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PREPARATION, CHARACTERIZATION AND STUDY OF THE BIOLOGICAL ACTIVITY OF NEW NO_2, NOVEL N_2O_2 LIGANDS AND THEIR COMPLEXES WITH [Co (II), Cu (II), Ni (II), Mn (II) AND Hg (II)] IONS

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ABSTRACT

A new two Schiff bases derivatives was synthesized and characterized with studying their biological activity and employed Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Mercury(II) complexes: 2-((Z)-4-((Z)-2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino) benzoic acid and (E)-4-(2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one. The first ligand were obtained through are action of Benzoin and 4-Aminoantipyrine while the second result from the condensation of the first ligand with 2-aminobenzoic acid. Ten new coordination compounds were synthesized and structurally characterized: $[Co(L_1)(Cl)]$, $[Cu(L_1)(Cl)]$ $[Ni(L_1)(Cl)]$, $[Mn(L_1)(Cl)]$, $[Hg(L_1)(Cl)]$, $[Co(L_2)]$, $[Ni(L_2)]$, $[Cu(L_2)]$, $[Mn(L_2)]$ and $[Hg\ (L_2)]$. All of the suggested chemical structures of the prepared ligands and metal complexes are confirmed by using FT-IR, UV, ^1H & ^{13}C-NMR spectra. Most of the prepared compounds show antibacterial activity to *Staphylococcus aureus*, *Escherichia coli*, *Bacillussubtilis* and *Pseudomonasaer*oginosa.

Key words: Characterization, Schiff bases, 2-Aminobenzoic acid, 4-Aminoantipyrine, Benzoin and biological activity.

INTRODUCTION

Schiff bases or imines are compounds formed by condensation of an active carbonyl group with primary amine[1-5]. These bases containing an amino group (R-C=N) which give the biological importance of these compounds[6]. Schiff's bases have been used extensively as ligands in the field of coordination chemistry. Furthermore the Schiff bases are very important tools for inorganic chemists as these are widely used to design molecular ferromagnetism, in catalysis, in biological modeling applications, as liquid crystals and as heterogeneous catalysts[7-10]. Schiff bases have been widely used as ligands because of high stability in the coordination compounds and their good solubility in common solvents, they are regarded as privileged ligands[11-19]. Tridentate and tetra ligands containing imine groups have also been used as the modulators of structural and electronic properties of transition metal centers[20]. The π-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well[21,22]. Thermo chemical properties of Schiff bases have attracted much researcher attention in view of their ability to coordinate metal ions[23-26],

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acting as tri and tetra dentate ligands in metal chelates involving a NO_2 and N_2O_2 Schiff bases donor atom sets. Schiff bases composed of NO_2 and N_2O_2 donor atoms are important chelating ligands for designing supramolecular synthase[27-29], medicinal and catalytically useful metal complexes[30-32]. Schiff base and their metal complexes are very popular due to their diverse chelating ability. They play an important role in both synthetic and structural research because of their preparation accessibility and structural diversity[33-34].

Hence, the aim of this work is to describe the preparation, characterization and biological evaluation of sensitive transition metal complexes with new two ligands type of triandtetradentate Schiff bases (Fig. 1 and 2). Metal complexes with two new ligands may be used as precursors for synthesis of new compounds.

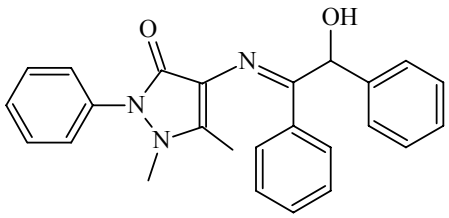


Fig. 1: (E)-4-(2-hydroxy-1, 2-diphenylethylideneamino)-1, 5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one

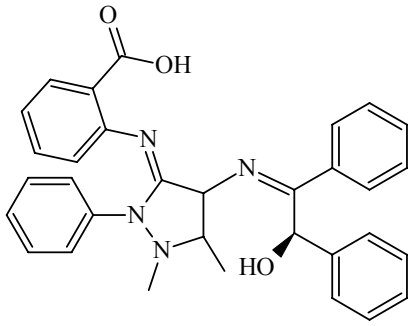


Fig. 2: 2-((Z)-4-((Z)-2-hydroxy-1, 2-diphenylethylideneamino)-1, 5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino) benzoic acid

