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Research Article

Synthesis , Physicochemical Studies and biological estimation of new mixed ligand complexes from hetrocyclic compounds

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ABSTRACT
The purpose of this research is to synthesize a new mixed ligand Schiff base complexes of Co(II),Ni(II),Cu(II), Zn(II), Cd(II), and Hg(II),which are formulated from the Schiff base (L) that resulted from ortho-phathalaldehyde (2-PA) with 4-chloroaniline(4-NA). Diagnosis of prepared Ligand and its complexes is done by spectral methods as ^{1}H–NMR, mass spectrometer, FTIR, UV-Vis, molar conductance, elemental microanalyses, atomic absoption and magnetic susceptibility. The analytical studyofall new complexes has shown octahedral geometries. Organic performance study of ligand Schiff base and its complexes reveals different activities agansit four types of bactria; two gram (+) and two gram (-) .

Keywords: ligand , schiff base, microanalyses, biological activity.

INTRODUCTION

The chemical compounds that derived from aldehyde or keton and amines call Schiff bases[(1)], which have azo methine group (HC=N). this naming come from Hugo Schiff who discovered them[(2)]. The Schiff bases play a big role in coordination chemistry, medicine and industry until this time[(3-4)]. They have a lot of applications such as ; preparation of metal complexes[(5)], catalysts, drug and cosmetics[(6-7)] .Ortho phthalaldehyde (OPA) is chemical compound with formula ($C_7H_5O_2$). The stracture of this compound have two carbonyl groups. Due to its nucleophilic naturralists used as a reagent to analysis and determination of amino acids [(8-10)]. In chemistry (OPA) play abig role in the synthesis of hetrocyclic compounds by it reaction with primary amins [(11)]. Guguloth H. and et al. synthesied aseries of derivates by the condensation of (OPA) with primary amine derivates. The chemical compounds were tested by IR,^{13}C NMR, ^{1}HNMR, Mass and elemantal analysis. The biologycal activity have been tested against four types of bactrtia (Escherichia coli, Staphylococus aureus, Klebsiella pneumonia and Bacillus subtillus) and found they have antibactrial activity [(12)] . Abidentate Schiff base ligand synthesied by the reaction between (OPA) and glycel – glycin by Voguri H. and et al. followed preparation metal complexes [$M_2L(H_2O)_4]^{+2}$. The Schiff base ligand and its complexes have the octahydral shape that assisted to coordination with the metal ion Fe(II). All the synthesied compounds were tested by TGA analysis, ESR spectra, IR, mass spectra, and electronic spectroscopy. The biologycal activities of complexes were good against g- positive and gram- negetive [(13)]. Mishiyaso N. and et al. actored ortho- phthalaldehyde ortho protected tris hydroxyalkyl aminomethanes in the location of 1- propanethiol to endure of stable isoindols. The bulkiness of C_3symmetric primary amines derrived from tris hydroxymethyl aminomethan have purveied steric protection. The bulky group could be important for the stabilization of 1- alkylthio-2-alkyl-substituted isoindoles derived from ortho phthalaldehyde [(14)].

