

## Synthesis and Characterization of Complexes of Schiff Base [1, 2-Diphenyl -2- 2- {[1-(3-Amino-Phenyl)-Ethylidene]-Hydrazono Methyl}-Phenol] with Mn(II), Fe(II), Co(II), Cu(II), Zn(II), Cd(II), Ni(II), and Hg(II) Ions

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### Abstract

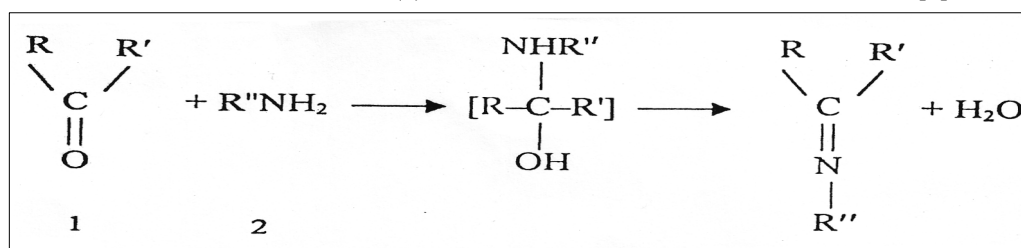
The new tridentate Schiff base ligand (HL)namely 2- {[1-(3-amino-phenyl)-ethylidene]-hydrazono methyl}-phenol containing (N N O)as donors atoms was prepared in two steps:Step (1): By the reaction of 3-aminoacetophenone with hydrazine monohydrate under reflux in methanol and drops of glacial acetic acid gave the intermediate compound 3-(1- hydrazono ethyl)-phenol amine.Step (2): By the reaction of 3-(1-hydrazono ethyl)-phenol amine with salicylaldehyde under reflux in methanol, gave the ligand (HL).The prepared ligand was characterized by I.R, U.V-Vis,1H- 13C NMR spectra and melting point and reacted with some metal ions under reflux in methanol with (1:1) ratio gave complexes of the general formula: [MCIL]. Where: M= Mn(II), Fe(II), Co(II), Cu(II), Zn(II), Cd(II), Ni(II), and Hg(II).Products were found to be solid crystalline complexes, which have been characterized through the following techniques:Molar conductivity .Spectroscopic Method [FTIR and UV-Vis], additional measurement magnetic suscepibility and Chloride content, The magnetic moment coupled with the electronic spectra suggested an tetrahedral geometry for all the complexes except[ NiCIL] is Square-planar.The nature of the complexes formed were studied by Mole Ratio and the stability constant of the complexes have also been studied.

**Key words:** spectral studies , tridentate Schiff base, 3-aminoacetophenone, hydrazine monohydrate complexes

### Introduction:

The term "Schiff bases" was firstly used to define those organic compounds which contain the functional group (-C= N-).Schiff's bases have several names; anils, azomethines, benzene's and benzylideneaniline,[1] these compounds were firstly prepared by Schiff in (1864), from a simple amines and for this reason, they were called " Schiff's bases "

The "Schiff's bases" could be obtained by condensation reaction between carbonyl compounds (1) and amine (2) by the intermediate of hemiamine, scheme (1), with formation of intermediate hemi amine. ,[2]



Scheme(1) Condensation reaction between carbonyl compounds and amine

Polydentate ligands, such as Schiff bases, assisted by metal ions, provide highly organized supramolecular metal complexes. Such complexes possess binding sites and cavities for various cations, anions and organic molecules [3-5].

Schiff base macrocycles have been of remarkable versatility in macrocyclic and supramolecular chemistry [6] and [7], and therefore they have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. In the area of bioinorganic chemistry the interest in the Schiff base complexes lies in that they provide synthetic models for the metal-containing sites in metallo proteins/enzymes and also contributed enormously to the development of medicinal chemistry, radio immunotherapy, cancer diagnosis and treatment of tumor [ 89] and [9]. In addition, some of the complexes containing N and O donor atoms are effective as stereo specific catalysts for oxidation [10]

In this paper we present the synthesis and study of some metal complexes with 2- {[1-(3-amino-phenyl)-ethylidene]-hydrazono methyl}-phenol. (HL)

