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Preparation and characterization of new Mixed ligand complexes For some transition metal ions (bivalent) with Schiff- Mannich and Schiff base ligands

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Abstract:

In this research, new mixed ligand complexes were prepared for complexes of some transitional element ions from the first transition series, which are: cobalt (II), nickel (II), and copper (II). The research included two paths:

First: The first path included the preparation of three polycyclic ligands derived from Isatin (L1, L2, and L3), all of these ligands were identified by measuring the melting point and infrared and ultraviolet-visible spectroscopy.

Second: The second path included the preparation of Mixed ligand complexes (L1and L2) with cobalt (II), nickel (II), and copper (II) ions. And Mixed ligand complexes (L1and L3) with ions of cobalt (II) and nickel (II). All the complexes of the new Mixed ligand were identified by the available analytical and spectroscopic methods. Based on the analytical data, the metal to ligands ratio was (1:1:1) and all complexes were characterized by various analytical techniques including (FT-IR and UV-Vis spectroscopy), CHN elemental analysis and determination using flame atomic

absorption spectroscopy The percent magnetic susceptibility and molar conductivity of metal ions in the prepared complexes and these metal complexes dissolved in DMSO at a laboratory temperature of 1×10^{-3} M were also studied. by means of infrared (IR) spectra, and when compared to the spectrum of the free ligands, it was observed that some bands were displaced and others disappeared, or a change in shape and intensity occurred, which indicates a coordination occur between the metal ions and the prepared ligands. As well as the ultraviolet-visible spectrum. And detecting the presence of chloride ion inside or outside the coordination sphere. Depending on these obtained results, we were able to conclude that ligands of L1 and L2 behaves like a bi-chelate ligands, which led to the formation of mixed ligand complexes (L1, L2) with the proposed geometry of the proposed hexahedral symmetry in the presence of two chloride ions inside the coordination sphere. . Whereas, the L3 ligand behaved like a tetragonal ligand, which led to the formation of mixed ligand complexes (L2, L3) with the proposed geometry of the proposed hexahedral symmetry

Keywords: Mixed ligand complexes , Transition Metal complexes , Schiff- Mannich ligands.

Introduction:

Mixed ligand complexes differ from traditional complexes in the sense that they are having at least two different kinds of ligands associated with the same metal ion in a complex. The presence of more than one type of ligand in a complex increases chances of variation in properties expected for the complex. This makes the researcher interested in the synthesis of mixed ligand complexes with varying properties. Synthesis and characterization of mixed ligand complexes is gaining importance day by day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publications are devoted to synthesis and characterization of mixed ligand complexes [1-6]. It is type of complex can be defined simply as compounds that contain more than one ligand in its chemical composition .Studies have shown that the use of Mixed ligand complexes in different analytical methods makes them more sensitive and selective in separating and quantifying different elements, as well as the possibility of predicting the mechanics of analytical reactions and studying the properties of different elements [7]. In this context, the researcher Atakilt Abeb prepared the complexes of the mixed ligands of phenanthroline with adenine and thymine for the copper (II) ion, and they were diagnosed by IR, UV-VIS spectroscopy, where he demonstrated the effectiveness of this compound as anti-inflammatory and antibacterial and used as in-vivo therapy[8]. A number of transition

metallic complexes that have mixed ligands including Schiff-bases were reported , such as Cu (II) complexes This includes the synthesis of ligands as first step from the reaction of salicylaldehyde with 2-aminophenol or 3-nitro amino benzene. Compounds were characterized by magnetic measurements, ESR, UV-VIS, FT-IR, C.H.N, and mass spectra. On the basis of the obtained data the creation of di nuclear Cu(II) complexes in which the suggested geometry is tetrahedral [9].

Four Novel mixed ligands Complexes were elaborated from two Schiff base ligand ((benzimidazol-2- phenyl)iminomethyl)phenol (HL_1) and 2-(1-Hbenzimidazol-2-yl)phenyl) imino)methyl) naphthol (HL_2) , copper salt ($CuCl_2.2H_2O$) and respectively 2-mercaptobenzothiazole or 2-aminobenzothiazole. The resulted data indicate that the copper is linked to ligands via deprotonated phenolic oxygen atom, nitrogen or sulphur atom of co-ligands and the coordination was realized through the azomethine group. X-ray powder diffraction analysis of complexes suggest that they possess monoclinic structure , orthorhombic structure and Rhombohedral structure for these complexes .The in vitro anticancer activities of these different complexes were evaluated and the results revealed an important cytotoxicity against lung human cancer A-549 and very good selectivity values of inhibitory concentration IC 50 [10] .

Mixed ligands complexes derived from Mannich reaction and Schiff-base are useful materials that have a variety of applications in human life. These include biomedical, analytical ,coordination chemistry, agriculture, industry, polymer chemistry and Environment [11,12].

In this paper, we report synthesis and characterization of a series of five mixed Ligand of Mannich reaction and Schiff-base complexes derived from Isatin , 4- Amino antipyrine and Sulphadiazine using Transition metal ions such as Co(II), Ni(II) and Cu(II) . These complexes are then characterized using molar conductance, magnetic measurements and spectral techniques such as IR and electronic spectra.