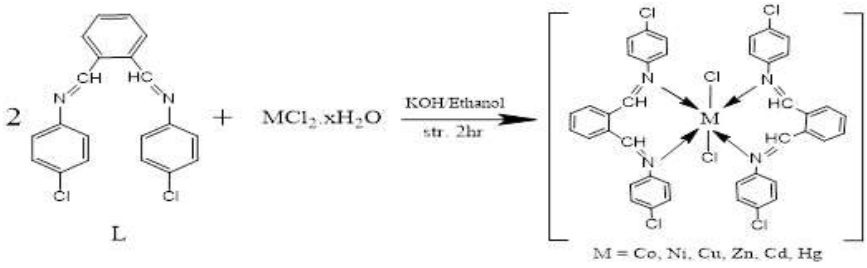
MATERIALS AND DEVICES

All chamicals have been bought from well known resources and they are of the highest purity; so,theydo not need to be further purified. Stuart Melting Point Kit is used to find the Melting points. Elemental micro analysis of the ligand is done by Euro (EA 3000) instrument. ^{1}H NMR spectra are obtained using Brucker DRX system (400 MHz). UV-Vis spectra are conducted don a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer in KBr discs on (4000-400) cm^{-1}range. The IR-spectra are verified by FTIR-8400SSpectrophotometer. The calculating of the complexes Metal contents (A.A.S) are conducted, using atomic absorption method by means of AA 620G Shimadzu spectrophotometer. The Chloride substances of compounds are specified by testing all complexes and decomposed with Nitric acid, and diluted with water. Magnetic measures results

are found out by using Bruker BM6 instrument at room temperature and the Faraday's method.

Synthesis of (1E,1'E)-1,1'-(1,2-phenylene)bis(N-(4-chlorophenyl) methanimine) (L):
A solution of o-phthalaldehyde(0.134g, 1 mol), melted in 5ml ethanol, and three drops of glacial acetic acid is mixed with a solution of 4-chloroaniline (0.254g,2mol) in 10 ml ethanol has beeninserted, and the product combination has been refluxed for 4h [10].By filteration, the resulted brown solid is composed,recrystallised from aceton absolute, and dried under m.p (179°C), yield84%Schem-1, fig. 1. The analytical and specteral methods are applied to verify the results.

Synthesis of the Mixed Ligand Complexes:
A stirred 1 mmol of metal chlorid in 10 ml ethanol;0.126g Mn(II)chloride, 0.237g Co(II) chlorid.$6H_2O$,0.237g Ni(II) chloride.$6H_2O$, 0.17Cu(II) chlorid.$2H_2O$,0.201g Cd(II) chlorid.H_2O, and 0.272 g Hg(II) chlorid, to which a solution of schiff base ligand (0.268g, 2mmol) in 5ml absolute ethanol,is added. The resultantmixture is stirred for sixty minutes and, then, is filtered and dried through anhydrous $CaCl_2$.The physical properties of schiff ligand and new compoundsare shown in table-1.



Scheme.1: The synthesis route of the ligand and their complexes

RESULTS AND DISCUSSION

In general, all the complexes are insoluble in water but soluble in DMSO and DMF. The compounds sensible features and CHN analysis are listed in table-1. The complexes is referred to as $[M(L)_2Cl_2]$ when M = metal (II) ions, (L=Schiff base ligand).

Table 1: The details of new Schiff ligand and their compounds

Complexes	code	M.wt	M.P°C	Theoretical (Calc.)				
				C	H	N	Cl	M
$C_{20}H_{14}N_2Cl_2$ Brown	L	353.25	176-179	67.9	3.77	7.88	19.97	-----
Ni $(L)_2Cl_2$ $C_{41}H_{31}NiN_4Cl_6$ Pail-brown	Lg1	851.12	240	57.86	3.64	6.58	24.96	6.65 (6.90)
$Cu(L)_2Cl_2$ $C_{40}H_{28}CuN_4Cl_6$ Brown	Lg2	840.95	250	57.34	3.71	6.70	25.32	7.25 (7.56)
Co $(L)_2Cl_2$ $C_{42}H_{34}CoN_4Cl_6$ Orange	Lg3	866.4	230	58.33	3.87	6.56	24.48	6.67 (6.80)
$Zn(L)_2Cl_2$ $C_{42}H_{34}ZnN_4Cl_6$ brown	Lg4	872.84	245	57.70	3.69	6.34	24.55	7.18 (7.49)
$Cd(L)_2Cl_2$ $C_{42}H_{33}CdN_4Cl_6$ Pail-brown	Lg5	918.86	250	54.67	3.45	6.36	23.23	11.98 (12.23)
Hg($L)_2Cl_2$ $C_{42}H_{34}HgN_4Cl_6$ Dark-brown	Lg6	1008.1	190-210	50.06	3.09	5.69	21.30	19.58 (19.9)

^{1}H-NMR Spectral: The ^{1}H-NMR spectrum of the (L) is recorded using DMSO-$d_6$at room temperature [15-17], as shown in table -2 figure-1. The singlet signal, which is revealed at (2.45

ppm), can be due to the solvent DMSO. The signals, which are appeared in the region (6.52-8.40 ppm), have been assigned to the protons of the aromatic rings of the free ligand.The two protons of azomethine group (HC=N) in the ligand show a single signal at (8.47 ppm) [18-20].