## 2. Experimental

All the chemicals were reagent grad (fluka & BDH) , and used as received., ethanol, methanol and dimethylforamaide(DMF) , benzene, and acetone and KBr , from (B.D.H. UV-Vis spectra were recorded on a (Shimadzu UV- 160A) Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a (Shimadzu, FTI R-8400S) Fourier Transform Infrared Spectrophotometer (4000- 400)  $\text{cm}^{-1}$  with samples prepared as KBr discs. Elemental micro analysis for the ligand was performed on a (C.H.N.S.O) Perkin Elemar 2400. While metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu AA 620G atomic absorption spectrophotometer. The Chloride contents of complexes were determined by potentiometric titration method using (686-Titro processor-665. Dosimat Metrohn Swiss). $^1\text{H}$  ,  $^{13}\text{C}$ -NMR and Mass spectrum was recorded on sorrier transform Varian spectrometer, operation at 300 MHz with tetra methyl saline (TMS) as internal standard in DMSO- $d_6$ , measurements were made at chemistry department, AL- albayt university, Jordan. In addition melting points were obtained using (Stuart Melting Point Apparatus). The proposed molecular structure of the complexes were drawing by using chem. office prog, 3DX (2006).

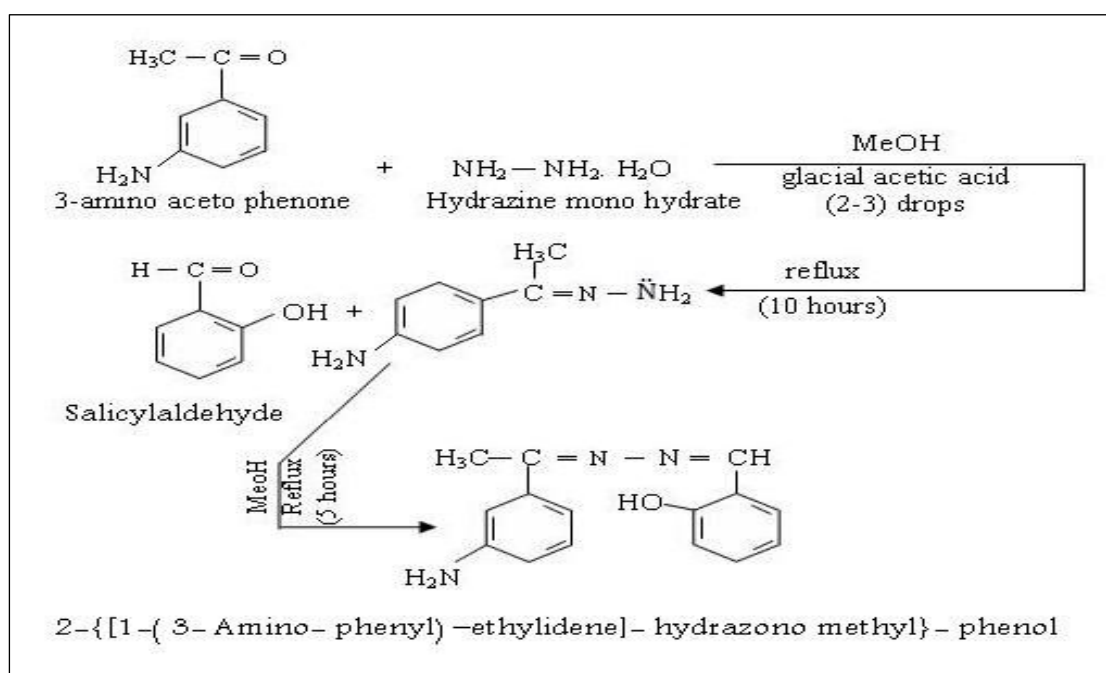
### Synthesis of the ligand (HL):

#### Preparation of intermediate material:

A solution of 3-amino aceto phenone (1.35gm, 9.06m mole) in methanol (5 ml) was added to hydrazine monohydrate (0.499 gm, 9.984 m mole) (0.476 ml), then (2-3) drops of glacial acetic acid was added slowly to the reaction mixture. The mixture was allowed to cool to room temperature. A brown solid was obtained by evaporation of methanol during (24 hours)., (1.1 gm), yield (81.48%) m.p (80°C.).