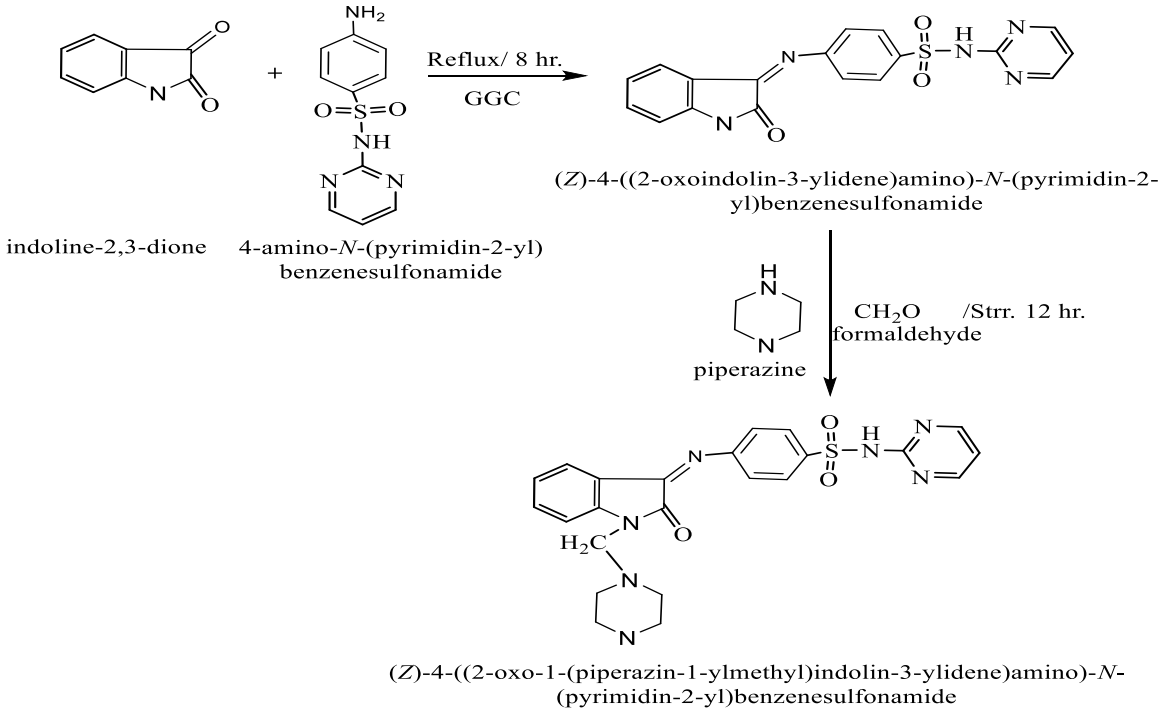
MATERIALS AND METHODS

All chemicals were purchased from Fluka ,Merck, Riedel –deHaën , Himedia, BDH, Sigma-Aldrich and Sharlut . Melting points were determined using a Model 9300 of the ligands and their complexes. UV-Vis spectra were recorded on a Shimadzu Model 1700 dual-band spectrophotometer. Magnetic susceptibility measurements were performed on a balanced magnet MSB-MKI using the Faraday method. Antimagnetic correction using Pascal's constant. FT-IR spectra were recorded on a Shimadzu FTIR 8400 spectrometer using KBr particles in the wavelength range 4000–400 cm −1 . CHN elemental analysis was performed using EURO 2012EA 300 CHN elements and melting

points of new complexes recorded by Electro Thermal 9300, Melting Point Engineering LTD.

1. Synthesis of Schiff – Mannich base ligand (L1) :

In order to prepare Schiff base as a first step including dissolving (0.147 gm, 0.001 ml) of Isatin in (30 ml) absolute ethanol in a rotating flask on a magnetic stirrer, then add (2-3) drops of glacial acetic acid to the mixture, then add (0.2 gm, 0.001 ml) of sulfadiazine With the sublimation process at a temperature of 75°C and for a period of (8 hr), then the precipitate was dried, washed, and recrystallized by ethanol, then the precipitate was dried (62%). In the second step the preparation of ligand including added (0.2 gm) of the first compound (Schiff base) was dissolved in (30 ml) absolute ethanol on the magnetic stirrer, then (1 ml) of formaldehyde was added to the mixture, then (0.06 gm) of Piperazine was added, and the mixture was left on the stirrer for a while (12 hr) then placed in the refrigerator for a period of (48 hr) after which the precipitate was dried, washed and recrystallized with ethanol. Its percentage is (75%) and its melting point was measured and it was (191-193)C°[13]. as shown in Scheme (1) .

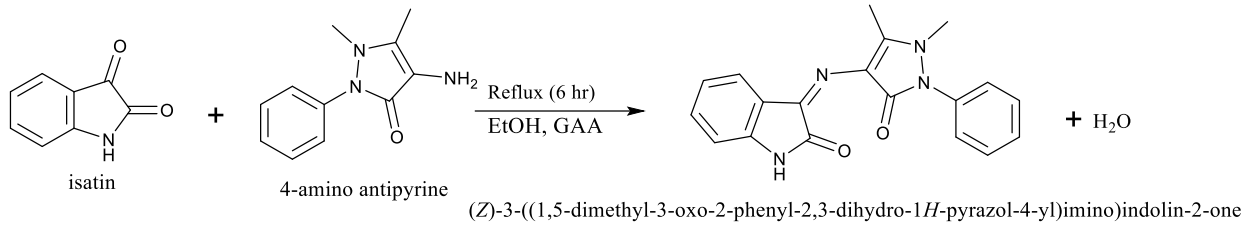


Scheme-1: Synthesis of Schiff – Mannich base ligand (L1).

2. Synthesis of Schiff base ligand (L2) :

The Schiff base ligand L2 (Z)-3-((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)imino)indolin-2-one.Was prepared according to the method of (M. A.

Hadi) [14] in a circular flask with a volume of (100 ml). (0.01 mole, 2.03 gm) of 4-aminoanitobarene was dissolved in ((15 ml of absolute ethyl alcohol) then (0.01 mole, 0.01 mole, 1.47 gm) of Isatin and (2-3) drops of Glacial acetic acid . The mixture was ascended for six hours [14] , then left to cool, and a bright orange precipitate was observed, then the precipitate was recrystallized from ethanol as it was dried over anhydrous calcium chloride, the percentage of the product (84%), melting point (165-168 ^{0}C), and the Scheme- 2 shows the method of preparation:



isatin

4-amino antipyrine

(*Z*)-3-((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)imino)indolin-2-one

Scheme-2: Synthesis of Schiff base ligand (L2).

