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Synthesis and Spectral Analysis of Some New Metal Complexes of Mixed Schiff Base Ligands.

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ABSTRACT

New series of Cd(II), Co(II), Cr(III), Fe(III), Ni(II) and Cu(II) complexes with ligand [2-Oxo-1,2-di hydro-indo (3-ylidene amino acetic acid)] (HL_1) and 1,10-phenanthroline (L_2) have been synthesized. The ligand (HL_1) which was prepared from (1-H Indoline-2,3-dione and glycine) and then react with 1,10-phenanthroline (L_2) to synthesize a mixed ligand. The prepared ligand was characterized by ^{1}H NMR spectroscopy, mass spectral analysis but the other physico-chemical techniques were characterized for all prepared compounds (ligands and their metal complexes) such as, melting point, (C.H.N) microanalysis, FT-IR, UV spectroscopy, Flame Atomic Absorption Spectrophotometer, the metal complexes were measured by conductivity to indicate the complexes are electrolyte or non electrolyte and magnetic susceptibility . The results were showed the formation and the high purity for ligands and their metal complexes, indicating that they are in a good agreement with the theoretical values.

Keywords: Spectral, Synthesis, Schiff Base, Metal Complexes

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INTRODUCTION

1, 10- phenanthroline is the parent of an important class of chelating agents. This chelating ligand which has high affinity for metal ions also posses π- acceptor capability which significantly contributes to the stabilization of their low valent metal complexes [1]. Isatin (1H-Indole-2,3-dione) is one of the most promising class of aromatic heterocyclic organic compounds having many interesting activity profiles and well-tolerated in human subjects [2], and it is an indole derivative [3] ,which that the indole ring system represents one of the most abundant and important hetero cycles in nature [4]. Amino acids are an organic compound containing an amino group, carboxylic group and any of various side groups. Amino acids are critical to life and have many functions in metabolism such as building blocks of proteins and forming parts of coenzyme as in s-adenosylmethionine, or as precursors of the biosynthesis of molecules such as hem [5]. The organic compounds which have azomethine group called Schiff bases [6] which it is a functional group that contains a carbon, nitrogen double bond, where the nitrogen atom connected to aryl group or alkyl group (R) but not hydrogen. [7]. It is one of the most important ligands which have form a several coordination complexes through association with general elements and specialize with transition metal . The first imine compound which prepared by German scientist that called Hugo Schiff from the condensation reaction between aldehyde or ketones with a primary amines[6]. Formation of Schiff base generally takes place under acid or base catalysis or with heat. Today Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures [8].The interaction of Schiff base compounds with metal ions and their metal complexes have been extensively investigated due to their wide range of applications in medicine and other application [9].

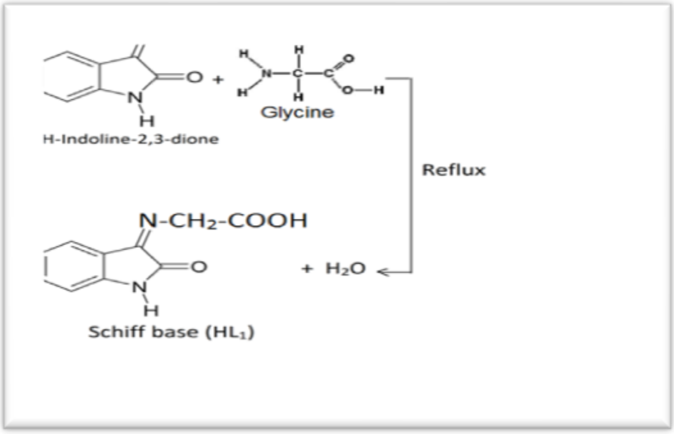
EXPERIMENTAL

Materials and measurements

All the organic and inorganic chemicals have been used in this research were of highest purity, were purchase from different companies (Sigma, Aldrich and BDH). The infrared spectra of the prepared compounds were recorded using IR presting 21, single beam path laser Fourier Transform infrared Spectrophotometer of Shimadzu Company as potassium bromide disc in the wavelength range of (4000-400) Cm^{-1}. The electronic spectra of the ligands and their metal complexes obtained by using UV-Visible Spectrophotometer type Shimadzu UV-160 at range (1100-200)nm, for 10^{-3}M solution of the ligands and their complexes in DMSO, using quartz cell of (1.0) cm length at room temperature. Elemental microanalysis (C.H.N) were performed from Euro vector, model (EA3000). The percentage of metals in complexes were determined by flame atomic absorption Spectrophotometer technique, using Nov AA350. The proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectrum of the prepared Schiff base ligand was performed on Brucker Amx 400 MHz Spectrometer with tetramethylsilane (TMS) as an internal standard. Mass Spectrum of the prepared Schiff base ligand was measured by using (5975C VL MSD with Tripe-Axis Detector). The Magnetic Susceptibility values of the prepared complexes were measured by using magnetic susceptibility balance Johnson matthey model (MSB-MKI). The molar Conductivity measurements of the prepared complexes were recorded by using Conductometer WTW with concentration(1×10^{-3}M) at (25˚C) ,and using solvent DMSO for them.