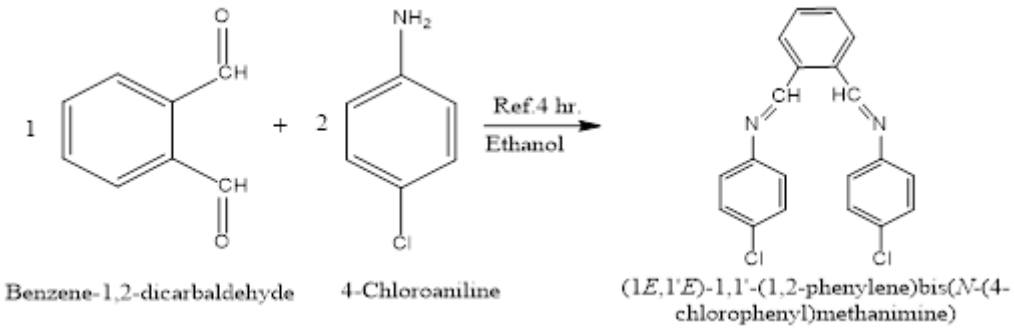


Table 2: 1H-NMR Spectral data for measured Land chemical shift in ppm

Ligand	Functional group	δ(ppm)
L	DMSO-d6	2.45
	Ar-H	6.52 – 8.40 (12H, m)
	N=C-H	8.47(2H, s)

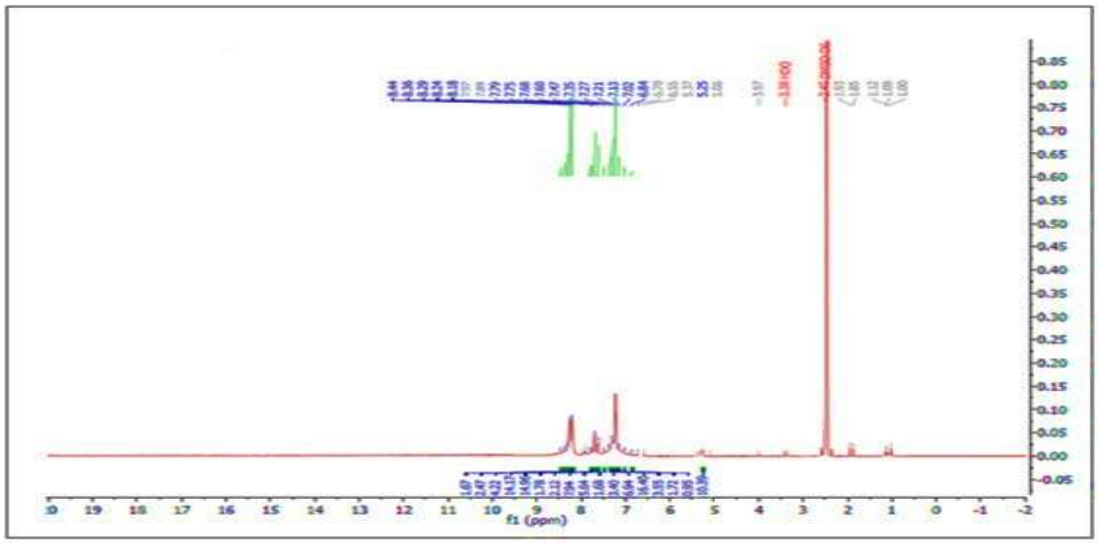


Fig.1: 1HNMR spectrum of (L)

Mass Spectrum:

