	1618(m)	1589(s)	1473(w)	1329(m)	1433(w)	663(w)	864(m)	447(m)	553(w)	571(w)
7.	3360(m)	-	3055(m)	2924(m)	2854(w)	1720(s)	-	1678(s)	1602(m)	1590(w)	1492(s)	1334(m)	-	-	878(m)	469(w)	-	574(w)
8.	3375(m)	-	3015(m)	2918(s)	2843(m)	1724(m)	-	1682(m)	1614(m)	1578(w)	1470(m)	1339(m)	1442(s)	719(w)	860(m)	430(m)	574(w)	586(w)
9.	3345(m)	-	3018(m)	2950(w)	2864(m)	1722(s)	-	1671(m)	1610(m)	1583(s)	1470(m)	1330(m)	1429(w)	709(w)	860(m)	453(m)	586(w)	575(w)
10.	3367(m)	3195(m)	3039(m)	2970(m)	2884(m)	-	1704(s)	1679(s)	1614(m)	1593(s)	1473(m)	1332(m)	-	-	849(m)	430(m)	-	586(w)

	m)	m)	m)					m)))))			
11.	3369(s)	3192(m)	3026(m)	2926(w)	2843(m)	-	1728(m)	1681(m)	1616(m)	1595(m)	1465(s)	1334(m)	1394(m)	698(m)	840(m)	476(w)	516(w)	582(w)
12.	3345(s)	3193(m)	3024(m)	2965(w)	2890(m)	-	1722(s)	1682(m)	1609(m)	1591(w)	1489(w)	1334(m)	1430(m)	698(w)	862(m)	465(w)	522(w)	577(w)
13.	3345(w)	3185(w)	3010(m)	2945(w)	2895(m)	-	1718(m)	1688(m)	1617(w)	1572(m)	1487(s)	1334(m)	1433(m)	642(w)	868(m)	468(m)	-	579(w)
14.	3345(m)	3189(m)	3024(m)	2965(w)	2890(m)	-	1707(s)	1666(m)	1609(m)	1591(w)	1489(w)	1334(m)	1430(m)	698(w)	849(m)	486(m)	519(w)	573(w)
15.	3336(s)	3195(m)	3024(m)	2976(m)	2860(m)	-	1703(s)	1677(w)	1610(m)	1596(s)	1485(w)	1338(m)	1430(m)	742(w)	860(m)	430(m)	573(w)	579(w)
16.	3338(s)	3198(m)	3039(w)	2918(s)	2843(m)	-	1730(m)	1680(m)	1610(m)	1560(w)	1454(w)	1337(m)	-	-	848(m)	448(m)	-	590(w)
17.	3369(s)	3192(w)	3026(m)	2926(w)	2843(m)	-	1728(s)	1681(m)	1616(m)	1563(w)	1456(w)	1334(m)	1494(m)	698(w)	846(m)	476(m)	566(w)	574(w)
18.	3325(s)	3189(m)	3010(m)	2945(w)	2895(m)	-	1723(m)	1688(m)	1616(m)	1572(m)	1487(s)	1334(m)	1433(m)	642(w)	860(m)	430(m)	554(w)	589(w)

W=weak , m=medium , s=strong , Ani=Aniline , Thy.=Thymine

NMR Results

The ^1H -NMR spectrum of the complex $[\text{Hg}(\text{L}_1)\text{Cl}_2]$ (Fig.4) showed a singlet at ($\delta\text{H}=2.51\text{ppm}$) assigned to the solvent protons (DMSO-d^6). The (O-CH_3) group displayed two singlets at ($\delta\text{H}=3.54\text{ppm}$), for the one adjacent to C-Cl group and ($\delta\text{H}=4.4\text{ppm}$) for the second (O-CH_3) which is coordinated to the metal center. this signal is shifted slightly down field and that is an indication of the coordination of methoxy oxygen atom. Also the spectrum showed a singlet at ($\delta\text{H}= 5.43\text{ppm}$) which is assigned to the protons of CH_2 group. The singlet of N-H group appeared at ($\delta\text{NH}=5.97\text{ppm}$). Two singlets also observed at ($\text{H}=6.86,6.71\text{ppm}$) belong to the aromatic C-H group a and b. Whereas a multiplet signal occur in the range ($=7.65_8.43\text{ppm}$) assigned to the protons of the benzene ring^[37]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Hg}(\text{L}_2)(\text{dppm})\text{Cl}_2]$ displayed a singlet at (-19.20ppm) (Fig.5) and that refer to the presence of one product. The negative value of the δP indicated that dppm behave as a bidentate chelate^[38]. The ^1H , ^{13}C , ^{31}P NMR data for compounds measured in DMSO-d^6 are given in (Table4).