Synthesis of [2-Oxo-1,2 di hydro-indo(3-ylidene amino acetic acid)] (HL_1)

1-H Indoline-2,3-dione (1.441 gm,0.009mol) was dissolved in absolute ethanol (10 ml) with stirring and heating because 1-H Indoline -2,3-dione was poor solubility at (20˚C) , glycine (0.735 gm,0.009 mol) was dissolved in absolute ethanol/distilled water (10 ml) and added to the 1-H Indoline-2,3-dione solution and then added 2-3 drops of glacial acetic acid . The mixture was heating under reflux at (60˚C) for (3 hours) after that a red solid was formed, then the red solid was collected by filtration and recrystalized from absolute ethanol , m. p. (258-260)˚C , yield (75)%. can be shown in Scheme (1).



Scheme (1): Synthesis of [2-Oxo-1,2 di hydro-indo(3-ylidene amino acetic acid)] Ligand

Synthesis of Metal Complexes

The Schiff base ligand (HL_1) (0.390 gm,0.001mmol) was dissolved in absolute ethanol (10 Cm^3). Ethanolic solution of 1,10-phenanthroline (L_2) (0.379gm, 0.001mmole) was add to the above solution. The ethanolic solution of $CuCl_2.2H_2O$ (0.380gm, 0.002mmole); $CoCl_2.6H_2O$ (0.478gm, 0.002mmole); $NiCl_2.2H_2O$ (0.478gm, 0.002mmole); $CrCl_2.6H_2O$ (0.507gm,0.001mmole); $CdCl_2.2H_2O$ (0.365gm, 0.001mmole) and $FeCl_3.6H_2O$ (0.295gm, 0.001mmole)] was added to the mixed ligands solution. The mixture was stirred and heated under reflux at temperature at (55-60°C) for one hours. The precipitate was collected by filtration, and dried for two hours.

RESULTS AND DISCUSSION

FTIR-spectra

The FTIR frequency of the free Schiff base ligand [2-Oxo-1,2-di hydro-indo (3-ylidene amino acetic acid)] (HL_1) showed broad band at (3460) cm^{-1} was attributed to the stretching vibration of (OH) of carboxylic group[10], the band at (3398)cm^{-1} due to the stretching vibration of (N-H)[11]. The band at (3062)cm^{-1} was attributed to stretching vibration of (C-H) aromatic [12], the bands at (2877) cm^{-1} and (2831)cm^{-1} assigned to the stretching vibration of (C-H) aliphatic of asymmetrical and symmetrical respectively [13]. The bands at (1716)cm^{-1} , (1620) cm^{-1} ,(1539)cm^{-1} ,(1118) cm^{-1} were assigned to the stretching vibration of (C=O) of carbonyl group [14], (C=N) [15] and (C-N). The infrared spectrum of the 1,10-phenanthroline ligand (L_2) showed strong band at (3387) cm^{-1} which belonged to stretching vibration of (OH) hydrate, bands at (3039) cm^{-1} and (3016) cm^{-1} assigned to stretching vibration of (C-H) aromatic of asymmetrical and symmetrical respectively [11]. The bands at (1585) cm^{-1} and (1558) cm^{-1} due to the stretching vibration of (C=N) [13], other band at (1138)cm^{-1} attributed to stretching vibration of (C-N) [16]. The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may be involved in coordination. The band at (1716) cm^{-1} belonged to (C=O) of carboxyl group in the free Schiff base ligand [2-Oxo-1,2-di hydro-indo (3-ylidene amino acetic acid)] (HL_1) wasn't changed in the complex Co^{+2} that indicate no coordinate this group with that above metal but it's coordinate with the other metal complexes due to change the frequency of (C=O) of carboxyl group in that (Cu^{+2}) metal complex [17] or change in the shape and intensity of the bands in the other metal complexes .Other group didn't coordinate with the metal Fe^{+3} complex was (N-H) in the free Schiff base ligand [2-Oxo-1,2-di hydro-indo (3-ylidene amino acetic acid)] (HL_1) at (3398)cm^{-1} but it's coordinate with the other metal complexes through changed it' s frequency in Ni^{+2}, Cr^{+3} metal complexes, change in the shape and intensity of the bands in the Co^{+2},Cu^{+2} metal complexes or disappeared in Cd^{+2} complex that mean coordinate this group with that metal complex . The bands at (2939-3066) cm^{-1} and (2796-2958) cm^{-1} were belonged to stretching vibration of (C-H) aromatic [15] and aliphatic symmetrical and asymmetrical respectively [18-20] for all metal complexes. The bands of (C=N) of the ligand (HL_1) and (L_2) which that (1539)cm^{-1} [21] and (1585)cm^{-1} [13] respectively were shifted to higher and lower frequency for all the metal complexes appeared at (1654-1512)cm^{-1}[22, 23] indicating participation of azomethine nitrogen in the interaction with the metal ion [24]. The medium sharp bands at (848)cm^{-1} belonged to the rocking vibration (OH) of water and that indicate the presence of water molecule inside the coordination sphere for Co^{+2},Cr^{+4}