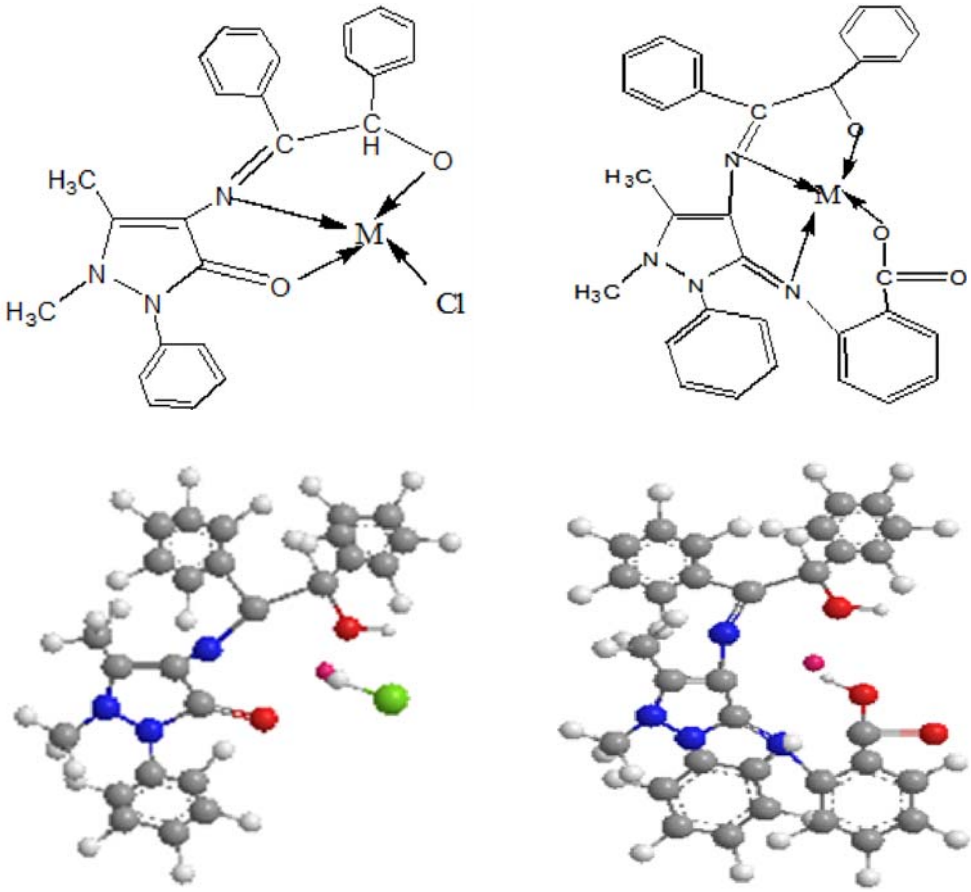
EXPERIMENTAL

Materials and methods

Materials: All chemicals benzoin, 4-aminoantipyrine, 4-aminobenzoic acid, and various metal (II) chlorides used were obtained from Merck products and used as received. The Methanol, Ethanol, DMSO, DMF and another solvents used in this study were of HPLC grade and purchased from Fisher Scientific Pittsburgh, PA Analytical grade chemicals were used throughout the study, unless otherwise stated.

Methods: Micro analytical data, ^{1}H- & ^{13}C-NMR spectra of the compounds were recorded at Brukerspecrospin ultra shield magnets 300 MHz instrument using tetramethylsilane (TMS) as an internal standard and DMSO-d_6 as a solvent in Sharif University of technology in Iran. Products were examined by FT-IR spectra were recorded on SHIMADZU FTIR–8400 Fourier Transform Infrared spectrophotometer as KBr disc. The chloride content for complexes were determined using potentiometric titration method on (686-Titro Processor- 665 Dosim A-Metrohm/Swiss. Magnetic susceptibility measurements were obtained at room temperature on the solid state applying Faraday's Method using Bruker BM6 instrumentat 298˚K. Micro analysis (C, H, and N%) of the synthesized compounds was carried out in the central service laboratory, College of Education for Pure Science, Ibn Al-Haitham using a CHN Analyzer on Perkin Elmer

2400 series II. Melting points were determined by using (start melting point Apparatus) type Digimelt (MSRS). The proposed molecular structure of the compounds were drawing by using Chem. Office Prog. 3DX (2006).



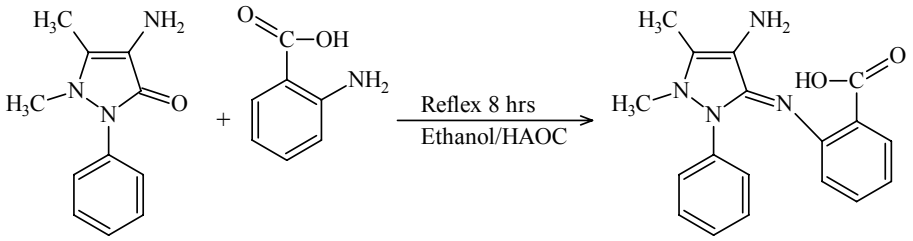
(a) **(b)**

Fig. 3: Molecular structure of (a)(E)-4-(2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one of the metal chelate complexes and (b) 2-((Z)-4-((Z)-2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)benzoic acid of the metal chelate complexes

Synthesis of Sciff bases ligands (L_1 & L_2)

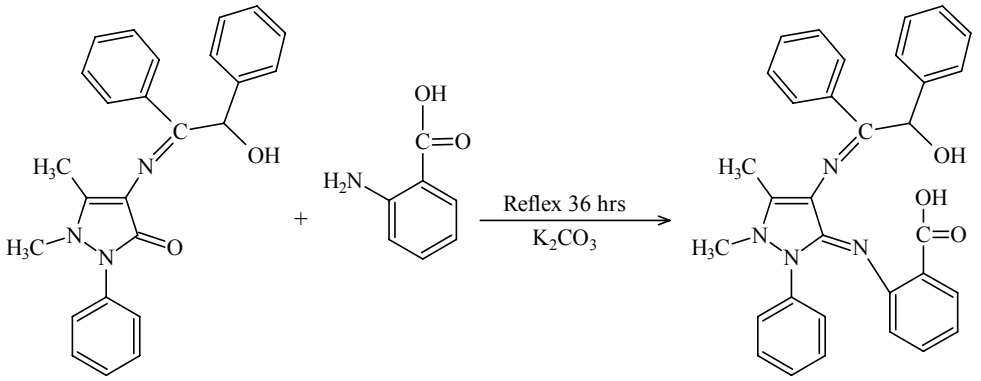
An ethanolic solution of (40 mL) 4-aminoantipyrine (4.06 g, 0.025 mmole) was added to an ethanolic solution of benzoin (3.14 g, 0.01 mmole) and three drops from glacial acetic acid. The resultant mixture was refluxed for *ca*. 8 hr. The solid product formed was filtered and recrystallized from ethanol[1,2].

An ethanolic solution of 2-((Z)-4-((Z)-2-hydroxy-1, 2-diphenylethylideneamino)-1, 5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino) benzoic acid (3.51 g, 0.01 mmole) was added to an ethanolic solution of 2-aminobenzoic acid (1.37 g, 0.01 mmole), and the resultant mixture was refluxed for *ca*. 36 hr after the addition of anhydrous potassium carbonate. The potassium carbonate was filtered off from the reaction mixture and the solvent was evaporated[3,4]. The yellow solid separated was filtered and recrystallized from ethanol as follows in (Scheme 1 and 2). The characteristic physical properties of two compounds are shown in Table 1.



(Z)-2-(4-Amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-yliden earnino)benzoix acid

Scheme 1: Synthesis route for the preparation of ligand (L_1)



2-((Z)-4-((Z)-2-Hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-yliden earnino)benzoix acid

Scheme 2: Synthesis route for the preparation of ligand (L_2)

Table 1: The physical properties, elemental analysis and molar conductance data of the Schiff base ligands and their complexes