Table 4 : ^1H , ^{13}C , ^{31}P NMR spectral data for L1, L2 and Hg (II) complexes .

no	Compound	Type of NMR	Chemical shift (ppm)
1.	(L ₁)	^1H	(DMSO-d^6):) $\delta\text{H}=2.51\text{ppm}$, ($\delta 3.76,3.82$)ppm(3H,s,) for 2OCH_3 , $\text{CH}_2=(\delta 5.07\text{ppm},2\text{H},\text{s})$, $\text{NH}=(\delta 6.16\text{ppm},1\text{H},\text{s})$, C-H-Ar ₁ =($\delta 6.78,6.74\text{ppm},1\text{H},\text{s}$), C-H-Ar ₂ =($\delta 6.73-7.71\text{ppm},4\text{H},\text{m}$)
		^{13}C	$\delta^{13}\text{C}=40.44\text{ppm}$ (DMSO-d^6), $\delta^{13}\text{C}=56.32,57.43\text{ppm}$ (2OCH_3), $\delta^{13}\text{C}=99.82\text{ppm}$ (CH_2), $\delta^{13}\text{C}=108.13-151.96\text{ppm}$ (Ar), $\delta^{13}\text{C}=161.91,165.39\text{ppm}$ (C=O)
2.	(L ₂)	^1H	DMSO-d^6):) $\delta\text{H}=2.50\text{ppm}$, $\text{CH}_3=(\delta 1.76\text{ppm},3\text{H},\text{s})$, ($\delta 3.75,3.82$)ppm(3H,s,) for 2OCH_3 , $\text{CH}_2=(\delta 4.47\text{ppm},2\text{H},\text{s})$, $\text{NH}=(\delta 5.52\text{ppm},1\text{H},\text{s})$, C-H-Ar ₁ =($\delta 6.96,6.70\text{ppm},1\text{H},\text{s}$), C-H=($\delta 7.25\text{ppm},1\text{H},\text{s}$), $\text{NH}=(\delta 10.91\text{ppm},1\text{H},\text{s})$,
		^{13}C	$\delta^{13}\text{C}=40.46\text{ppm}$ (DMSO-d^6), $\delta^{13}\text{C}=12.47$ (CH_3), $\delta^{13}\text{C}=56.05,56.65\text{ppm}$ (2OCH_3), $\delta^{13}\text{C}=59.94\text{ppm}$ (CH_2), $\delta^{13}\text{C}=98.65,111.03\text{ppm}$ (C=C), $\delta^{13}\text{C}=116.43-150.28\text{ppm}$ (Ar), $\delta^{13}\text{C}=152.19,165.35\text{ppm}$ (C=O)
3.	$[\text{Hg}(\text{L}_1)\text{Cl}_2]$	^1H	(DMSO-d^6):) $\delta\text{H}=2.51\text{ppm}$, ($\delta 3.54,4.00$)ppm(3H,s,) for 2OCH_3 , $\text{CH}_2=(\delta 5.43\text{ppm},2\text{H},\text{s})$, $\text{NH}=(\delta 5.97\text{ppm},1\text{H},\text{s})$, C-H-Ar ₁ =($\delta 6.71,6.86\text{ppm},1\text{H},\text{s}$), C-H-Ar ₂ =($\delta 7.65-8.43\text{ppm},1\text{H},\text{m}$),
		^{13}C	$\delta^{13}\text{C}=40.27\text{ppm}$ (DMSO-d^6), $\delta^{13}\text{C}=56.63,58.52\text{ppm}$ (2OCH_3), $\delta^{13}\text{C}=65.22\text{ppm}$ (CH_2), $\delta^{13}\text{C}=105.27-153.47\text{ppm}$ (Ar), $\delta^{13}\text{C}=160.61,174.38\text{ppm}$ (C=O)
4.	$[\text{Hg}(\text{L}_2)(\text{dppm})_2\text{Cl}_2]$	^1H	DMSO-d^6):) $\delta\text{H}=2.50\text{ppm}$, $\text{CH}_3=(\delta 1.73\text{ppm},3\text{H},\text{s})$, $\text{CH}_2(\text{dppm})=(\delta 1.24\text{ppm},2\text{H},\text{s})$, ($\delta 3.68,3.84$)ppm(3H,s,) for 2OCH_3 , $\text{CH}_2=(\delta 4.03\text{ppm},2\text{H},\text{s})$, $\text{NH}=(\delta 5.94\text{ppm},1\text{H},\text{s})$, C-H-Ar ₁ =($\delta 6.81,6.44\text{ppm},1\text{H},\text{s}$), C-H=($\delta 7.22\text{ppm},1\text{H},\text{s}$), $\text{NH}=(\delta 10.94\text{ppm},1\text{H},\text{s})$, C-H-Ar ₂ =($\delta 7.20-$