metal complexes , the broad bands at (3240)cm^{-1},(3437)cm^{-1} and (3414)cm^{-1} were attributed to the (OH) of carboxyl group in the metal complexes Co^{+2},Fe^{+3} and Cd^{+2} respectively, other bands at (1199-1141) cm^{-1} were belonged to (C-N) for all metal complexes. The new bands that observed in all metal complexes at (567-493) cm^{-1} and (478-424) cm^{-1} were due to the (M-N) and (M-O) respectively [25, 26], these are summarized in the Table (1).

Table 1: IR spectral data of the ligands and their metal complexes (cm^{-1})

Compounds	**υ OH**	**υ (C- H) ar.**	**υ (C-H) ali.**	**υ (C=N)**	**υ (C=O) Carbonyl**	**υ (C=O) CarboXyl**	**υ (N-H)**	**υ (C-N)**	**υ (M-N) and M-O)(**
Schiff base (HL_1)	3460	3062	2877-2831	1539-1512	1620	1716	3398	1118	- -
L_2 (1,10-phenanthroline)	3387 hydrate.	3039-3016	-	1585-1558	-	-	-	1138	- -
$[Co(HL_1)(L_2)(H_2O)Cl]$	3240 848	3062	2870-2796	1585-1516	1666-1620	1716	3398	1141	547 447
$[Cr_2(HL_1)(L_2)(H_2O)_2]^{+4}$	848	3062-2939	2881-2827	1550-1519	1620	1716	3367	1195	567 451
$[Cu(HL_1)(L_2)]$	-	3047-3012	2873-2812	1581	1620	1724	3398	1145	493 424
$[Fe(HL_1)(L_2)Cl_2]Cl$	3437	3059-3008	2958-2881	1516	1620-1581	1732	3394	1141	528 459
$[Cd(HL_1)(L_2)Cl](H_2O)$	3414	3047-3008	2958-2889	1585-1512	1647-1620	1716	-	1141	555 478
$[Ni(HL_1)(L_2)Cl](H_2O)$	-	3066	2870-2835	1654-1620	1670	1705	3240	1199	555 455

The ^{1}H-NMR spectrum indicated the multiplete ranged between (δ=6.806-6.821 ppm) was attributed to the aromatic protons of the ligands (HL_1) [27] .The singlet signal showed at (δ=8.195 ppm) due to the proton of the amide group of the ligands (HL_1) [28]. The singlet signal appeared at (δ=2.505-2.508ppm) can be assigned to the solvent DMSO of the ligands (HL_1) [29]. The singlet signal appeared at (δ=4.002-4.176 ppm) was attributed to the protons of the $(-CH_2-)$ of the ligands (HL_1) [16]. The singlet signal appeared at (δ=10.35 ppm) was attributed to the proton of carboxylic group of the ligands (HL_1) [11] ,which that can be shown in fig.(1).