#### Preparation of the ligand (HL):

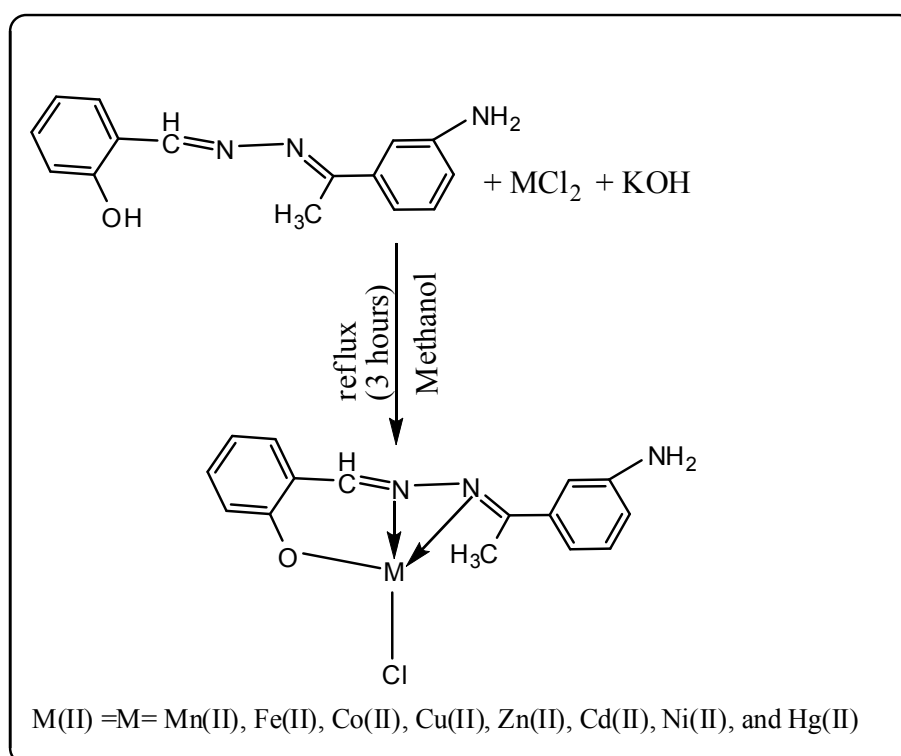
A solution of (0.24 gm, 1.610 m mole) of intermediate compound in methanol ( 5 ml) was added to salicylaldehyde (0.202 gm, 1.656 m mole). The reaction mixture was refluxed for (5 hours) with stirring, filtered and the filtrate was allowed to dry at room temperature. A deep yellow solid was obtained .Weight is (0.36 gm), yield (89%), m.p (131° C). The new ligand was prepared according to the general method shown in schemes (2).



Scheme (2)The synthesis route of the ligand (HL)

General procedure for the synthesis of metal complexes[MCIL ]

All complexes of ligand (HL) were synthesized by a similar method, shown in scheme (3).



Scheme (3): Schematic representation of synthesis of complexes

### 3. Results and Discussion

Generally, the complexes were prepared by reacting the respective metal salts with the ligand using 1:1 mole ratio, i.e. one mole of metal salt : one mole of ligand (HL). The formula weights and melting points, are given in (Table I). Based on the physicochemical characteristics (Table I), it was found that all the complexes were non-hygroscopic, stable at room temperature and appears as powders with high melting points. Ligand (HL) is soluble in (N,N-dimethylformamide (DMF), dimethylsulphoxide (DMSO), methanol (MeOH), ethanol (EtOH), and completely insoluble in water (H<sub>2</sub>O), benzene (C<sub>6</sub>H<sub>6</sub>), and acetone. Generally, the complexes were prepared by reacting the respective metal salts with the ligand using using 1:1 mole ratio, i.e. one mole of metal salt : one mole of HL. The weights and melting points are given in (Table I) based on the physicochemical characteristics, it was found that all the complexes were non-hygroscopic, stable at room temperature and appears as powders with high melting points. The solubility of the complexes of were studied in various solvents. They are not soluble in water. All complexes are soluble in (DMF) and (DMSO) solvent. The complexes were analyzed for their metal by atomic absorption measurements and chloride contents were determined by standard methods. (Table-1) for all complexes gave approximated values for theoretical values. The observed molar conductance (Table 1) values measured in (DMF) in 10<sup>-3</sup>M solution lie in the (11-6.7 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) range, indicating their electrolytic nature with (1:1). [11]

#### Fourier transform infrared spectroscopy (FTIR) spectrum of the ligand (HL):

The (FTIR) spectrum of the ligand (HL), table(2) displayed two bands at (1620), (1566) cm<sup>-1</sup> are due to the ν(N=C-CH<sub>3</sub>) and ν(N=C-H) stretching vibration respectively. The band at (3450) cm<sup>-1</sup> is assigned to ν(N-H) stretching vibration. The band at (981) cm<sup>-1</sup> was assigned to (N-N) stretching vibration[12].