3. **Synthesis of Schiff base ligand (L3) :**

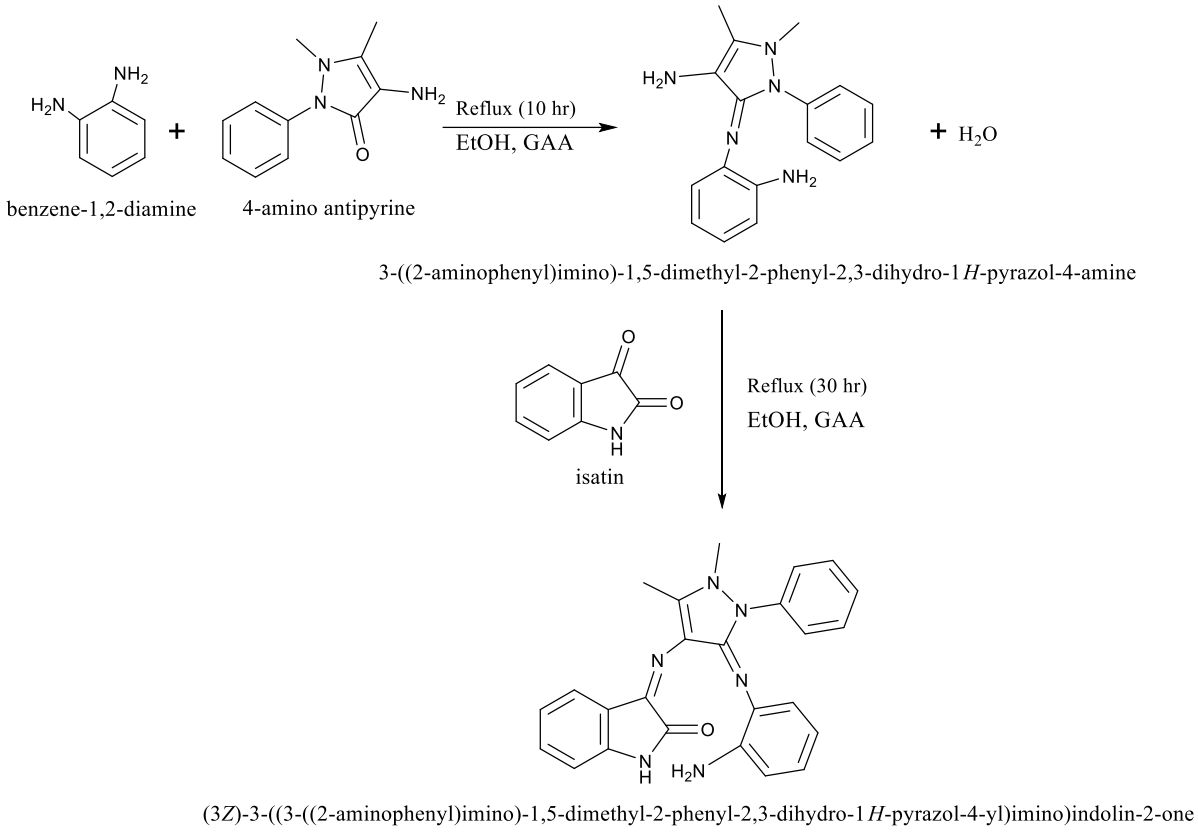
The Schiff base ligand L3 prepared in two steps:

3.1 Preparation of the compound DMAA

Preparation of the compound DMAA [15]. In a round flask of volume ((100 ml) (0.01 mole, 2.03 gm) of 4-amino antipyrine was dissolved in (15 ml) of absolute ethyl alcohol, then (0.01 mol, 1.08 gm) of 3- was added to it. benzene 1,2-Diamine and (2-3) drops of glacial acetic acid. The mixture was ascended for ten hours, then left to cool. An orange precipitate was observed, then the precipitate was recrystallized from ethanol and dried over anhydrous calcium chloride. Melting (153-155 ^{0}C) and Scheme-3 showing the method of preparation.

3.2 Preparation of the Ligand L3

In the second step of preparing the L3 Schiff base, (0.01 mol, 2.933 gm) of the compound prepared in step (3.1) (DMAA) was dissolved in (50) ml of absolute ethanol and (0.01mol, 1.47 gm) of dissolved Isatin was added to it in (50) ml of absolute ethanol and (2-3) drops of glacial acetic acid, and the mixture rose for thirty hours [16] , then it turned brown. It was left to cool, and the ligand (L3) precipitated in the form of a brown solid. It was filtered, dried, and recrystallized from hot absolute ethanol. It was also dried over anhydrous calcium chloride. The percentage was (83%) and the melting point (170-171) ^{0}C. The preparation reaction is shown in the Scheme-3 :



Scheme-3: Synthesis of Schiff base ligand (L3).

The physical properties of the three ligands had listed in Table 1.

4. Synthesis of Mixed Ligand complexes :

4.1 Mixed Ligand complexes of Co (II),Ni (II) and Cu(II) with (L1 and L2)

The metal complexes were prepared in a molar ratio (1:1:1) (M:L1:L2) by dissolving (0.477 gm) (0.001 mol) of solid ligand L1 as a primary ligand with (0.332 gm) (0.001 mol) of ligand L2 as co-ligand in (15ml) of ethyl alcohol. Added to (0.001 mol) for each of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ dissolved in (15 ml) of ethyl alcohol, The resultant mixtures were refluxed for one hour. The complexes produced were isolated by evaporation, filtered off and dried under vacuum. The physical properties of the studied complexes were listed in Table 1. Schemes 4 illustrate the procedure steps for preparing metal complexes with mixed ligands L1 and L2.