Compds.	Formula	Molecular weight	Colour	Yeild %	M.P. (°C)	% Elemental analysis Found (Calculated)				
						C	H	N	M	Cl
L_1	$C_{25}H_{23}N_3O_2$	396.46	Yellow	78	175	74.17 (74.54)	5.62 (5.73)	9.93 (10.57)	-	-
[Co(L_1)Cl]	$C_{25}H_{22}ClCoN_3O_2$	490.85	Blue	81	254	60.77 (61.17)	4.46 (4.52)	8.59 (8.56)	11.85 (12.01)	6.67 (7.22)
[Ni(L_1)Cl]	$C_{25}H_{22}ClNiN_3O_2$	490.61	Green	66	200	60.80 (61.20)	4.12 (4.52)	8.09 (8.56)	11.43 (11.96)	6.79 (7.23)
[Cu(L_1)Cl]	$C_{25}H_{22}ClCuN_3O_2$	495.46	Brown	72	231	60.15 (60.60)	4.06 (4.48)	8.54 (8.48)	12.27 (12.83)	6.88 (7.16)
[Mn(L_1)Cl]	$C_{25}H_{22}ClMnN_3O_2$	486.85	White	89	212	60.34 (61.68)	4.17 (4.55)	8.68 (8.63)	10.65 (11.28)	6.56 (7.28)
Hg(L_1)Cl]	$C_{25}H_{22}ClHgN_3O_2$	632.50	Clouress	90	241	47.10 (47.47)	3.00 (3.51)	6.69 (6.64)	31.25 (31.71)	5.19 (5.61)
L_2	$C_{32}H_{28}N_4O_3$	516.22	Orange	75		73.73 (74.40)	5.35 (5.46)	10.41 (10.85)	-	-

Cont…

Compds.	Formula	Molecular weight	Colour	Yeild %	M.P. (°C)	% Elemental analysis Found (Calculated)				
						C	H	N	M	Cl
[Co(L_2)]	$C_{64}H_{54}CoN_8O_6$		Pink	76	200	70.11 (70.52)	4.56 (4.99)	9.79 (10.28)	5.63 (5.41)	-
[Ni(L_2)]	$C_{64}H_{54}Ni\ N_8O_6$		Green	81	210	70.28 (70.53)	4.70 (4.99)	9.83 (10.28)	5.59 (5.39)	-
[Cu(L_2)]	$C_{64}H_{54}Cu\ N_8O_6$		Black	70	217	69.86 (70.22)	4.64 (4.82)	9.35 (9.88)	5.27 (5.32)	-
[Mn(L_2)]	$C_{64}H_{54}MnN_8O_6$		White	74	234	70.09 (70.77)	4.65 (5.01)	9.92 (10.32)	5.61 (5.06)	-
Hg(L_2)]	$C_{64}H_{54}HgN_8O_6$		Clouress	66	213	61.76 (62.41)	4.33 (4.42)	8.97 (9.10)	15.89 (16.28)	

Synthesis of metal (II) complexes

A solution of metal (II) chlorides in ethanol (2 mmole) was stirred with ethanolic solution of the Schiff base (2 mmole), for ca. 2 h on a magnetic stirrer at 50°C. The solid complex precipitated was filtered off and washed thoroughly with ethanol and dried in vacuous, recrystallized from a hot of (10 mL) ethanol, a coloured precipitate was formed[5,6]. The physical properties of complexes were listed in Table 1.

Table 2: Infrared spectral data (wave number $\bar{v}$) cm^{-1} for the ligands [(L_1), (L_2)] precursors and their complexes

Compd.	υ(OH)	υ(OH)	υ(C-H) aromatic	υ(C-H) aliphatic	υ(HC=N) imine	υ(C=O) Ketone	υ(C=O) carboxyl	υ(C=O) carboxyl	υ(C=C)	υ(C-O)	M–N M–O
L_1	3466	3466	3061	2920	1660	1739	-	1739	1591	1170	-
[Co(L_1)Cl]	-	-	3078	2945	1647	1707	-	1707	1566	1217	573 421
[Ni(L_1)Cl]	-	-	3041	2978	1641	1712	-	1712	1557	1221	586 427
[Cu(L_1)Cl]	-	-	3025	2955	1639	1709	-	1709	1560	1207	569 428
[Mn(L_1)Cl]	-	-	3037	2917	1445	1714	-	1714	1558	1228	566 420
[Hg(L_1)Cl]	-	-	3023	2928	1636	1710	-	1710	1560	1226	570 431
L_2	3406 2889	3406	3059	2956	1662	-	-	-	1593	1176	-
[Co(L_2)$_2$]	-	3390	3082	2910	1639 1608	-	as1568 s 1396	-	1558	1196	555 489
[Cu(L_2)$_2$]	-	3394	3066	2918	1646 1610	-	as 1539 s 1327	-	1550	1207	590 489
[Ni(L_2)$_2$]	-	3371	3052	2904	1650 1612	-	as 1546 s 1408	-	1562	1201	586 470

Cont…

Compd.	υ(OH)	υ(OH)	υ(C-H) aromatic	υ(C-H) aliphatic	υ(HC=N) imine	υ(C=O) Ketone	υ(C=O) carboxyl	υ(C=O) carboxyl	υ(C=C)	υ(C-O)	M–N M–O
$[Mn(L_2)_2]$	-	3364	3076	2915	1645 1607	-	as 1548 s 1327	-	1548	1205	578 447
$[Hg(L_2)_2]$	-	3367	3061	2920	1651 1600	-	as 1562 s 1396	-	1558	1200	559 470

RESULTS AND DISCUSSION

The Schiff base ligands (L_1 and L_2) are yellow and orange crystals, but the prepared complexes of these ligands vary in colour depending of metal ion. All the prepared compounds are stable at room temperature[6]. They are in solublein water but soluble in MeCN, DMF and DMSO. The ligands are interaction with Cu(II), Co(II), Ni(II), Mn(II) and Hg(II) chlorides, yields of complexes corresponding to the general formulas $[M(L_1)Cl]$ and $[M(L_2)]$ where M = Cu(II), Co(II), Ni(II), Mn(II) and Hg(II); L_1 = $C_{25}H_{23}N_3O_2$ & L_2 = $C_{32}H_{28}N_4O_3$. These stoichiometric assignment were supported by the microanalytical data. The low molar conductance values of the complexes (7-18 ohm cm^2 mol^{-1}) support their neutral nature as in Table 3)[7, 8].