#### (U.V-vis) spectrum of the ligand (HL):

The (U.V-Vis) spectrum of (HL) exhibits a high intense absorption peak at (301nm) (33222.59 cm<sup>-1</sup>), (ε<sub>max</sub> =1609 molar<sup>-1</sup>.cm<sup>-1</sup>) and (278 nm) (35971.223 cm<sup>-1</sup>), (ε<sub>max</sub> =1484 molar<sup>-1</sup>. cm<sup>-1</sup>) which are assigned to (n → π\*) and (π → π\*) transition respectively [13], table (3).

#### <sup>1</sup>H-NMR spectrum of the ligand (HL):

The <sup>1</sup>H-NMR spectrum of the (HL) in DMSO-d<sub>6</sub> shows proton of (O-H) group (ph-OH) of the ligand appeared as a singlet signal at (9.051) ppm. The three protons of carbon (C15) appeared as a singlet signal at (2.338) ppm. The multiple signals at (7.003, 7.028, 7.1), (6.5, 6.8, 8.1) ppm. Are due to aromatic hydrogen of carbon (C13, C14, C3), (C12, C10, C2, C4 and C7) respectively [14]. Table (4).

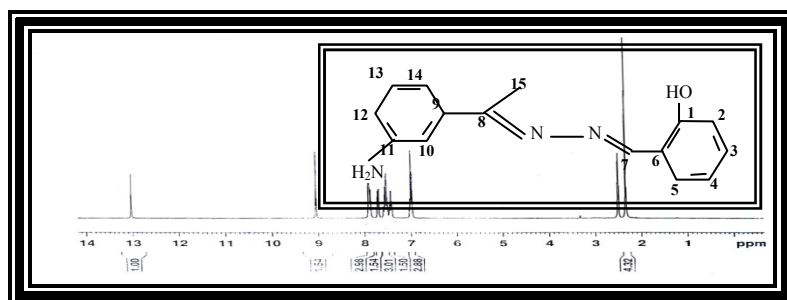


figure (3)  $^1\text{H}$  NMR spectrum of ligand (HL)

$^{13}\text{C}$ -NMR spectrum of the (HL):

$^{13}\text{C}$ -NMR of the ligand (HL), figure (4), table (5) in (DMSO- $d_6$ ) shows the chemical shifts as follow [14].

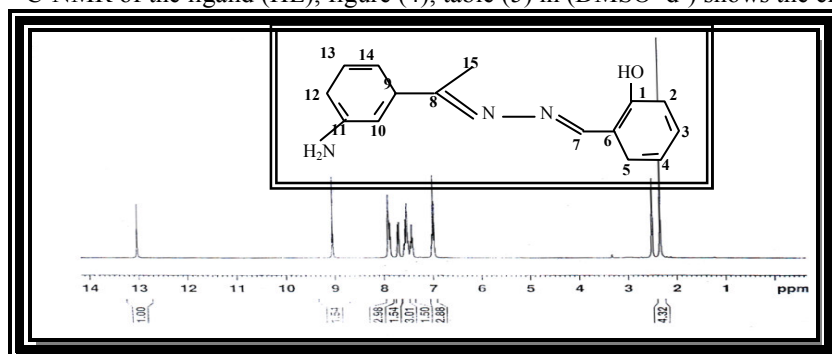


Figure (4)  $^{13}\text{C}$ -NMR spectrum of ligand (HL)

The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligand to the central metal ions. The characteristic vibrations and assignments of ligand (HL) and its complexes as KBr spectra discs are described (Table -2), Some new bands of weak intensity observed in the regions around (510-599) $\text{cm}^{-1}$  and (430-541)  $\text{cm}^{-1}$  may be ascribed to M-N and M-O vibrations, respectively [15-16].