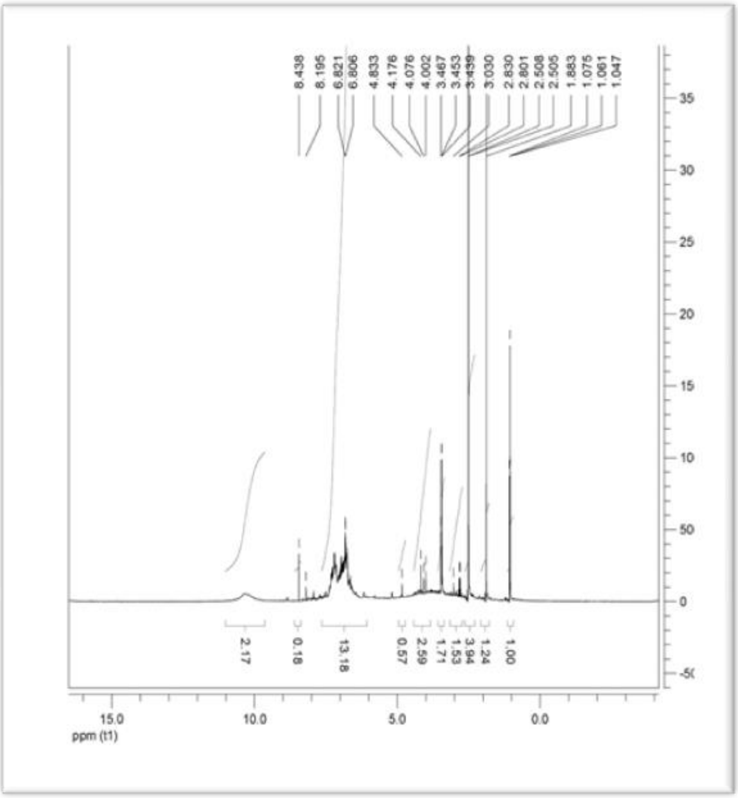


Figure 1: ^{1}H-NMR spectrum of Schiff base Ligand (HL$_1$)

The main high resolution mass spectrometer of the prepared Schiff base ligand [2-Oxo-1,2-di hydro-indo (3-ylidene amino acetic acid)] (HL$_1$) as shown in fig. (2).The molecular ion peak was observed at m/z=204(M). The fragmentation pattern of the molecular ion of the ligand was illustrated in scheme 2.