Table 3: Electronic spectral data of the ligands and their metal complexes

Compounds	μ_{eff}	Mol. Cond. ohm.$cm^2$$mole^{-1}$	Absorption bond (nm, cm^{-1})	Transition	
L_1	-	-	343 nm (29154 cm^{-1}) 289 nm (34602 cm^{-1})	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-
$[Co(L_1)Cl]$	4.21	7	617 nm (16207 cm^{-1})	$^4A_2 \rightarrow {}^4T_{1(P)}$	Tetrahedral
$[Ni(L_1)Cl]$	3.8	9	419 nm (23866 cm^{-1})	$^3T_2 \rightarrow {}^3T_1$	Tetrahedral
$[Cu(L_1)Cl]$	2.5	12	411 nm (24330 cm^{-1})	$^2E \rightarrow {}^2B_2$	Tetrahedral
$[Mn(L_1)Cl]$	5.57	15	423 nm (23640 cm^{-1}) 562 nm (17793 cm^{-1})	$^6A_1 \rightarrow {}^4A_{1(G)}$ $^6A_1 \rightarrow {}^4E_{(G)}$	Tetrahedral
$[Hg(L_1)Cl]$	Dia.	10	367 nm (27247 cm^{-1})	C.T	Square planar
L_2	-	-	309 nm (32362 cm^{-1}) 275 nm (36363 cm^{-1})	$n \rightarrow \pi^*$ $\pi \rightarrow \pi$	-
$[Co(L_2)]$	4.34	16	804 nm (12437 cm^{-1}) 487 nm (20533 cm^{-1})	$^4A_2 \rightarrow {}^4T_{1(F)}$ $^4A_2 \rightarrow {}^4T_{1(P)}$	Tetrahedral
$[Cu(L_2)]$	1.90	18	643 nm (15552 cm^{-1}) 522 nm (19157 cm^{-1})	$^2B_1g \rightarrow {}^1B_1g$ $^1A_1g_{(F)} \rightarrow {}^2Eg$	Square planar
$[Ni(L_2)]$	Dia.	13	806 nm (12406 cm^{-1}) 421 nm (23752 cm^{-1})	$^1A_1g_{(F)} \rightarrow {}^2Eg$ $^1A_1g \rightarrow {}^1B_2g$	Square planar
$[Mn(L_2)]$	5.72	8	407 nm (24570 cm^{-1}) 546 nm(18315cm^{-1})	$^6A_1 \rightarrow {}^4A_{1(G)}$ $^6A_1 \rightarrow {}^4E_{(G)}$	Tetrahedral
$[Hg(L_2)]$	Dia.	17	330nm (30303cm^{-1})	C.T	Square planar

NMR Spectrum

The ^{1}H NMR spectrum of the first new Schiff base L_1 in DMSO-d_6 solution showed the following signals in δ ppm at: (2.072, singlet, 1H for -OH Hydroxyl group of benzoin); (2.377, singlet, 3H for = C-CH_3); (2.479, singlet, 6H for DMSO protons); (3.385, singlet, 3H for = N-CH_3 group of antipyrine compound); (5.17, singlet, 1H, -CH-OH group of benzoin compound); and the rang at (6.540-8.126) for 3 benzene ring protons[9].

The ^{1}H NMR spectrum of the second new Schiff base L_2 in DMSO-$d_6$solution showed the following signals in δ ppm at: (2.072, singlet, 1H for -OH hydroxyl group of benzoin); (2.377, singlet, 3H for =C-CH_3); (2.479, singlet, 6H for DMSO protons); (3.385, singlet, 3H for = N-CH_3 group of benzoin compound); (5.17 single, 1H -CH-OH group of benzoin compound); the rang at (6.540-8.126) for 4 benzene ring protons); and (13.36, single, 1H for -OH carboxyl group of 2-aminobenzoic acid)[10].

The ^{13}C NMR spectrum of L1 in DMSO-d6 solution showed the signals at: (14.10 for = C-CH_3 group); (35.75 for N-CH_3 group); (40.80 for DMSO); (80.05 attributed to -C-OH moiety); (107.43 for = C-N); (122.70~149.88 to 3 benzene rings. The peak observed at 159.61 for C=O carbonyl group of antipyrine compound; and the signal at 165.19 for the C=N imine group[11].

The ^{13}C NMR spectrum of L_2 in DMSO-d_6 solution shows the signals at: (14.10 for =C-CH_3 group); (35.75 for N-CH_3 group); (40.80 for DMSO); (80.05 attributed to -C-OH moity); (107.43 for = C-N); (122.70~149.88) to 4 benzene rings. The peak observed at 159.61 for C=O carbonyl group of antipyrine compound; and the signal at 165.19 for the C=N imine group. The peaks observed at 159.19 and 165.19 are attributable to the two C=N imine groups, respectively. The peak observed at 165.19 is due to the acidic CO-OH group present in the 2-aminobenzoic acid[12].

Infrared spectral analysis

Infrared spectra of metal complexes of the Schiff base ligand were compared with that of the Schiff base in order to determine the coordination sites that may involve in chelation. These FT-IR data of the compounds were summarized in Table 1. The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom[13]. The O-H stretching frequency of the ligand (L_1) exhibits broad weak intensity band in the 3000-3500 cm^{-1} range, which is assigned to the intra molecular hydrogen bond O-H...N=C. This band disappeared in the spectra of the complexes. A strong sharp absorption band around 1660 cm^{-1} in the spectrum of the Schiff base ligand can be assigned to the C=N stretching. In all the complexes, this band is shifted to lower frequencies in the range (1636-1647 cm^{-1}) upon complexation with the metal, which can be attributed to the coordination of the imine nitrogen to the metal center[15].

However, strong band at 1739 cm^{-1} in the spectrum of the free ligand, which was attributed to the C=O but shifted towards lower frequencies at range (1707-1714 cm^{-1}) also indicated the coordination of oxygen atom of these carbonyl group[17]. The frequency of the alcoholic oxygen (C-O) of the free ligand at 1170 cm^{-1} was shifted to lower frequency ($\Delta\upsilon$ = 15-28 cm^{-1}) in the complexes, suggesting the participation of alcoholic group(C–O) inchelation[18]. The new bands between (569-585 cm^{-1}) and (420-431 cm^{-1}) were assigned to stretching frequencies of υ(M-O) and υ(M-N), respectively[19,20]. Therefore, from the IR spectra, it is concluded that (L_1) behaves as a tridentate ligand with ONO donor sites coordinating to the metal ions via the azomethine N, carbonyl Oatomand deprotonated alcohol O atom.