			7.90ppm,20H,m)
5.	[Hg(L ₂)(dppm) ₂ Cl ₂]	³¹ P	-19.20

S; singlet ; D ; doublet ; t ; triplet ; m ; multiplet

Antimicrobial activity

(Table5) illustrates the result of antibacterial activity of . Mannich Base ligands (L₁,L₂) and their metal Complexes against two types of bacteria *pseudomonas aeruginosa* (gram negative) and *staphylococcus aureus* (gram positive). The Compounds were evaluated in vitro for their antibacterial activity against the tested bacteria by disc diffusion method^[39,40] the bacterial species were obtained from biological department/college of science/ Tikrit university. Nutrient agar was used for bacterial screening, DMSO was used as solvent and Ciprofloxine ,Ampicillin and Amoxllin (1x10⁻³g/ml) as Control.

The ligands were inactive (Conc., 1x10⁻⁴ mg/ml) or relatively shows narrow spectrum of activity (Cenc:1X10⁻³ mg/ml).Metal Complexes exhibited different activity against the *Pseudomonas aeruginosa* and *staphylococcus aureus* (Conc,1X10⁻²,1x10⁻³mg/ml)The results obtained suggest that the Complexion metals enhanced antibacterial activity of Mannich Base ligand Figure (6,7)

Table5: Antibacterial activity of ligands and some complexes.

No.	Complexes	Conc. mg/ml	<i>Pseudomonas aeruginosa</i>	<i>Staphylococcus aureus</i>
1.	L ₁	1 x 10 ⁻⁴	-	-
		1 x 10 ⁻³	+	+
		1 x 10 ⁻²	+	+
2.	[Co(L ₁)(pph ₃) ₂]Cl ₂	1 x 10 ⁻⁴	+	-
		1 x 10 ⁻³	+++	+++
		1 x 10 ⁻²	+++	+++
3.	[Ni(L ₁)Cl ₂]	1 x 10 ⁻⁴	+	+
		1 x 10 ⁻³	++	+
		1 x 10 ⁻²	+++	+++
4.	[Hg(L ₁)Cl ₂]	1 x 10 ⁻⁴	+	+
		1 x 10 ⁻³	+	++
		1 x 10 ⁻²	+++	+++
5.	L ₂	1 x 10 ⁻⁴	-	-
		1 x 10 ⁻³	+	+
		1 x 10 ⁻²	++	++
6.	[Co(L ₂)Cl ₂]	1 x 10 ⁻⁴	-	-
		1 x 10 ⁻³	++	+
		1 x 10 ⁻²	+++	+++