4.2 **Mixed Ligand complexes of Co (II) and Ni (II) with (L2 and L3)**

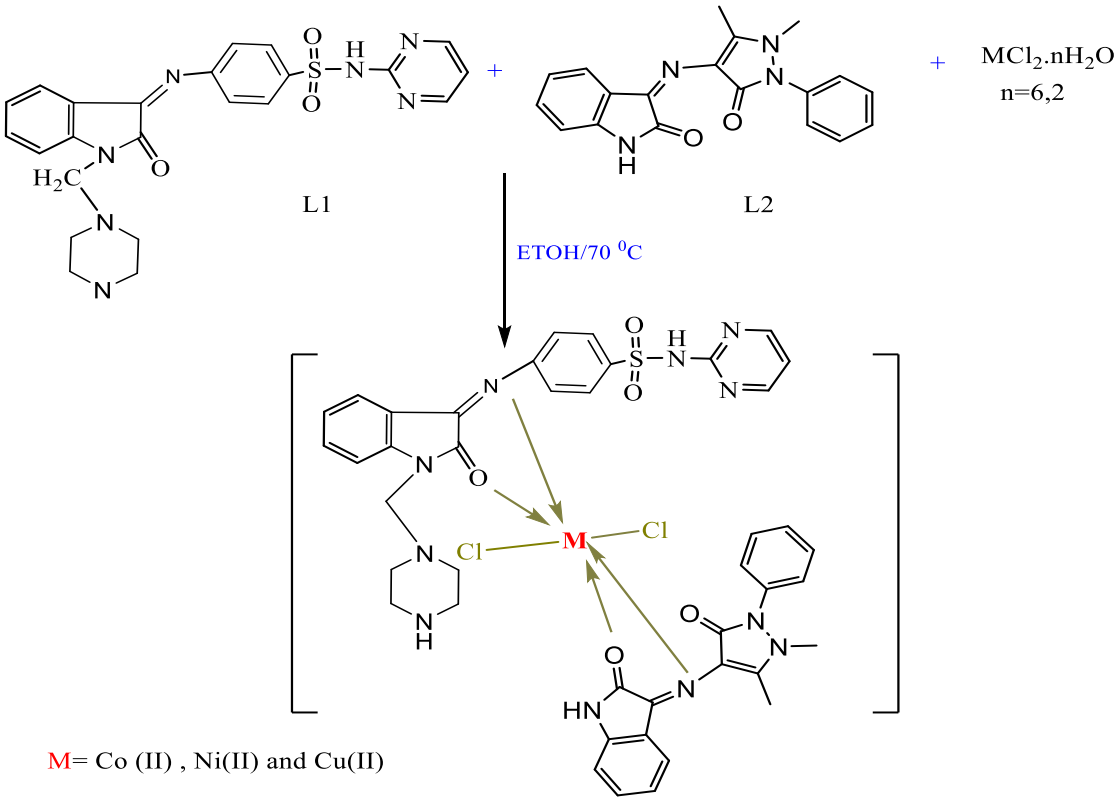
The metal complex was prepared in a molar ratio (1:1:1) (M:L2:L3) by dissolving by dissolving (0.422 gm) (0.001 mol) of solid ligand L3 as a Primary with (0.332 gm) (0.001 mol) of ligand L2 as Co- ligand in (15ml) of ethyl alcohol. Added to (0.001 mol) for each of $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ dissolved in (15 ml) of ethyl alcohol, The

resultant mixtures were refluxed for one hour. The complexes produced were isolated by evaporation, filtered off and dried under vacuum. The physical properties of the studied complexes were listed in Table 1. Schemes 4 illustrate the procedure steps for preparing metal complexes with mixed ligands L2 and L3.

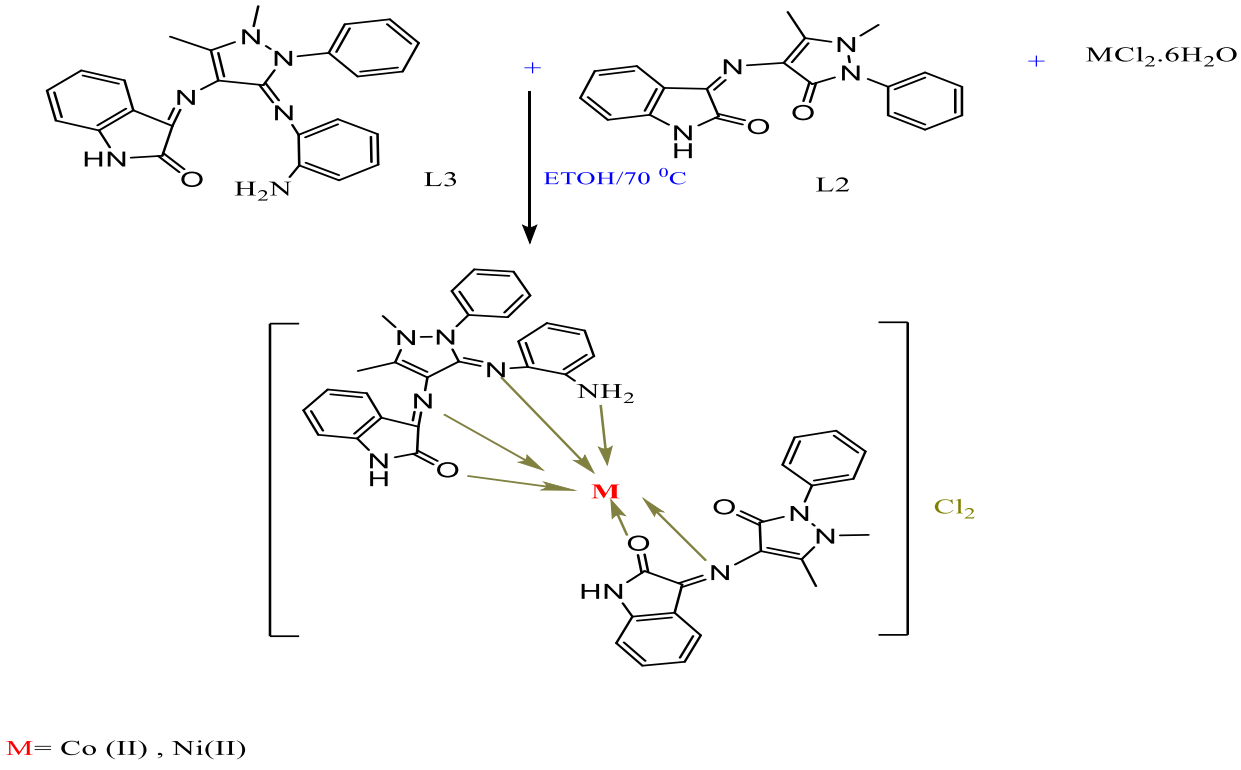
The physical properties of the mixed ligand complexes are listed in Table 1. Schemes 4 and 5 illustrate the procedure for preparing these metal complexes with mixed ligands.

Table (1) Physical properties of the ligands L1,L2 ,L3and their novel metal Mixed ligand complexes.