The FT-IR spectrum of the ligand (L_2) showed the peak at (3406 cm^{-1}) attributed to O-H alcoholic group, (3388-2544 cm^{-1}) due to intramolecular hydrogen bonded -OH alcohol groups of alcohol and carboxylic acid[18]. This bands were absent in the spectra of complexes indicating the dissociation indicating the dissociation of the carboxylic proton on complexation and involvement of alcohol anionic oxygen in coordination[22]. IR spectra of ligand (L_2) showed two peaks at (1662, 1620 cm^{-1}) υ(C=N) and absence of C=O peak at around (1707-1739 cm^{-1}) indicates the Schiff base (L_2) formation, which were shifted to lower frequencies at (1651-1639) cm^{-1} and (1610-1636) cm^{-1} in the spectrum of the complex, showing the participation of C=N nitrogen in the coordination to the metal ion[23]. The ligand acts as a tetra dentate chelating agent, bonded to the metal ion via the two nitrogen atoms of (–C=N) azomethine group, oxygen atom of (COOH) carboxylate group and oxygen atom of C-OH alcohol for the Schiff base. Moreover, the strong band at 1176 cm^{-1} due to (C-O) alcohol in the ligand was shifted to the 1130-1138 cm^{-1} in the spectra of complexes. Further, the spectrum showed bands at (1539-1568) cm^{-1} and (1408-1327) cm^{-1}, which assigned to $\upsilon_{asym}(COO^-)$ and $\upsilon_{sym}(COO^-)$, respectively in the free ligand spectrum, was shifted to lower frequency and appeared at (1510) cm^{-1} and (1317) cm^{-1}.[23] The alcoholic C-O stretching vibration that appeared at (1176 cm^{-1}) in Schiff base shifted towards higher frequencies (20-31) cm^{-1} in the complexes. This shift confirms the participation of oxygen in the C-O-M bond. Finally, the appearance of two non-ligand bands in the two ranges (555-590) cm^{-1} and (447-489) cm^{-1} in all the complexes could be assigned to the stretching frequencies of υ(M-O) and υ(M-N), respectively, which further confirm that the ligand is tetra dentate in nature[24].y. Therefore, from the IR spectra, it is concluded that H2L behaves as a tetra dentate ligand with ONNO donor sites coordinating to the metal ions via the azomethine N and deprotonated alcoholic O atoms

Electronic spectra and magnetic moments

Within the UV spectrum of the ligands (L_1 and L_2), we observed the existence of 2 absorption bands assigned to the transitionsn → π* and π → π* at 343 nm (29154 cm^{-1}) and 289 nm (34602 cm^{-1}) for L_1 and 309 nm (32362 cm^{-1}) and 275 nm (36363 cm^{-1}) for L_2, respectively. These transitions were also in the spectra of the complexes, but they shifted to lower frequencies[25].

The electronic spectrum of data of the metal complexes in DMSO solution are given in Table 4. The nature of the ligand field around the metal ion has been deduced from the electronic spectra.

In the electronic spectrum of cobalt(II) complex of L_1 a single broad band at 617 nm (16207 cm^{-1}) has been observed, which is attributed to 4A2 → 4T1(P) transition[16]. This confirms the presence of tetrahedral geometry for cobalt complex. While the Electronic spectrum of cobalt (II) complex of L_2 shows two peaks at 804 nm (12437 cm^{-1}) and 487 nm (20533 cm^{-1}) are assigned for the 4A2 → 4T1(F) and 4A2 → 4T1(P) transitions[26]. This confirms the presence of tetrahedral geometry for cobalt complex.

Nickel (II) complex of L_1 has a (d8) configuration giving peak, found at 419 nm (23866 cm^{-1}) is assigned 3T2 → 3T2 excitation. The magnetic moment is 3.8 B. M. Thus, the tetrahedral geometry has been suggested for the nickel complex. While the electronic spectrum of Nickel (II) complex of L_2 shows two peaks at 421 nm (23752 cm^{-1}) and 806 nm (12406 cm^{-1}) are assigned for the 1A1g(F) → 2Eg and 1A1g → 1B2g transitions[27], respectively. It is a diamagnetic complex. Therefore, square planar geometry has been assigned for this complex.

The electronic spectrum of copper(II) complex of L_1 showed one high intense absorption peak at 411 nm (24330 cm^{-1}), which has been assigned to 2E → 2B2 transition. Its magnetic moment is 2.5 B.M. A tetrahedral geometry has been assigned for this Cu(II) complex[28]. Also the electronic spectrum of copper(II) complex of L_2 showed two bonds of appreciable intensity at 643 nm (15552 cm^{-1}) and 522 nm (19157 cm^{-1}),

which have tentatively been assigned to $^2B_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g}(F) \rightarrow {}^2Eg$ transitions, respectively. The magnetic moment is 1.90 B.M. Thus the square planar geometry has been assigned for this complex.

The absorption spectrum of manganese(II) complex of L_1 exhibited two bonds at 423 nm (23640 cm^{-1}) and 562 nm (17793 cm^{-1}), which are assignable to 6A1→ 4A1(G) and 6A1→ 4E (G) transitions respectively[29]. It is magnetic moment is 5.57 B.M. Therefore, tetrahedral geometry has been assigned for this complex. While the absorption spectrum of manganese (II) complex of L_2 showed two bonds at 407 nm (24570 cm^{-1}) and 546 nm (18315 cm^{-1}), which have been assigned to 6A1 → 4A1 (G) and 6A1 → 4E (G) transitions, respectively. The magnetic moment is 5.72 B.M. Thus the tetrahedral geometry has been assigned for this complex[30].

The complex mercury (II) of L_1 and L_2 is diamagnetic giving peaks, found in L_1 at 367 nm (27247 cm^{-1}) and found at 330 nm (30303 cm^{-1}) in L_2 were assigned to charge transfertransitions. The absence of absorption peaks in the visible region indicated no (d-d) electronic transition happened; this a good result for square planar[31].

Biological activity

The antibacterial activity of the synthesized ligands (L_1), (L_2) andtheir complexes, were tested utilizing the agar diffusion technique[32]. The organism tested was *Staphylococcus aureus*, *Escherichia coli*, *Bacillus* and *Pseudomonas.* The agar media were inoculated with test organisms and a solution of the tested compound 100 μg/mL) was placed separately in cups (6 mm diameter) in the agar medium. The inhibition zones were measured after 24 hrs incubation. Separate studies were carried out with the solution alone of DMSO and the showed no activity against any bacterial strains[33-35]. The results of these studies revealed that the ligands and metals complexes showed an effective in the inhibition of all type bacterial. Biological activity of the previous compounds in inhibition of bacterial growth could be attributed to one of the following mechanisms, the first mechanism is by the inhibition of the bacterial cell wall synthesis by bounding to the precursor of the cell wall, and second mechanism revealed that some antibodies have similar stereo structure to substrate. All standards also screened under the similar condition for comparison. Results of all given activities of above compounds were given in (Tables 4 (a, b).