The UV- Vis spectra of the prepared complexes dissolved in (DMF) ( $10^{-3}$  M) have been measured and the data obtained were included in (Table- 3). Again the large bathchromic shift of the ( $\lambda_{\text{max}}$ ) assigned to ( $\pi-\pi^*$ ) and ( $n-\pi^*$ ) transitions of the ligand suggesting the involvement of the ligand in the bond formation with the metal ion. [13]The magnetic moment has been determined in the solid state by Faraday's method. Table (6).

Cd (II), Zn(II) and (II) complexes are diamagnetic in nature and their electronic spectra do not furnish any characteristic d-d transitions except charge transfer (CT) bands as expected for  $d^{10}$  systems in the visible region, that is a good result for Zn(II), Cd(II) and Hg(II) tetrahedral complexes. [17-18]

Table (1) Some physical properties of the ligand (HL) and its metal complexes

No	Compound	m. p °C	Color,	Yield%	M. wt	$\Lambda_m$ $\Omega^{-1}$ $\text{mol}^{-1}$ $\text{cm}^2$	Found (calc.)%	
							Cl	Metal
-	(HL)	131	Deep yellow	89	252	2.4	—	—
1	[MnCl]L	360 dec	Dark green	73	342.39	6.1	(10.35) 9.81	(14.52) 13.21
2	[FeCl]L	360 dec	Dark violet	80	343.3	5.5	(10.32) 10.64	(14.72) 13.25
3	[CoCl]L	360 dec	Deep orange	53	346.38	5.8	(10.23) 11.12	(15.42) 16.53
4	[NiCl]L	360 dec	Yellow green	80	346.16	1.2	(12.14) 11.54	(15.38) 14.92
5	[CuCl]L	360 dec	Dark green	53	350.99	11- 6.7	(10.09) 9.11	(16.7) 15.80
6	[ZnCl]L	360 dec	Yellow	80	352.82	5.6	(10.04) 10.13	(16.81) 15.11
7	[CdCl]L	225	Deep yellow	74	400.04	6.3	(8.86) 9.11	(25.81) 23.92
8	[HgCl]L	213	Dark yellow	78	488.04	6.7	(7.26) 8.16	— —

dec.= decomposition, Calc. = calculated, ( )= theoretical

Table (2) Infrared data (wave number  $\nu$ )  $\text{cm}^{-1}$  of the (HL) and its complexes

No	Compound	$\nu(\text{N}=\text{C}-\text{CH}_3)$	$\nu(\text{N}=\text{C}-\text{H})$	$\nu(\text{HO}-\text{H})$ hydrogen bonding	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{C})$ arom.	$\nu(\text{C}-\text{H})$ arom.	$\nu(\text{C}-\text{H})$ aliph	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$	Other bands
-	(HL)	1620	1566	3500	3450	1496	3058	2921	981	—	—	$\delta(\text{N}-\text{H})=1615$
1	[MnCl L]	1605	1539	3479	3350	1465	3058	2920	1031	599	541	$\delta(\text{N}-\text{H})=1600$
2	[Fe (HL)]	1605	1535	3464	3475	1467	3058	2372	1031	601	466	$\delta(\text{N}-\text{H})=1600$
3	[Co ClL]	1604	1525	<b>3566</b>	3552	1461	3055	2970	1049	510	480	$\delta(\text{N}-\text{H})=1668$
4	[Ni ClL]	1610	1533	<b>3459</b>	3300	1467	3058	2921	1031	525	460	$\delta(\text{N}-\text{H})=1600$
5	[Cu ClL]	1608	1531	3450	3600	1465	3058	2966	1047	538	430	$\delta(\text{N}-\text{H})=1654$
6	[Zn ClL]	1608	1529	3440	3600	1461	3058	2956	1026	545	440	$\delta(\text{N}-\text{H})=1662$
7	[Cd ClL]	1618	1530	3420	3521	1458	3060	2655	1093	574	455	$\delta(\text{N}-\text{H})=1600$
8	[Hg ClL]	1614	1523	3400	3630	1456	3052	2927	1029	582	445	$\delta(\text{N}-\text{H})=1610$