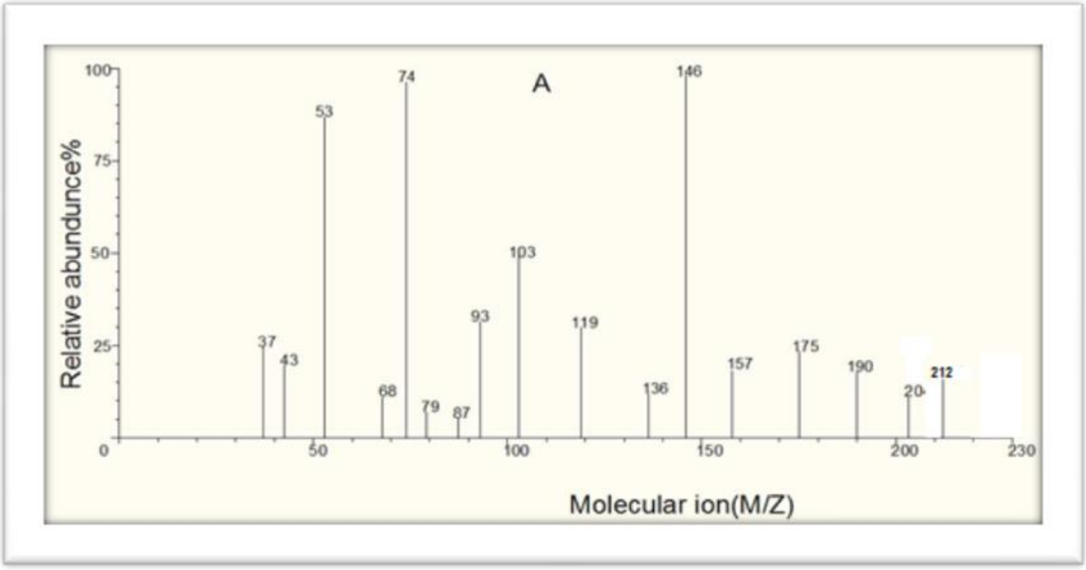
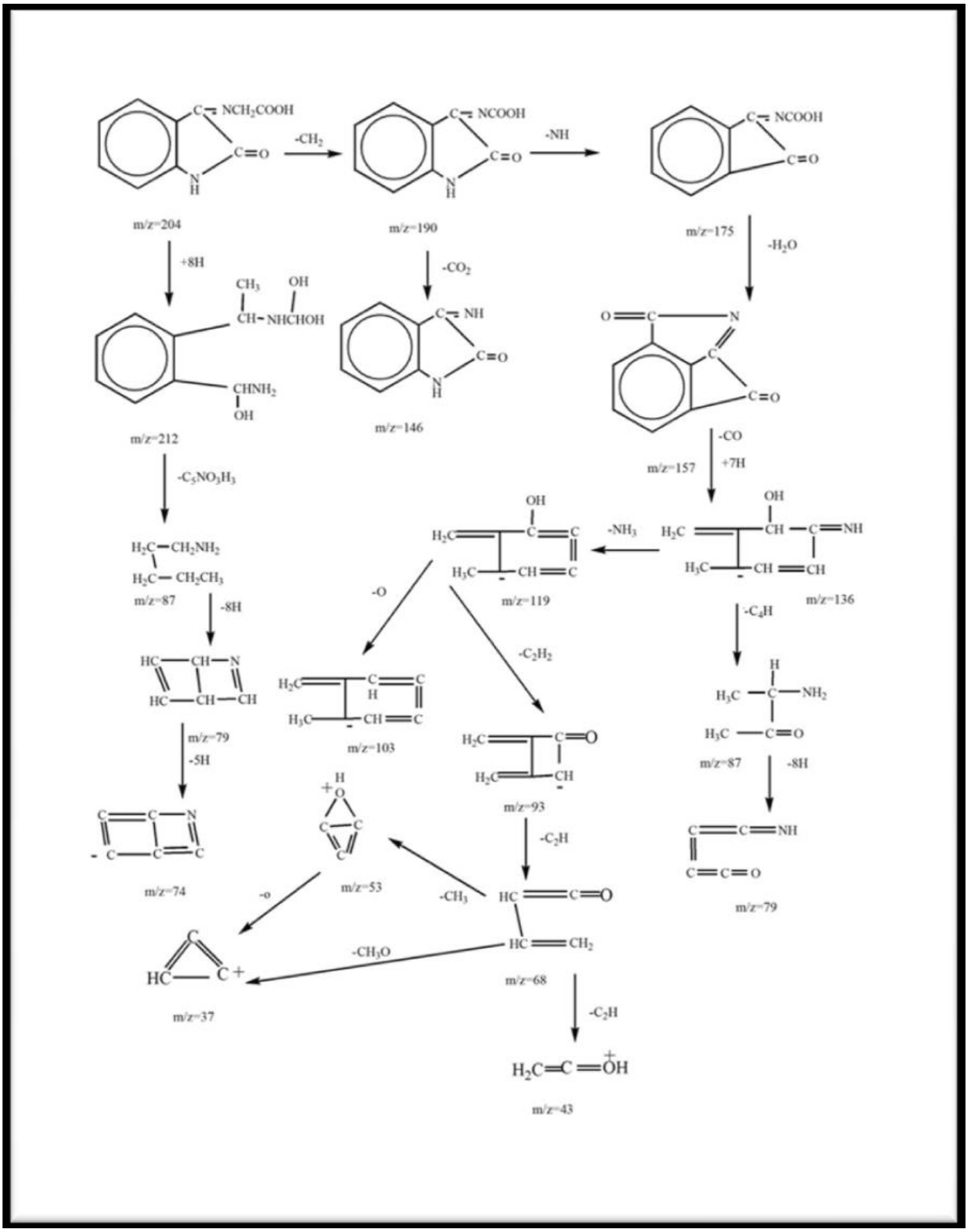


Figure 2: Mass spectrum of Schiff base Ligand (HL$_1$)



Scheme (2): The fragmentation pattern of the free Schiff base ligand (HL_1)

The measurements of the molar conductivity of the prepared complexes were carried out using DMSO (10^{-3}M) as a solvent at room temperature. The values indicate that all the metal complexes are non-electrolyte nature except the ferric complex is electrolyte.

The magnetic moments of Co(II), Cr(III), Cu(II), Fe(III), Cd(II) and Ni(II) were found to be 3.86, 3.88, 2.83, 1.75. 0.0 and 3.00 B.M. respectively within the expected values.

The microanalysis (CHN) of the free Schiff base ligand and the metal complexes are in a good agreement with the calculated values, also the data of metal and chloride contents of the complexes were in a good agreement with the theoretical values. All the results were illustrated in tables 2 and 3.