Table 4(a): Diameter of zone of inhibition (mm) of L_1

Comp.	L_1	[Co(L_1)Cl]	[Ni(L_1)Cl]	[Cu(L_1)Cl]	[Mn(L_1)Cl]	[Hg(L_1)Cl]
Escherichia Coli	10	9	12	11	18	17
Staphylococcus aureus	8	12	10	9	8	13
Bacllus	12	15	17	14	15	19
pseudmonas	7	8	11	10	14	12

Table 4 (b): Diameter of zone of inhibition (mm) of L_2

Comp.	L_2	[Co(L_2)]	[Ni(L_2)]	[Cu(L_2)]	[Mn(L_2)]	[Hg(L_2)]
Escherichia Coli	6	9	10	8	14	16
Staphylococcus aureus	5	10	9	12	15	11
Bacllus	4	6	8	4	10	13
pseudmonas	3	7	5	9	8	11

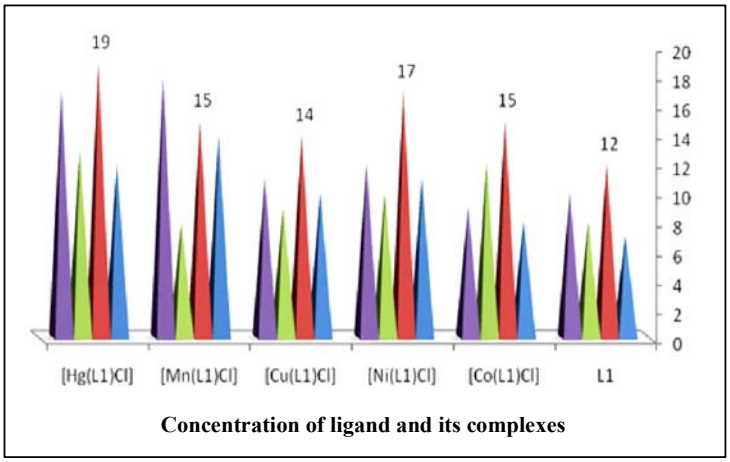


Fig. 4: Difference between the antimicrobial activity of ligand (L_1) & metal complexes

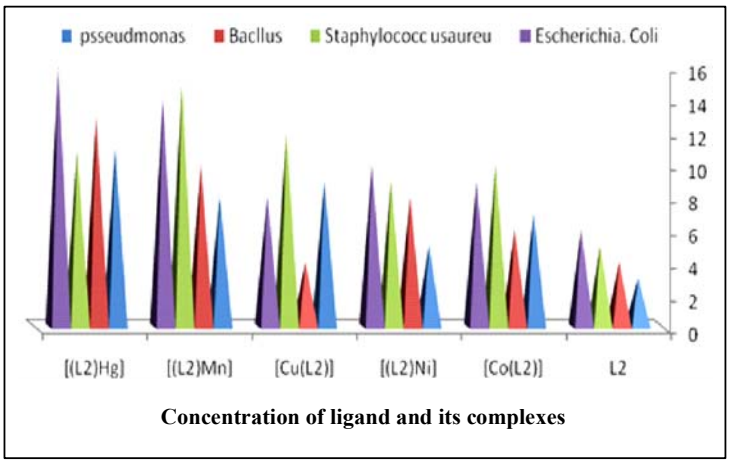


Fig. 5: Difference between the antimicrobial activity of ligand (L_2) & metal complexes

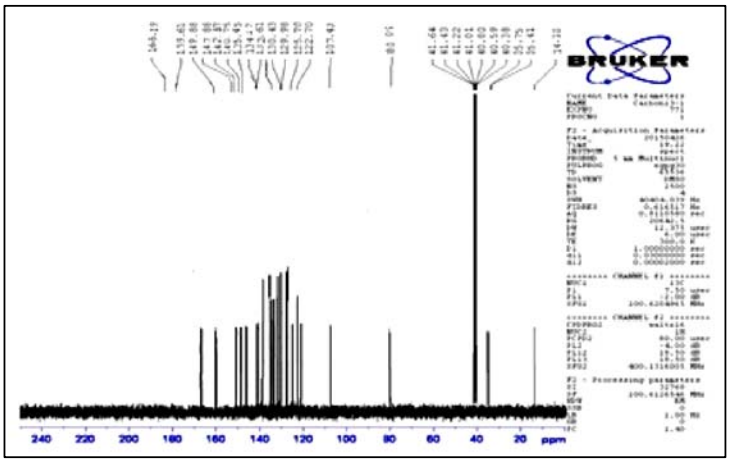


Fig. 6: ^{13}C- NMR of Ligand (L_1)

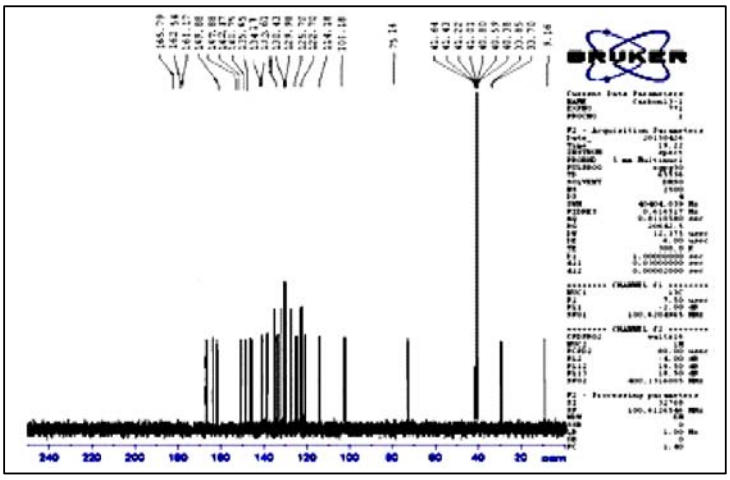


Fig. 7: ^{13}C- NMR of Ligand (L_2)