aliph. = aliphatic, arom. = aromatic,  $\delta$  = Bending,  $\nu$  = stretching

Table 3- Electronic Spectral data of the studied compounds

No	Compound	$\lambda$ nm	$\nu$ $\text{cm}^{-1}$	$\epsilon_{\text{max}}$ molar $^{-1}$ . $\text{cm}^{-1}$ )	Assignments	Coordination
-	(HL)	278 301	35971.22 33222.59	1484 1609	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	—
1	[MnCIL]	306 357 395	32679.73 28011.20 25316.45	2166 927 776	Ligand field C.T ${}^6A_1 \rightarrow {}^4T_2$	Tetrahedral
2	[FeCIL]	281 344 373	35587.18 29069.76 26809.65	1548 1343 925	Ligand field C.T ${}^5E \rightarrow {}^5T_2$	Tetrahedral
3	[CoCIL]	307 357 394	32573.28 28011.20 25380.71	2284 1645 1624	Ligand field C.T ${}^4T_{1(p)} \rightarrow {}^4A_2$	Tetrahedral
4	[NiCIL]	306 394	32679.73 25380.71	2123 1273	Ligand field $b_2g \rightarrow b_1g$	Square-planar
5	[Cu CIL]	308 403	32467.53 24813.89	2109 1239	Ligand field ${}^2T_2 \rightarrow {}^2E$	Tetrahedral
6	[Zn CIL]	308 400	32467.53 25000	2308 1599	C.T C.T	Tetrahedral
7	[Cd CIL]	306	32679.73	1877	C.T	Tetrahedral
8	[Hg CIL]	306 388	32679.73 25773.19	1654 1200	C.T C.T	Tetrahedral

Table (4)  ${}^1\text{H-NMR}$  data for the ligand (HL) measured in (DMSO- $d_6$ ) and chemical shift in ( $\delta$  ppm)

Compound	Function. group	$\delta$ ppm
(HL)	-OH	9.051 (s)
	C15 – H3	2.338
	C3 – H	7.1
	C12 – H	6.5
	C4 – H, C2 – H, C10 – H	6.8
	C7 – H	8.1
	C13 – H	7.003
	C14 – H	7.028
	DMSO	2.5

$\delta$  = singlet

Table (5)  $^{13}\text{C}$ -NMR spectrum of the ligand (HL) measured in (DMSO- $d_6$ ) and chemical shift in ( $\delta$  ppm)

Compound	Funct. group	$\delta$ ppm
(HL)	C15	12.2
	C10	115.6
	C2	115.8
	C12	117.4
	C6	118.4
	C14	119
	C4	121.2
	C13	129.4
	C5	130.037
	C9	133.11
	C3	133.891
	C11	146.8
	C1	157.298
	C7	163.7
	C8	164.6
DMSO	2.5	

Table (6) Data of magnetic moment ( $\mu_{\text{eff}}=\text{B.M.}$ ) of solid at 298 k and suggested structure chemical structure of complexes

Complexes	$X_g \times 10^{-6}$ gram susceptibility	$X_m \times 10^{-6}$ molar susceptibility	$X_A \times 10^{-6}$ atom susceptibility	$\mu_{\text{eff}}$ B.M. expt.	$\mu_{\text{eff}}$ B.M. calc	Suggested structure
[Mn ClL]	17.485	6.608	6.457	3.722	3.922	Tetrahedral
[Co ClL]	21.675	8.278	8.127	4.2	4.40	Tetrahedral
[Cu ClL]	3.825	1.453	1.3029	1.551	1.762	Tetrahedral

<sup>a</sup>spin only value<sup>[18]</sup>, expt: experimental, calc. : calculated

The composition of the complexes [Ni Cl L], [Cu Cl L] and [Zn Cl L] formed in solution have been established by mole ratio method, the results reveals (1:1) metal to ligand ratio.

The mole - ratio curves to these complexes in (DMF) are painted in figures (5), (6) and (7). The absorbance value against mole-ratio values are summarized in tables (7), (8) and (9).

Table (7) The absorbance values against mole-ratio values of complex [Ni Cl L] in solution ( $1 \times 10^{-3}$  mol.  $\text{L}^{-1}$ ) in DMF at ( $\lambda = 301$  nm)

No. of compounds	L:M	Absorbance
1	0.5: 1	0.86
2	1: 1	1.00
3	2: 1	1.01
4	3: 1	0.97
5	4: 1	1.06