Table 2: The physical properties of ligands and their metal complexes, magnetic succeptibility and molar conductivity of complexes

Compound	Color	M.wt	Yield %	M.P (C$^{\circ}$)	Molar Conductance (μs/cm^{-1})	$\mu_{eff.}$ (B.M)
Schiff base (HL_1)	Reddish brown	204	75	260	-	-
$[Co(HL_1)(L_2)(H_2O)Cl]$	Dark-green	494.9	60	100	16	3.86
$[Cr_2(HL_1)(L_2)(H_2O)_2]^{+4}$	Dark-brown	522	59	100	20	3.88
$[Cu(HL_1)(L_2)]$	Light-Green	445.5	75	280	12	2.83
$[Fe(HL_1)(L_2)Cl_2]Cl$	Red	544.85	85	282	34	1.75
$[Cd(HL_1)(L_2)Cl]H_2O$	Light-pink	548.4	80	300	9	0
$[Ni(HL_1)(L_2)Cl]H_2O$	Dark – brown	494.7	65	191	15	3.00

Table 3: Microanalysis of free ligands and their metal complexes

Compounds	Elemental microanalysis (calc.) Found%			Cl %	M (Calc.) Found %
	C %	H %	N %		
Schiff base (HL_1)	(58.82) 59.16	(3.92) 4.18	(13.72) 14.31	-	-
$[Co(HL_1)(L_2)(H_2O)Cl]$	(53.34) 51.93	(3.43) 4.32	(11.31) 10.07	(7.07) 7.09	(11.90) 12.69
$[Cr_2(HL_1)(L_2)(H_2O)_2]^{+4}$	(50.57) 49.69	(3.44) 3.50	(10.72) 11.01	-	(19.92) 19.97
$[Cu(HL_1)(L_2)]$	(59.25) 58.69	(3.14) 3.39	(12.57) 13.31	-	(14.25) 14.35
$[Fe(HL_1)(L_2)(Cl)_2]Cl$	(48.45) 46.01	(2.93) 3.39	(10.27) 11.03	(19.27) 19.03	(10.25) 10.01
$[Cd(HL_1)(L_2)Cl]H_2O$	(48.14) 47.93	(3.09) 3.88	(10.21) 11.78	(6.38) 6.93	(20.49) 20.33
$[Ni(HL_1)(L_2)Cl]H_2O$	(53.36) 53.01	(3.43) 4.83	(11.31) 12.13	(7.07) 6.93	(11.86) 10.01

The electronic spectra indicated that the color of the transition metal complexes that prepared are different from the color of their metal salts and ligands and this is good indication of coordination the central metal ion with the free Schiff base ligands through the donor atoms of their ligands . The electronic spectrum of the free Schiff base ligand (HL_1) showed three absorption bands at (271 nm,36900cm^{-1}) and (348nm, 28735 cm^{-1}) which were belonged to (π-π^*) electronic transition of benzene ring and (n-π^*) electronic transition of (C=N) group respectively [30, 31] . The electronic spectrum of the ligand (1,10-phenanthroline) (L_2) observed absorption band at (281 nm,35587cm^{-1}) assigned to (π-π^*) electronic transition of azo methine group [32] .

The electronic spectrum of the Fe^{+3} complex showed four absorption bands at (275 nm,36363cm^{-1}), (430 nm,23256 cm^{-1}), (515nm,19417cm^{-1}) and (995 nm,10050 cm^{-1}) assigned to ($\pi \rightarrow \pi^*$) electronic transitions, the second electronic transition assigned to [$^6A_1g \rightarrow {}^4T_1g$] and the third belonged to [$^6A_1g \rightarrow {}^4T_2g(D)$] and [$^6A_1g \rightarrow {}^4T_1g(G)$] that mean the geometry of this complex is octahedral [33]. The electronic spectrum of the Cr^{+3} complex observed three absorption bands at (281 nm,35587cm^{-1}),(775 nm,12953cm^{-1})and (788nm,12690cm^{-1}) were attributed to the ($\pi \rightarrow \pi^*$) electronic transitions, [$^4A_2g_{(F)} \rightarrow {}^4T_1g_{(F)}$] electronic transitions and [$^4A_2g_{(F)} \rightarrow {}^4T_2g_{(F)}$] electronic transitions respectively, that mean the geometry of this complex is octahedral [34]. The spectrum of Cu^{+2} complex displays two bands: the first band with high intensity and high molar absorptivity appeared at (276nm, 36231cm^{-1}) attributed to intra-ligand, the other absorption band at (758nm, 13192cm^{-1}) attributed to (d-d) electronic transition type [$^2Eg \rightarrow {}^2T_g$], that mean the geometry of this complex is octahedral [35]. The spectrum of Co^{+2} complex displays three bands: the first band with high intensity and high molar absorptvity appeared at (276nm, 36231cm^{-1}) attributed to L.F., the second band at (510nm,19608cm^{-1}) can be assigned to [$^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$] electronic transition and the last electronic transition (972nm,10288cm^{-1}) can be assigned to [$^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$] , that mean the geometry of this complex is octahedral [38].