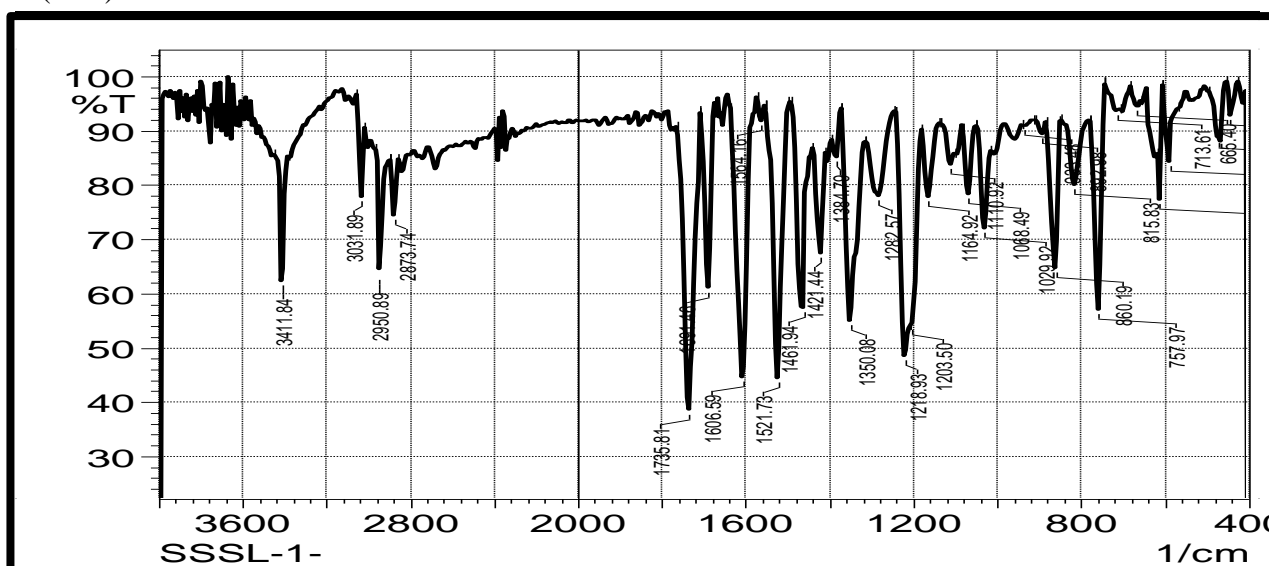
7.	[Co(L ₂)(dppm)]Cl ₂	1 x 10 ⁻⁴	+	+
		1 x 10 ⁻³	+	++
		1 x 10 ⁻²	+++	+++
8.	[Ni(L ₂)(pph ₃) ₂]Cl ₂	1 x 10 ⁻⁴	+	-
		1 x 10 ⁻³	+++	++
		1 x 10 ⁻²	+++	+++
9.	[Hg(L ₂)Cl ₂]	1 x 10 ⁻⁴	-	-
		1 x 10 ⁻³	++	+
		1 x 10 ⁻²	+++	+++
10.	[Hg(L ₂)(pph ₃) ₂]Cl ₂	1 x 10 ⁻⁴	+	+
		1 x 10 ⁻³	++	++
		1 x 10 ⁻²	+++	+++

(-) = There is no inhibition

(+) = Inhibition of 5 - 10 mm diameter

(++) = Inhibition of 15 - 20 mm diameter

(+++)= Inhibition of 25 to 30 mm diameter



(Fig. (1) Infrared spectrum of [L1]

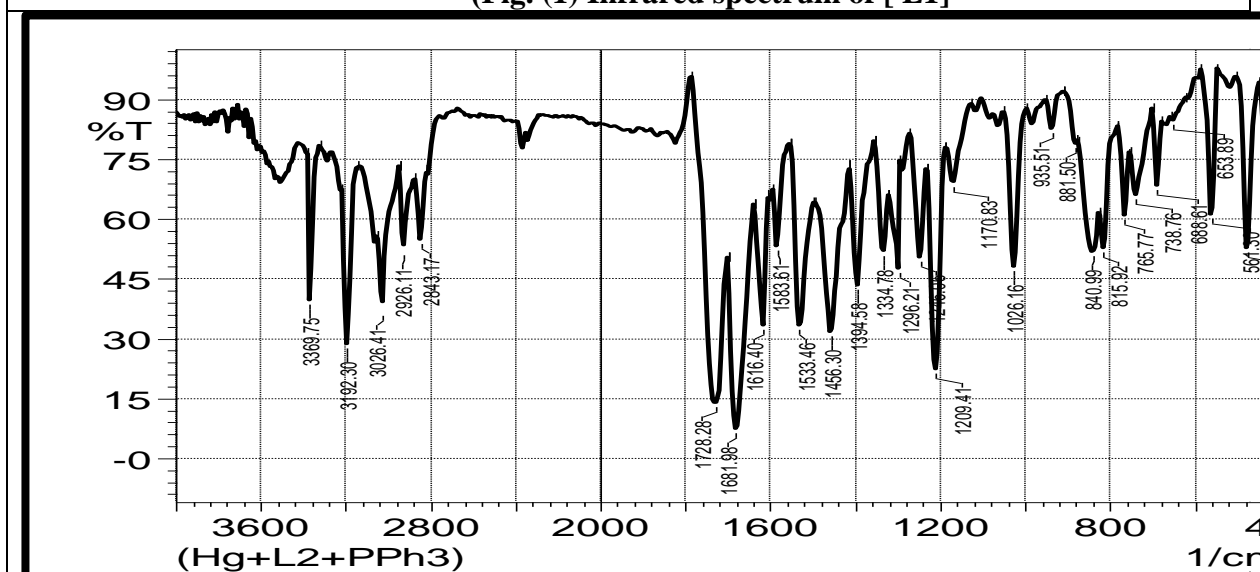


Figure (2) Infrared spectrum of $[\text{Hg}(\text{L}_2)(\text{pph}_3)_2\text{Cl}_2]$