Mass Spectrum of Schiff base ligand is carried out in order to determine its molecular weight and fragmentation pattern as explained in table – 3 fig. 2, which shows that the base peak m/z is 353.4. The first fragmentation at m/z = 282 duo to absence group $[C_3HCl]^+$. The peak at m/z = 245 is assigned to losing group $[C_3H2]^+$. The other peak at m/z = 205 is referred to group $[N=CH-C]^+$. The fragmentation at m/z = 178.1 is due to loosing group $[C_2H_2]^+$, while the peak at m/z = 77 is assigned to absence group $[C7H4N]^+$ [21-23].

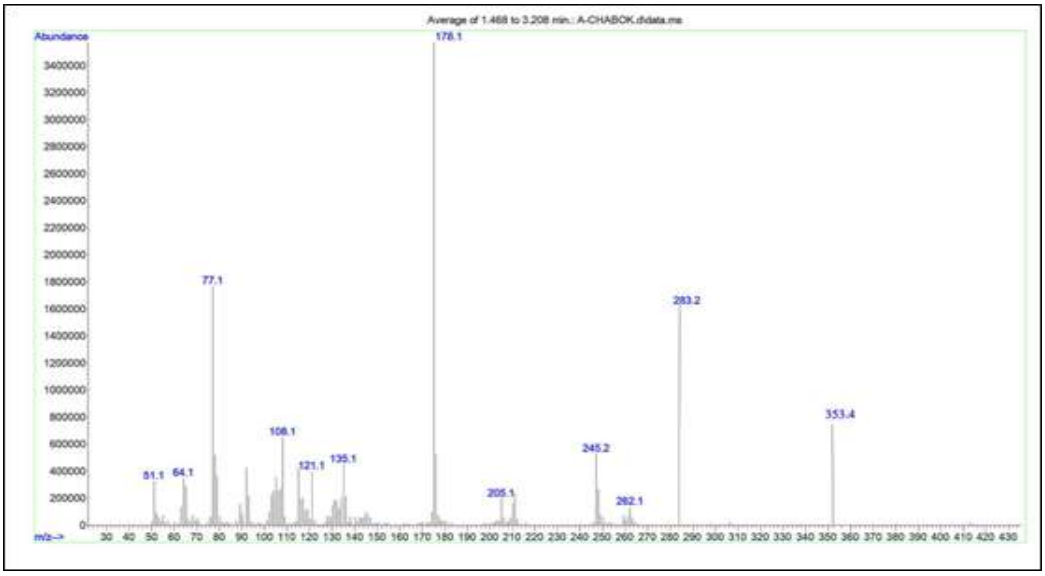


Fig.2: The fragmentation data for the (L)

FTIR Spectra

The FTIR spectra of the synthesized Schiff base ligand(L) and complexes, which are in KBr disc in range of (4000-200) cm^{-1},show that the weak absorption band at 3117 cm^{-1}refersto the (C-H) aromatic stretching vibration while the bands in the regions(3053-3142) cm^{-1} refer to υ(C-H) aromatic of complexes[24]. The medium band at 1625 cm^{-1} is assigned to the azomethine group (HC=N) stretching vibration of ligand, while the band at (1610-1664) cm^{-1}refer to (HC=N) of complexes[25].The (C=C) stretching vibration is allocated at 1567 cm^{-1} for ligand, while the bands at (1545-1569)$cm^{-1}$are assigned to the (C=C) stretching vibration of complexes [24] .The bands that show weak absorption in range (268-297)cm^{-1}refer to (C-Cl) stretching vibration[26]. The FTIR spectrum of all complexes show new bands in the regions (544-558) cm^{-1}which refer to υ(M-N) modewhile the bands (256 - 295) cm^{-1} refer to (M-Cl) stretching vibration[27]. Table -3 shown the FT-IR details of ligand and complexes.