The spectrum of Cd^{+2}complex do not furnish any characteristic d-d transitions because it is diamagnetic in nature and its electronic spectra appears two bands: the first electronic transition with high intensity and high molar absorptvity appeared at (272nm, 36764cm^{-1}) attributed to intra-ligand and the second electronic transition (783nm, 12771cm^{-1}) attributed to M→L ,CT [39]. The results are summarized in the table (6) and some of them are illustrated in figures (3-5).

Table 4: UV-Vis Spectra of metal ion complexes derived from mixed of Schiff base ligands (HL_1) and 1, 10-phenanthroline (L_2) ligands.

Compound	λ_{max} (nm)	Wave number (cm^{-1})	ABS.	ε_{max} $Molar^{-1}$ $.cm^{-1}$	Assignment
Schiff base (HL_1)	271 348	36900 28735	1.911 1.038	1911 1038	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
L_2 (1,10-phenanthroline)	281	35587	2.420	2420	$\pi \rightarrow \pi^*$
$[Co(HL_1)(L_2)(H_2O)Cl]$ Octahedral	276 965 972	36231 10362 10288	2.257 0.001 0.003	2257 1 3	L.F. $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$ $^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$
$[Cr_2(HL_1)(L_2)(H_2O)_2]^{+4}$ Octahedral	281 772 788	35587 12953 12690	2.443 0.001 0.004	2443 1 4	$\pi \rightarrow \pi^*$ $^4A_2g_{(F)} \rightarrow {}^4T_1g_{(F)}$ $^4A_2g_{(F)} \rightarrow {}^4T_2g_{(F)}$
$[Cu(HL_1)(L_2)]$ Octahedral	276 758	36231 13192	2.210 0.018	2210 18	Intra-ligand $^2Eg \rightarrow {}^2T_2g$
$[Fe(HL_1)(L_2)Cl_2]Cl$ Octahedral	275 430 515 995	36363 23256 19417 10050	2.263 0.405 0.542 0.001	2263 405 542 1	$\pi \rightarrow \pi^*$ $^6A_1g \rightarrow, {}^4T_1g$ $^6A_1g \rightarrow, {}^4T_2g_{(D)}$ $^6A_1g \rightarrow {}^4T_1g_{(G)}$
$[Cd(HL_1)(L_2)Cl](H_2O)$ Octahedral	272 783	36764 12771	1.995 0.028	1995 28	Intra-ligand M→ L ,CT
$[Ni(HL_1)(L_2)Cl](H_2O)$ Octahedral	272 494 697 767	36764 20242 14347 13038	2.005 0.065 0.001 0.001	2005 65 1 1	Intra-ligand $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(P)}$ $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ $^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$