No	Chemical formula	Color	M.wt g/Mol	m.p °C	Yield%	R_f
1	L1= $C_{23}H_{23}N_7O_3S$	light brown	477.54	191-193	75	0.61
2	L2= $C_{19}H_{16}N_4O_2$	Orange	332.36	165-168	85	0.58
3	L3= $C_{25}H_{22}N_6O$	Dark Brawn	422.49	170-171	81	0.73
4	$[Co(L1)(L2)Cl_2]$	Dark brown	939.74	189-220	78	0.78
5	$[Ni\ (L1)(L2)Cl_2]$	Purple	939.50	207-245	82	0.81
6	$[Cu\ (L1)(L2)Cl_2]$	Orange	944.35	146-150	80	0.69
7	$[Co(L3)(L2)]Cl_2$	Reddish brown	884.69	>300	83	0.86
8	$[Ni(L3)(L2)]Cl_2$	red	884.45	270-273	81	0.54



Scheme- 3: Synthesis of the new complexes with mixed ligands (L1 and L2)



Scheme- 4: Synthesis of the new complexes with mixed ligands (L3 and L2)

5. Results and discussion:

All of our mixed ligand complexes are soluble in DMF, DMSO, methanol and ethanol. They are also stable in air. Ligands and their mixed ligand complexes were characterized by elemental analysis, table (2), molar conductivity, magnetic susceptibility, FTIR, and UV-Vis. The analytical data (C, H, N, S) of the complexes are consistent with the experimental data. The data show a metal to ligands ratio of (1:1:1) (M:L1:L2) and (1:1:1) (M:L3:L2) respectively as shown in Table 2.

Table (2) The Elemental Analysis of the ligands L1,L2 , L3 and their novel metal Mixed ligand complexes.

No	Formula	Calc.(Found) %				
		C%	H%	N%	S%	M%
1	L1= $C_{23}H_{23}N_7O_3S$	57.85 (57.91)	4.85 (4.90)	20.53 (20.39)	6.71 (6.49)	-----
2	L2= $C_{19}H_{16}N_4O_2$	68.66 (68.41)	4.85 (4.40)	16.86 (16.71)	-----	-----
3	L3= $C_{25}H_{22}N_6O$	71.07 (71.23)	5.25 (5.41)	19.89 (19.62)	-----	-----
4	$[Co(L1)(L2)Cl_2]$	53.68 (53.57)	4.18 (4.32)	16.40 (16.20)	3.41 (3.60)	6.27 (6.30)
5	$[Ni\ (L1)(L2)Cl_2]$	53.69 (53.45)	4.18 (4.39)	16.40 (16.75)	3.41 (3.85)	6.25 (6.12)
6	$[Cu\ (L1)(L2)Cl_2]$	53.42 (53.56)	4.16 (4.23)	16.32 (16.62)	3.39 (3.55)	6.73 (6.34)
7	$[Co(L3)(L2)]Cl_2$	59.74 (59.61)	4.33 (4.29)	15.83 (15.92)	-----	6.66 (6.49)
8	$[Ni(L3)(L2)]Cl_2$	59.75 (59.58)	4.33 (4.11)	15.84 (15.66)	-----	6.64 (6.58)

5.2 FTIR Spectra studies:

The FTIR spectra compartment between the complexes with the free ligands in order to determine the changes that occurred during the Complexation [17,18], all data are registered in table (3) .

The infrared spectra of the Schiff bases are considered one of the important techniques in addition to other spectral studies, especially within the range (400-1750 cm^{-1}) of the spectrum. This region includes most of the absorption bands of the active groups in the prepared ligands. Therefore, this region is characterized by its importance, as it includes the absorption bands For C=N aggregates belonging to azomethine groups, absorption bands of the aromatic C=C bond, and stretching bands belonging to the C=O ketone group belonging to isatin. Among the factors affecting stretching and bending vibrations are the nature of the compound and the associated aggregates, and the nature of these aggregates in terms of electronic density and structure Stereoisomers and their symmetry, hydrogen bonds and coordination strength [19].

As well as the presence of ions outside the coordination sphere, these factors lead to changes in the shape, energy level, and symmetry of the ligand molecule when coordination occurs between it and the metal ion as a result of the emergence of the coordination bond, and this leads to a change in the intensity and location of the main bundles of the metallic complex.

The spectrum of the ligand (L1) shows a band at frequency at 1608cm^{-1} belonging to the azomethine group (C=N). The spectrum of the ligand (L2) shows a band at frequency 1585cm^{-1} belonging to the azomethine group (C=N) too. These two bands were compared with stretch bands in the spectra of the mixed ligand complexes of ligands L1 and L2 with cobalt (II), nickel (II) and copper (II) ions, and a change in the shape and intensity of these bands was observed, in addition to the (C = O) band belonging to the primary ligand L1, which showed a change in shape, intensity and frequency shift towards frequencies Lower or higher is an indication of obtaining coordination from the oxygen atom of the carbonyl group. Also, two new bands appeared, the two bonds (M-O) and (M-N), which appeared in the spectrum of the complexes and were not present in the ligands. It indicates the occurrence of a coordination process between ligands and their mixed complexes with the metal ions under study .

The spectrum of the (L2) appears at frequency (1585 cm^{-1}) due to the stretching of the bond C=N. This band has been compared with stretch bands in the spectrum of nickel (II) and cobalt (II) mixed ligand complexes, as its shift towards Frequency (1591-1593) cm^{-1}, respectively. The shift in the band is due to the sharing of the electron doublet of the nitrogen atom of the two azomethine groups mentioned .

A broad vibration band appeared at (3153cm^{-1}) attributed to the stretching of the N-H bond present within the isatin molecule in the ligand L2. No significant change was observed in the location and shape of this band when compared with the spectrum of the complex of the mixed ligand L3and L2, which clearly indicates that no process has taken place. The tautomerism of the two nitrogen atoms and the carbonyl group of the carbon atom (2) in the isatin molecule, which indicates that the L2 ligand molecule does not lose its proton and shares it in coordination with the metal ion. The spectrum of ligand L3 also showed a strong stretching band at (3153cm^{-1}) attributed to the stretching vibrations of the NH_2 group. A significant change in the location and shape of this band was observed when compared with the spectra of the Co (II) and Ni (II) complexes, which clearly indicates the involvement of the nitrogen atom of the amine group in the coordination process[20].