Table 3: FTIR details of cm-1 free ligands and its compounds

Compound	υ(C-H) aromatic	υ(C=N)	υ(C=C)	υ(C-Cl)	υ(M-N)	υ(M-Cl)
L	3117	1625	1567	278	----	----
Lg1	3133 3062	1652	1557	254	553 546	256
Lg2	3131 3076	1644	1545	255	553	287
Lg3	3130 3075	1664	1553	289	561	284
Lg4	3120 2974	1610	1548	297	544	265
Lg5	3142 3053	1654	1583	273	584	283
Lg6	3118 3058	1644	1569	268	558	295

Electronic Spectra, Molar Conductivity, and Magnetic Moments

The UV-Vis. for ligand and its complexes were shown in table- 4. The three peaks for the ligand's spectrum at (257) nm assigns to ($\pi \rightarrow \pi^*$) electronic shift while the two peaks in (339-345) nm refer to ($n \rightarrow \pi^*$). The UV- Vis. spectrum of Lg_1exhibits five absorption peaks, the peaks at (268, 341) nm due to intra ligand in comparison with the spectrum of ligand. The peak at (386) nm refers to charge transfer while the two weak peaks at (740, 792) nm indicate to (d-d) electronic transition type ^4T_1g (F) $\rightarrow ^4A_2g$ (F) and ^4T_1g (F) $\rightarrow ^4T_2g$ (F) respectively. This improve that

there is an octahedral shape around Co (II) complex [28-29]. The two peaks of UV-Vis. spectrum for Lg_2 at (279,329) nm attributed to intra ligand and the peak at (362) nm attributed to charge transfer (C.T.), while the other weak peaks at (785, 840) nm refer to (d-d) electronic transitions types ^3A_2g (F) $\rightarrow ^3T_1g$ (F) and ^3A_2g (F) $\rightarrow ^3T_2g$ (F) respectively which support the octahedral structure around metal ion Ni (II) [30]. The UV-Vis. spectrum of Lg_3 shown three absorption peaks; the heights intensity at (361) nm due to charge transfer (C.T.), and the peak at (263) nm assigned to intra ligand, while the weak peak at (791) nm is due to $^2Eg \rightarrow ^2T_2g$. this coordination agree with the octahedral structure around the metal ion Cu (II) [31] .The UV-Vis spectra of Lg_4, Lg_5 and Lg_6 shows peaks with strong intensity at (266, 259 and 275) nm consecutively, and there refer to charge transfer (C.T.) which have diamagnetic formant depending on electronic arrangement. Theysupport that there is an octahedral structure around Zn (II), Cd(II) and Hg(II)[32- 33]. All the values of μe_{ff} (BM) for the synthesized complexes are listed in table-4- which refer that octahedral structure around the metal ions [34]. From noting the values molar conductivity in the table -5- finding all the complexes are non electrolytes.

Table-4: Spectral and magnetic moments (nm) of the complexes

Compounds	$\lambda_{max.}$	$\bar{\upsilon}$ cm^{-1}	$\epsilon_{max.}$ $mol^{-1}.L.cm^{-1}$	Assignments	Molar Cond.	μe_{ff} (BM)
L	257 339 354	38911 29499 28249	876 2010 1130	$\pi \rightarrow \pi^*$ n $\rightarrow \pi^*$ n $\rightarrow \pi^*$	---	---
Lg_1	268 341 386 740 792	37313 29326 25907 13514 12626	1261 1974 1643 85 28	Intra-ligand Intra-ligand Intra-ligand C.T $^6A_1g \rightarrow ^4T_2g(G)$	1.07	4.83
Lg_2	279 329 362 785 840	35842 30395 27624 12738 11905	1062 1234 1445 28 14	Intra-ligand Intra-ligand C.T. $^4T_1g(F) \rightarrow ^4A_2g(f)$ $^4T_1g(F) \rightarrow ^4T_2g(f)$	1.92	4.74
Lg_3	263 361 791	38023 27701 12642	1000 1017 16	Intra-ligand Intra-ligand C.T. $^3A_2g(F) \rightarrow ^3T_1g(F)$ $^3A_2g(F) \rightarrow ^3T_2g(F)$	1.56	4.35
Lg_4	266 363	37594 27545	1011 2331	Intra-ligand C.T. $^2Eg \rightarrow ^2T_2g$	0.87	Dia.
Lg_5	259 379	38610 26385	1120 2170	Intra ligand C.T.	0.81	Dia.
Lg_6	275 377	36364 29240	1150 2052	Intra ligand C.T.	1.67	Dia