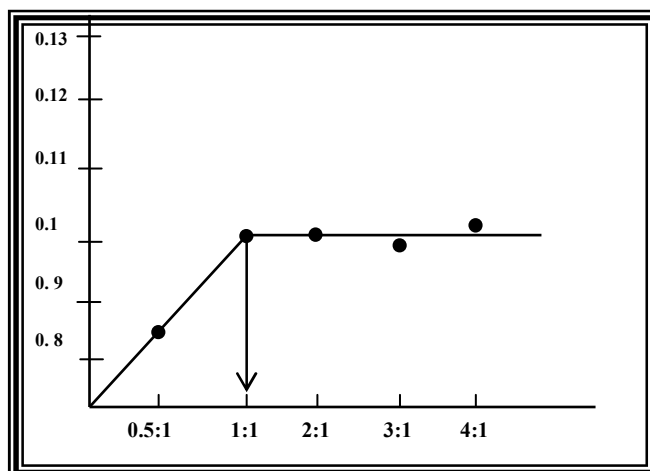


Fig (5) The mole-ratio curve to complex [Ni Cl L] in solution ( $1 \times 10^{-3}$  mole.  $L^{-1}$ ) at ( $\lambda = 301$  nm)

Table (8) The absorbance values against mole-ratio values of complex [Cu Cl L] in solution ( $1 \times 10^{-3}$  mol.  $L^{-1}$ ) in DMF at ( $\lambda = 295$  nm)

No. of compounds	L:M	Absorbance
1	0.5: 1	0.391
2	1: 1	0.46
3	2: 1	0.474
4	3: 1	0.5
5	4: 1	0.45

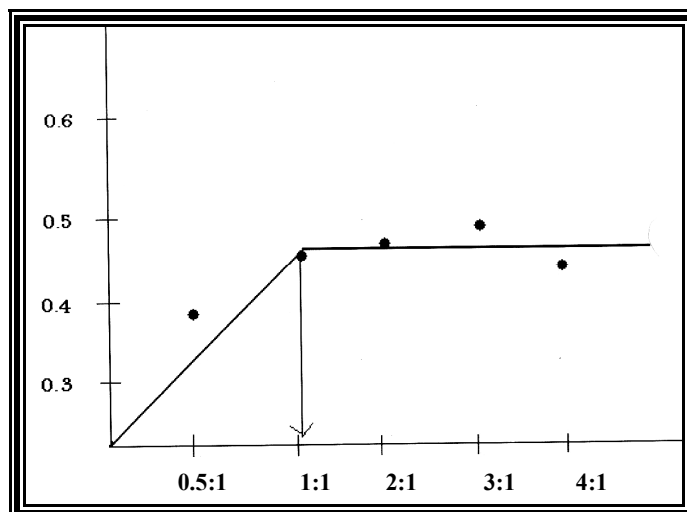


Fig (6) The mole-ratio curve to complex [Cu Cl L] in solution ( $1 \times 10^{-3}$  mole.  $L^{-1}$ ) at ( $\lambda = 287$  nm)

Table (9) The absorbance values against mole-ratio values of complex  $[Zn Cl L]$  in solution ( $1 \times 10^{-3}$  mol.  $L^{-1}$ ) in DMF at ( $\lambda = 265$  nm)

No. of compounds	L:M	Absorbance
1	0.5: 1	0.04
2	1: 1	0.06
3	2: 1	0.061
4	3: 1	0.058
5	4: 1	0.06

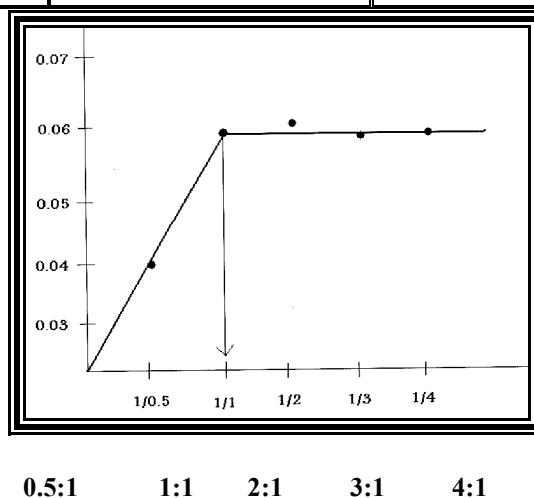


Fig (7) The mole-ratio curve to complex  $ZnCl L$  in solution ( $1 \times 10^{-3}$  mole.  $L^{-1}$ ) at ( $\lambda = 265$  nm)

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