The spectra of the metallic complexes also showed a new absorption band of weak intensity and at a low frequency (424-455cm^{-1}) and (497-555cm^{-1}) devoid of the ligands L2 and L2 spectra. These bands are attributed to the vibration frequency of the (M-O) and (M-N)bands , respectively. Figures (3-6) (3-8) show the spectra of each of the mixed ligands L2 and L3 complexes. Table (3) shows the results of the study of the infrared spectra of the L2 and L3 ligands and their mixed ligand with the cobalt (II) and nickel (II).

Table (3) FTIR spectra for L1,L2,L3 ligands and their mixed complexes calculated in cm^{-1}

Compounds	NH_2	C=O	C=N	C-N	M-N	M-O	Other
L1	3475 3417	1742	1585	---	---	---	C=O 1649
L2	3250 3250 3201	1742	1584 1668	1591	---	--	C=C 1616
[CO (L_1) (L_2)Cl_2]	3427	1701	1649	1593	555 516 551	456 441	C=C
[Ni (L_1) (L_2) Cl_2]	3377 3412	1732	1653	1593	516 551 497	---	----
[Cu(L_1) (L_2) Cl_2]	3202.02	1735.93	1616.35	---	549.71	466.77	OH 3473.60

L3	**3250.05**	**1724.36**	**1668.43 1591.27**	**---**	**----**	**---**	**C=C 1458.18**
$[Co(L3)(L2)]Cl_2$	**3427.51**	**1701.22**	**1649.14 1618.28**	**---**	**555.50 516.92**	**455.20**	**C=C 1460.11**
$[Ni(L3)(L2)]Cl_2$	**3412.08**	**1732.08**	**1653.00 1593.20**	**---**	**551.64 497.64**	**441.70**	**C=C 1458.18**