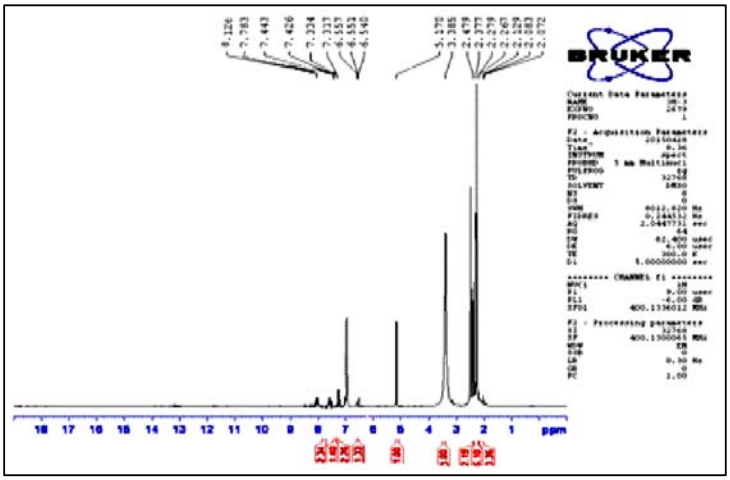


Fig. 8: ^{1}H- NMR of Ligand (L_1)

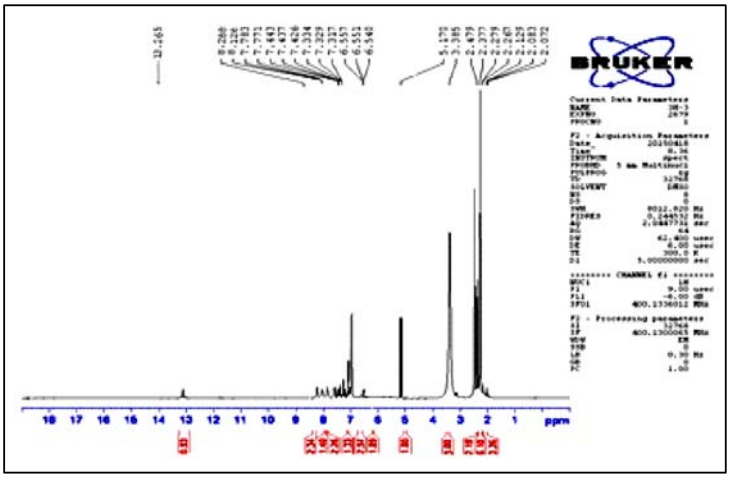


Fig. 9: ^{1}H- NMR of Ligand (L_2)

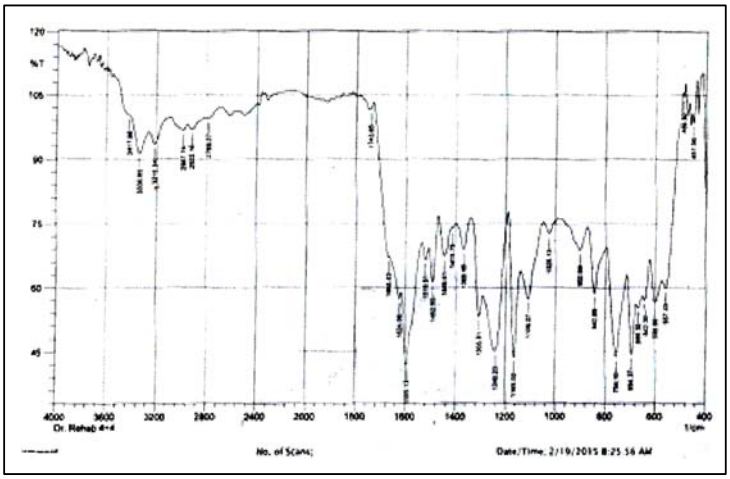


Fig. 10: IR spectrum of ligand (L_1)

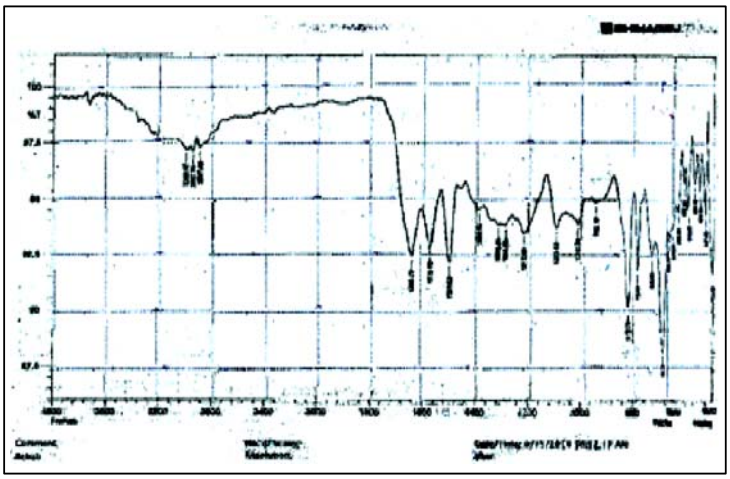


Fig. 11: IR spectrum of ligand (L_2)

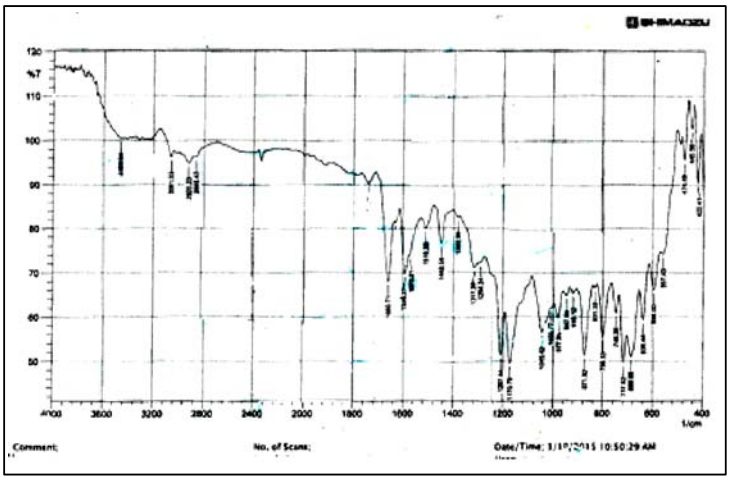


Fig. 12: IR of Complex [Ni (L_1)Cl]

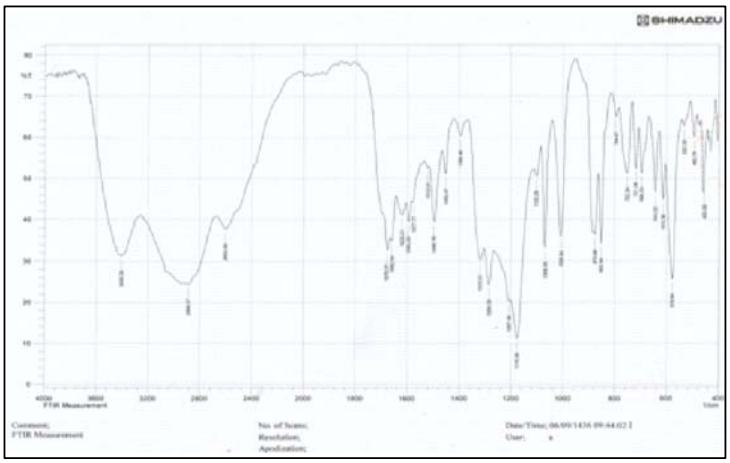


Fig. 13 IR of Complex [Mn(L_2)]