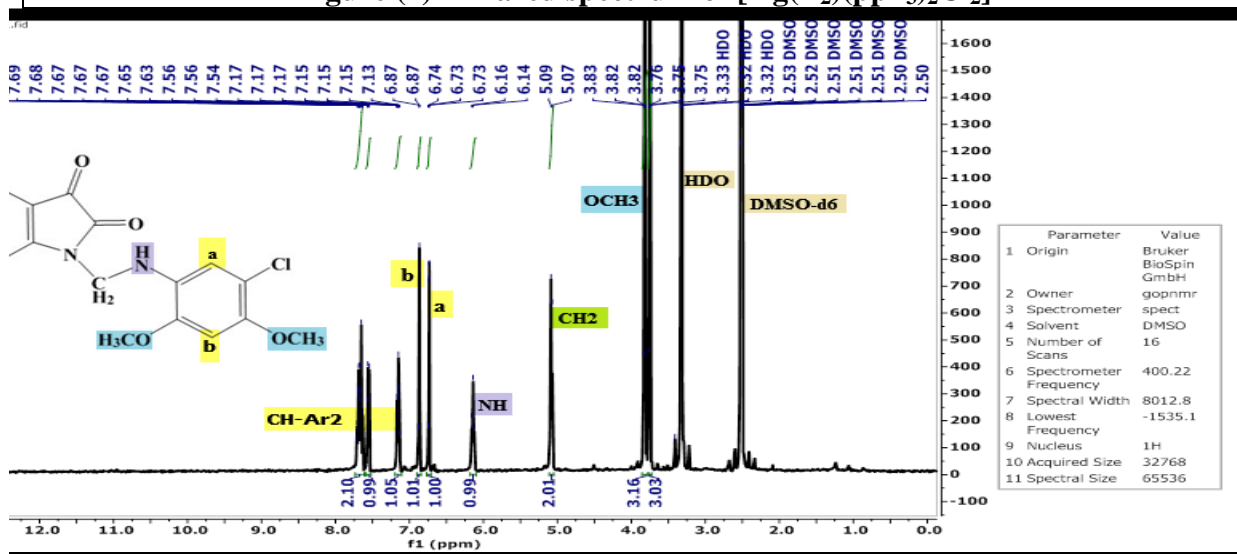


Figure 3: $^1\text{H-NMR}$ spectrum of the ligand $[\text{L}_1]$

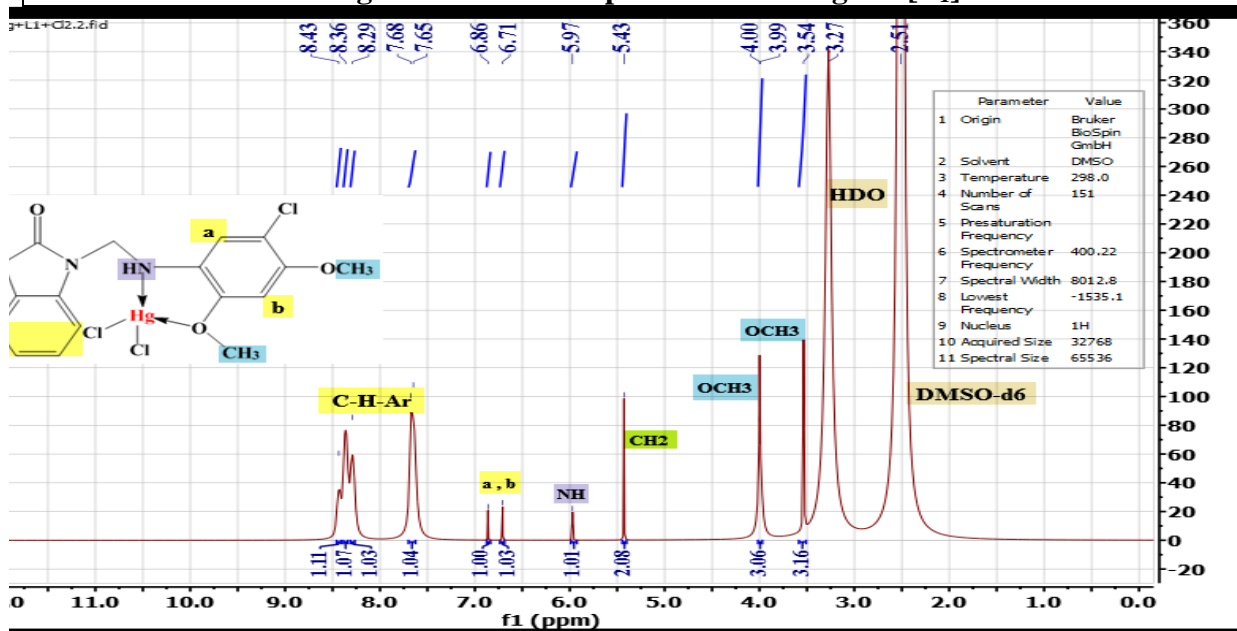
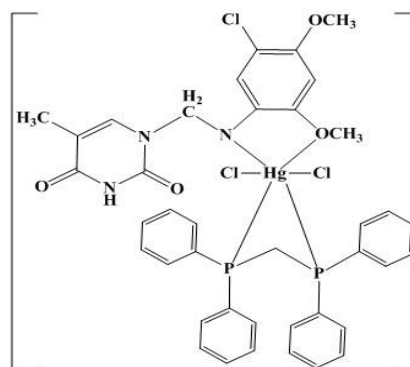