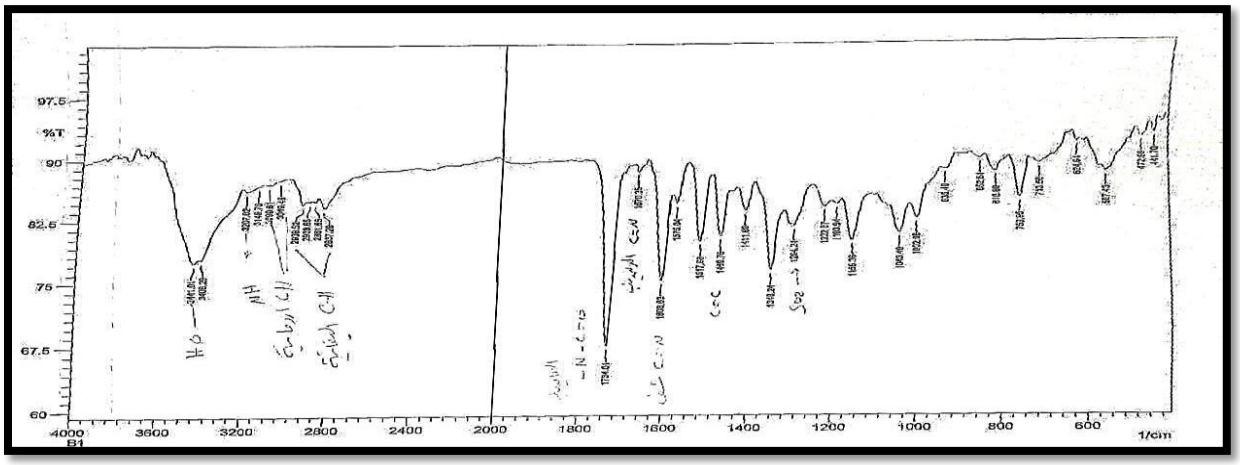


Fig (1): FTIR-spectra of the ligand L1

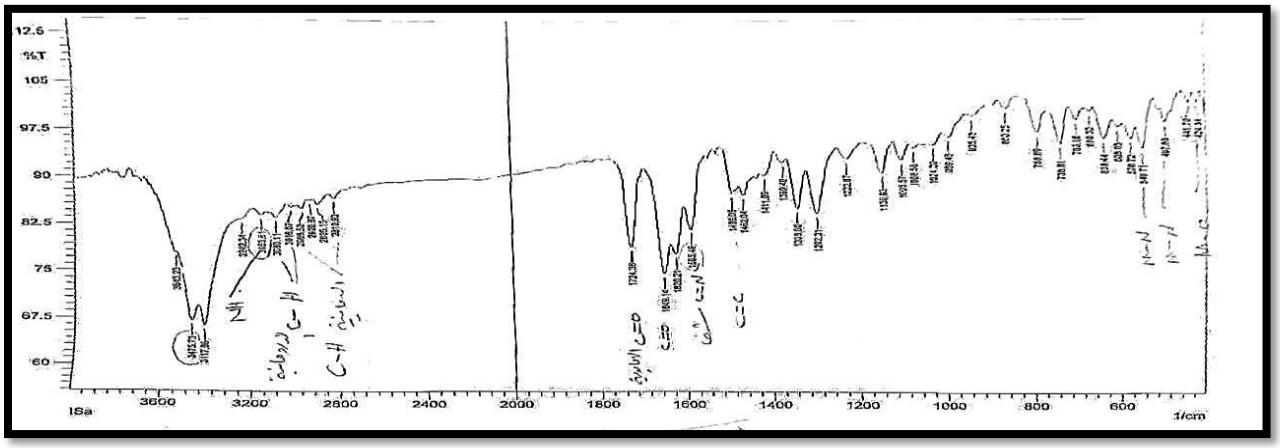


Fig (2): FTIR-spectra of the ligand L2

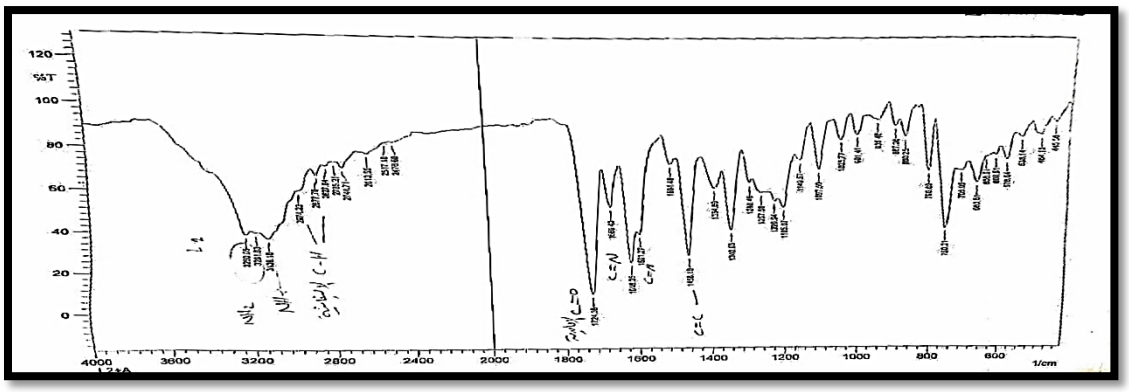


Fig (3): FTIR-spectra of the ligand L3

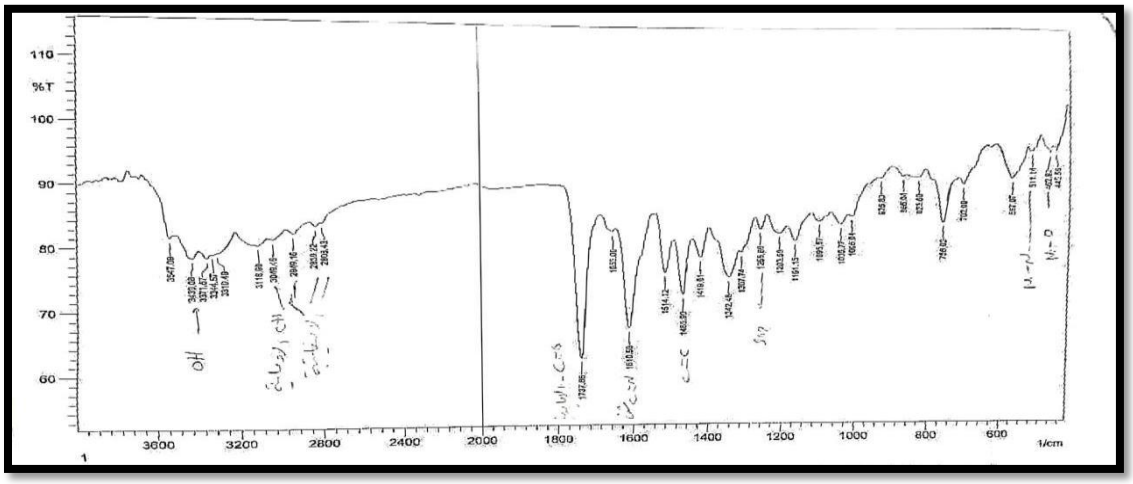


Fig (4): FTIR-spectra of mixed ligand L1 and L2 complex with Co(II)

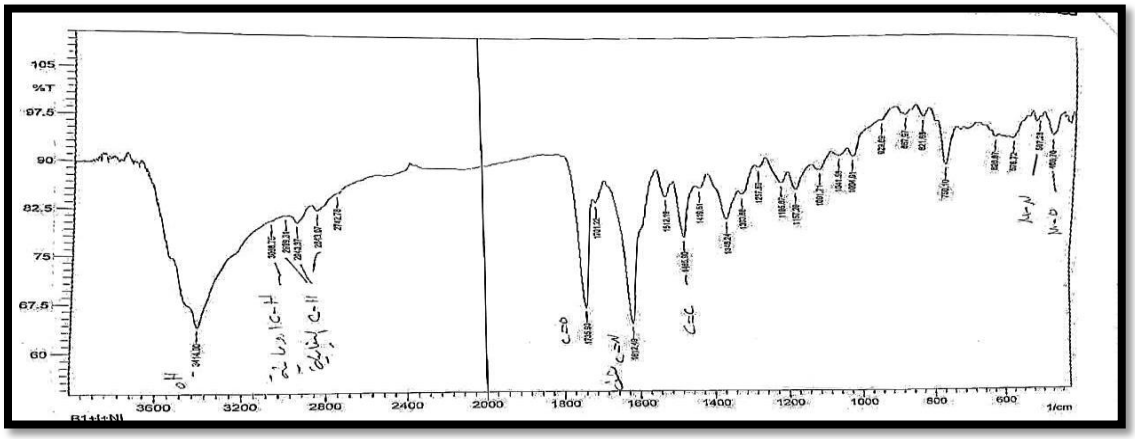


Fig (5): FTIR-spectra of mixed ligand L1 and L2 complex with Ni(II)

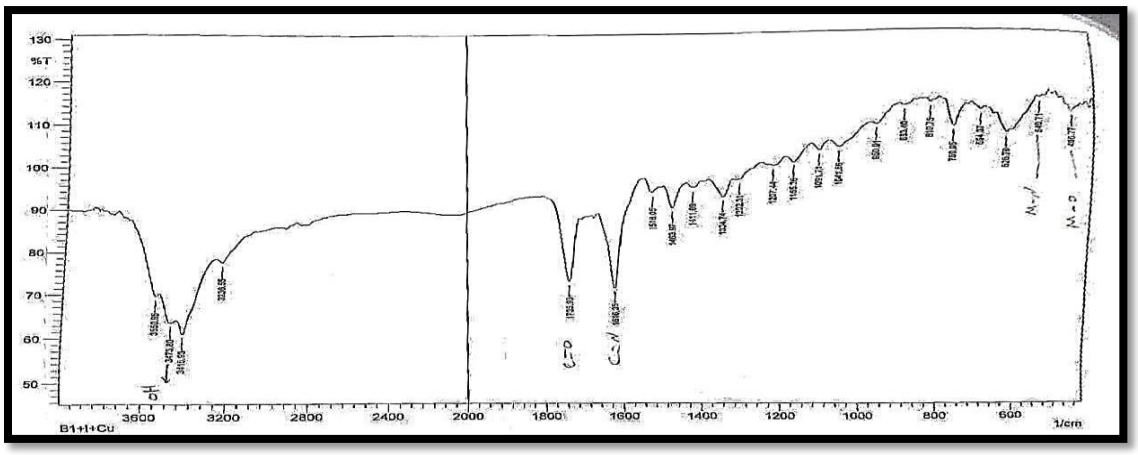


Fig (6): FTIR-spectra of mixed ligand L1 and L2 complex with Cu(II)