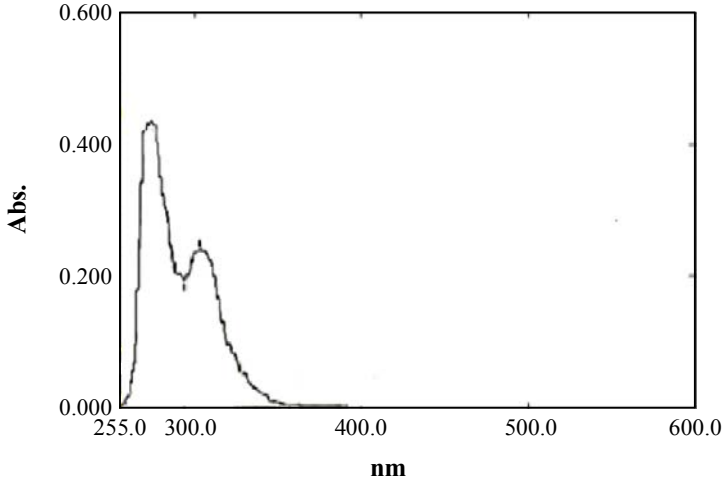


Fig. 14: Electronic spectrum of (L_1)

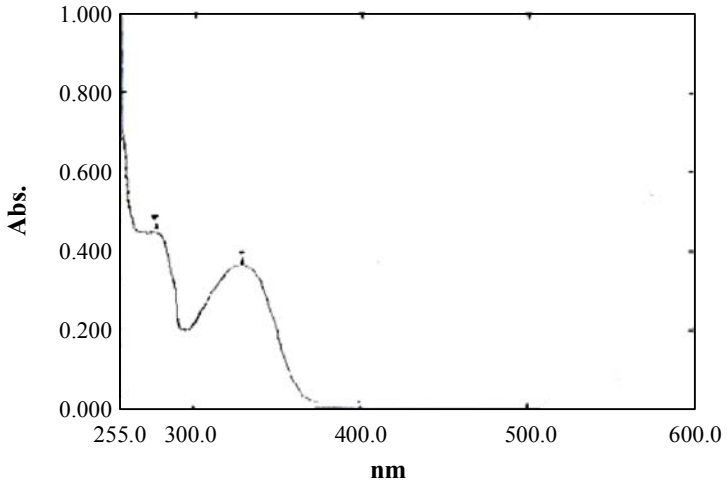


Fig. 15: Electronic spectrum of (L_2)

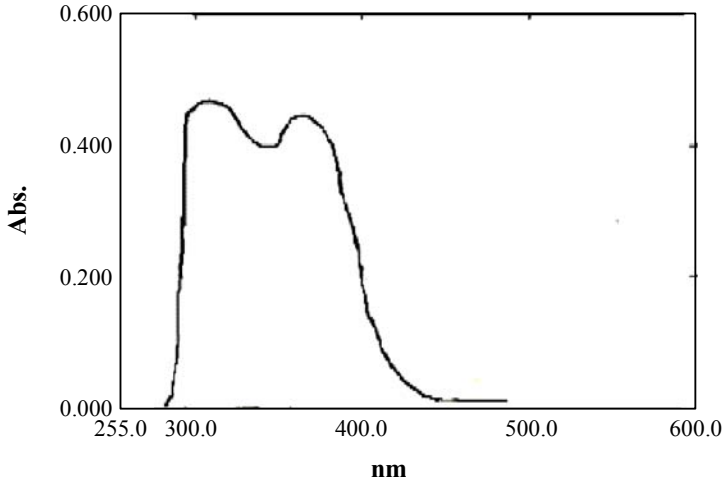


Fig. 16: Electronic spectrum of [Cu(L_1)Cl]

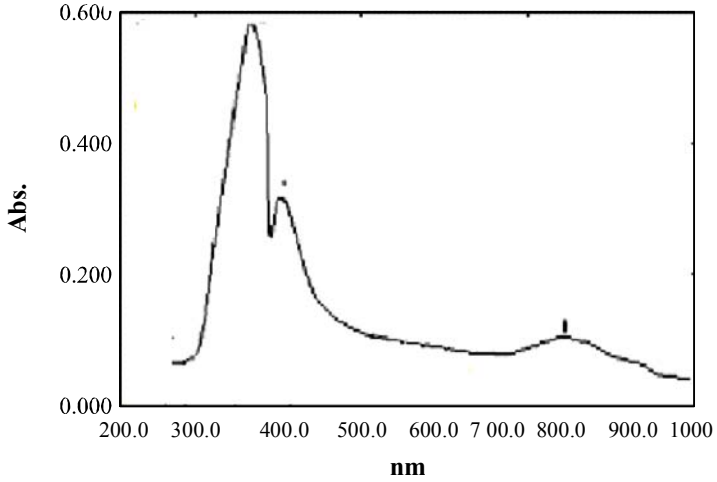


Fig. 17: Electronic spectrum of [Ni (L_2)]

CONCLUSION

From the elemental analysis, molar conductivity, UV–Vis magnetic, IR, ^{1}H-& ^{13}C-NMR spectral data, it is possible to determine the type of coordination of the ligand in their metal complexes. Based on these data, Tetrahedral and Square planar geometries are assigned to these complexes. The new Schiff ligands (L_1), (L_2) and metal complexes were prepared Co (II), Cu (II), Ni (II), Mn(II) and Hg(II) complexes. The metal (II) ions were coordinated with O atom for hydroxyl group (O-H), O atom for carbonyl group (C=O) and N atom for imine group (H-C=N) of ligand (L_1), while the complexes for ligand (L_2) b were coordinated with O atom for hydroxyl group (O-H), O atom for carboxyl group (C=O) and two N atoms for imine groups (H-C=N). Spectroscopic, structural and magnetic data show that all complexes are four-coordinate metal complexes owing to the ligation of the Schiff bases.

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