Figure 4: $^1\text{H-NMR}$ spectrum of the complex $[\text{Hg}(\text{L}_1)\text{Cl}_2]$



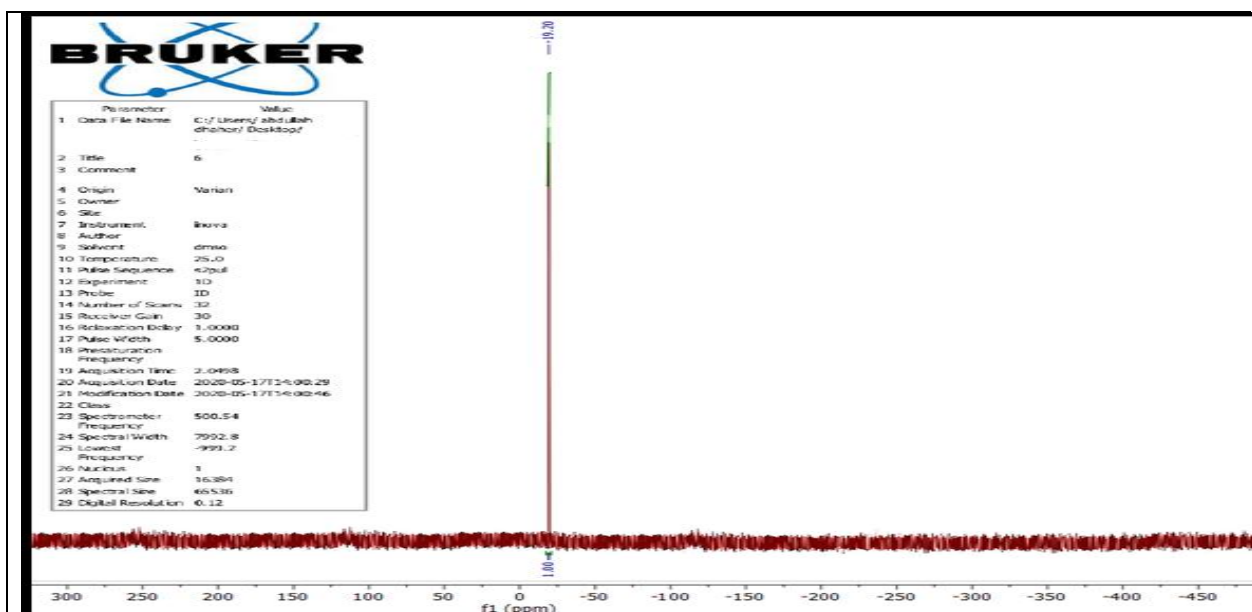


Figure 5: ^{31}P -NMR spectrum of the complex $[\text{Hg}(\text{L}_2)(\text{dppm})_2\text{Cl}_2]$



(Fig.7) The inhibitory activity of the complex $[\text{Hg}(\text{L}_2)\text{Cl}_2]$ against bacteria *Pseudomonas aeruginosa*



(Fig.6) The inhibitory activity of the complex $[\text{L}_2]$ against bacteria *Pseudomonas aeruginosa*

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