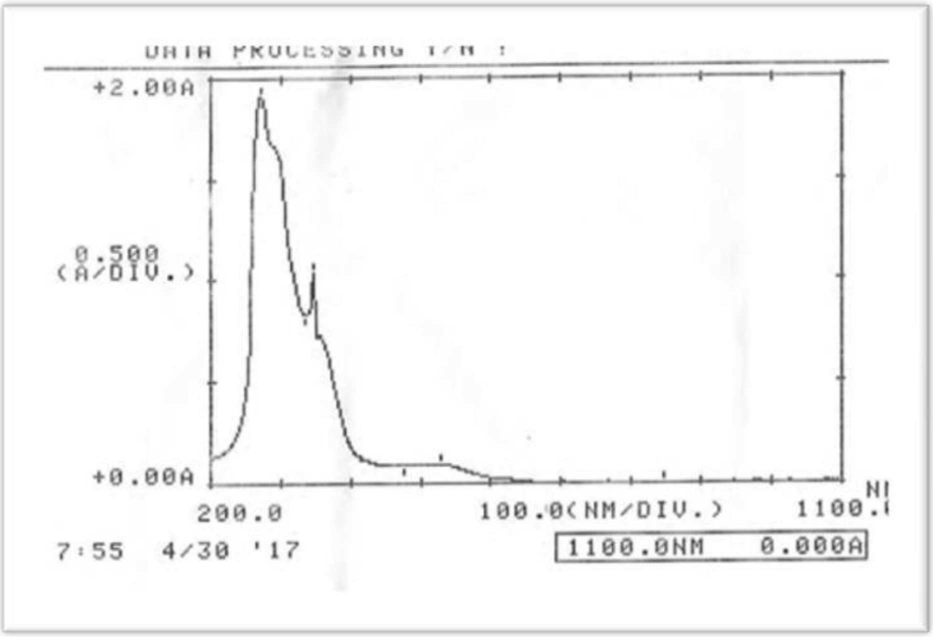


Figure 3: Electronic spectrum of (HL_1) ligand .

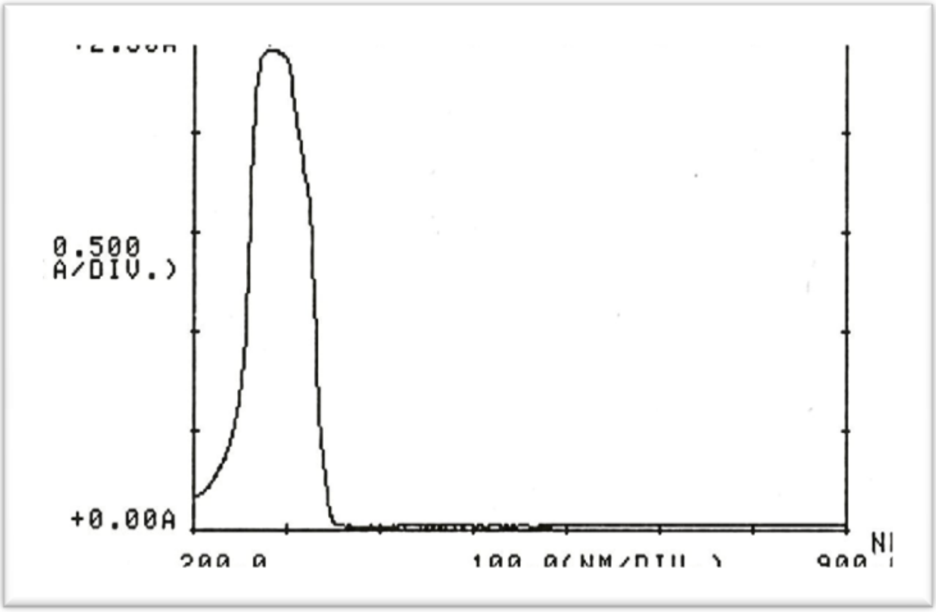


Figure 4: The electronic spectrum for 1, 10-phenonthroline (L_2) ligand.

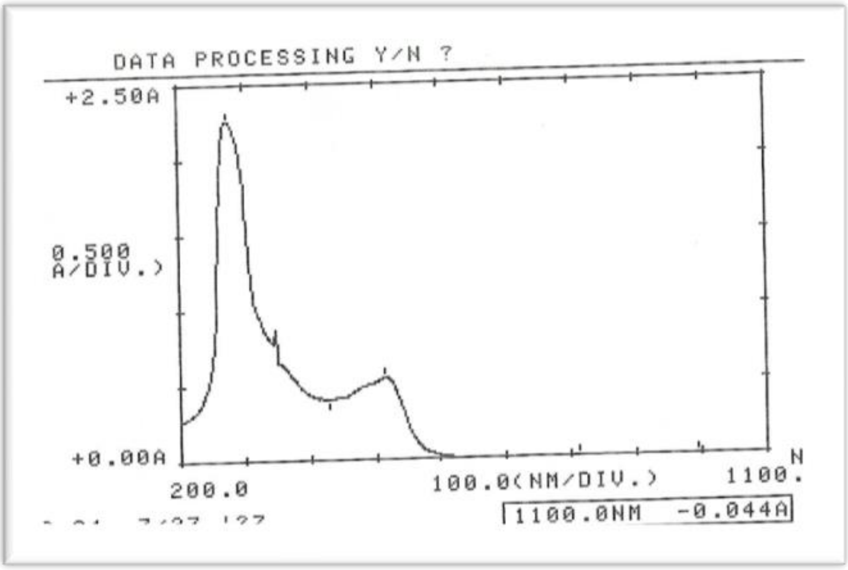


Figure 5: The electronic spectrum of [Fe (Hl1)(L2)Cl2]Cl.

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