Biological Activity

The Schiff base ligand and its complexes are tested with four bacteria; psuedomonas aruginosa, Escharia coli, Staphylococcus aureus and Streptococcus pyogenes,using disc diffusion technique[19-20].The chemical solutions of the biological studyare prepared by using the solvent of dimethyl sulfoxide (DMSO), and they are provided as a single concentration of 1×10^{-3}M. The dishes are incubated at room temperature for 24 h.The criterion applied for measuring the intensity of the synthetic chemical compound effect on the outgrowth of cultivated specific bacteria strainsare the inhibition zones(IZ) in mm, which are formed after 24h.The synthesized shiff base ligand and (CoII) complex do not reveal any activity toward bactria type (G+) while they show good activity toward bactria type (G-). The two complexes (NiII and CuII) show good activity toward all types of bacteria gram(+) and gram (-). The complex of (Zn II) shows a very good activity toward all types of baceria except Streptococcus pyogenes. The high activity toward bacterias is shwon by the complexes of (Hg II , Cd II). (The detalais are shown in table 5.

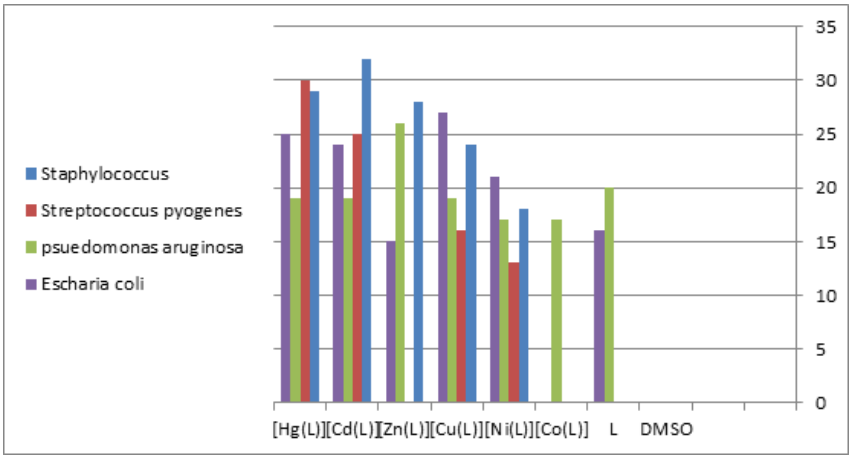


Fig.3: The (ZI) mm of (L) and its Complexes

Table 5: biological activity of the ligand and complexe

Compound	Staphylococcus aureus	Streptococcus pyogenes	psuedomonas aruginosa	Escharia coli
L	---	---	20	16
[Co(L)]	---	---	17	---
[Ni(L)]	18	13	17	21
[Cu(L)]	24	16	19	27
[Zn(L)]	28	---	26	15
[Cd(L)]	32	25	19	24
[Hg(L)]	29	30	19	25

CONCLUSION

It has been concluded from the synthesis of the results and the characterizations of the new Schiff base, which is derived from o-phathalaldehyde with 4-chloro aniline that the formed Ligand is coordinated with metal ions through the N as a donor atom. It is also revealed from the analysis of he results of the electron spectra and the magnetic susceptibility of all complexes that have octahedral geometry. The antibacterial activities of the synthesized complexes shown that Lg_5, Lg_4 and Lg_6 have good activity toward three types of bacteria while Lg_2 and Lg_3 shown activity against all types of bacteria. The Lg_1 and ligand shown activity against two types and not shown any activity against the other.

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