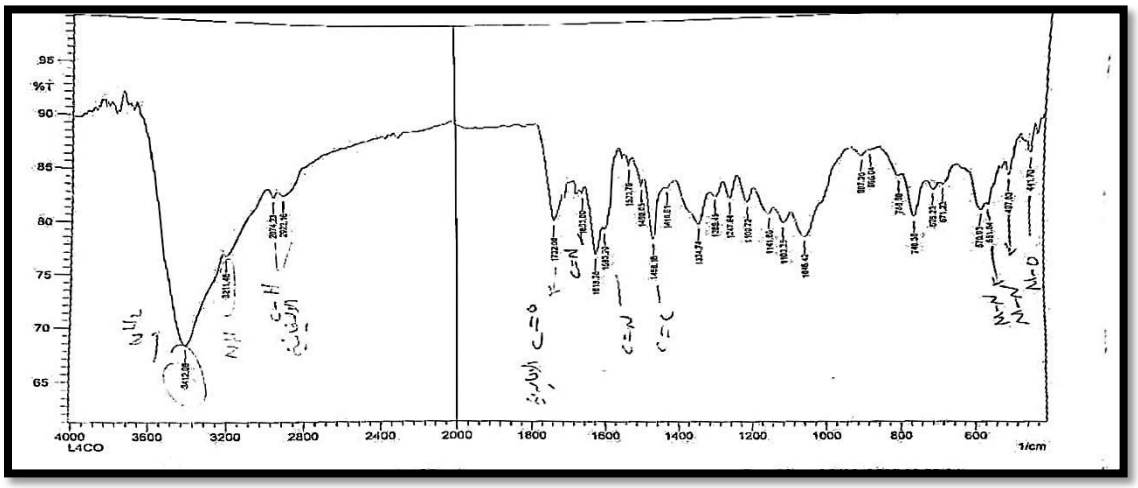


Fig (7): FTIR-spectra of mixed ligand L3 and L2 complex with Co(II)

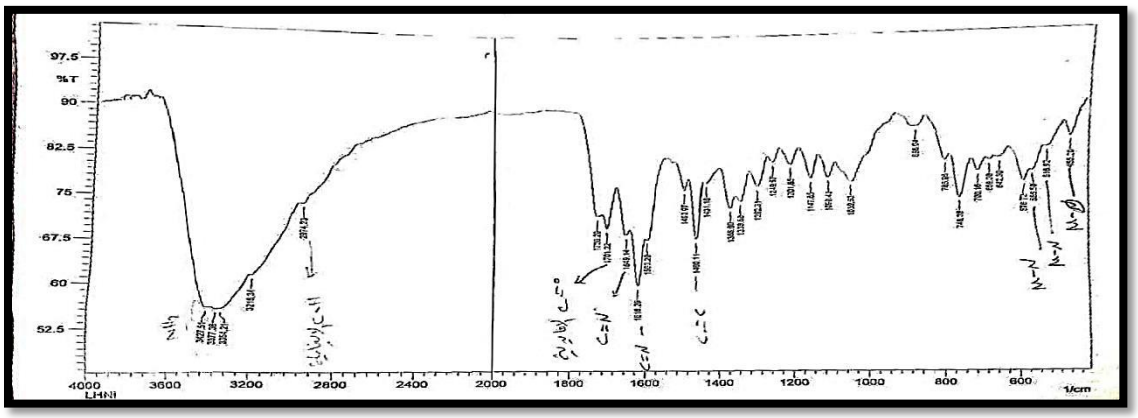


Fig (8): FTIR-spectra of mixed ligand L3 and L2 complex with Ni (II)

5.3 Magnetic susceptibility:

The magnetic susceptibility results were list in the table(4) where the value of magnetic moment of mixed ligand Complexes of Co(II) ,Ni (II) and Cu(II),which indicates the presence of the paramagnetic characteristic [21,22].

5.4 Molar Conductivity Measurements :

By the results acquired, it is obvious that the measurements of molar electric conductivity for the solutions of metallic complexes with the Schiff- Mannich base ligands in concentration of (1×10^{-3}) molar each complex at the research laboratory temperature and by using DMSO solvent , ranged between (7.55-19.88) S. $cm^2.mol^{-1}$ and (73.61, 78.29) S. $cm^2.mol^{-1}$ respectively listed in the data of these Measurements tableted in table(4), The lack of ionic characters of the mixed ligand complexes of L1,L2 and the ionic characters of the mixed ligand complexes of L3,L2 were obvious. These results are matching to what was detailed in the collected works for metallic complexes[23,24].

Table (4) Magnetic susceptibility and Molar Conductivity values .

Compounds	μ_{eff} (B. M)	Conductivity $S.mol^{-1}.Cm^2$
[CO (L_1) (L_2)Cl_2]	4.86	19.88
[Ni (L_1) (L_2) Cl_2]	2.98	10.22
[Cu(L_1) (L_2) Cl_2]	1.76	7.55
[Co(L3)(L2)]Cl_2	4.85	73.61
[Ni(L3)(L2)]Cl_2	3.41	78.29

5.5 Electronic Transition spectra studies:

The absorption electronic transitions spectra are very valuable in the assessment of effects equipped thru other methods of essential investigation.

Fig.9 the ligand (L1) spectrum in solvent (DMSO) showed three absorption peaks, two at (240nm) and (284nm) due to the electron transition of the type ($\pi \rightarrow \pi^*$) while the third peak was attributed at (441 nm) to the electron transition ($n \rightarrow \pi^*$) due to the ligand having double bonds with atoms having unshared electron pairs [22,23].

The spectrum in Fig.10 of the ligand (L2) in solvent (DMSO) showed two absorption peaks, one at (315nm) due to the electron transition of the type ($\pi \rightarrow \pi^*$) while the second peak was attributed at (449 nm) to the electron transition ($n \rightarrow \pi^*$) due to the ligand having double bonds with atoms having unshared electron pairs [23].

The spectrum in Fig.11 of the ligand (L3) in solvent (DMSO) showed two absorption peaks, one at (295nm) due to the electron transition of the type ($\pi \rightarrow \pi^*$) while the second peak was attributed at (435 nm) to the electron transition ($n \rightarrow \pi^*$) due to the ligand having double bonds with atoms having unshared electron pairs [24].

The spectra of the ligands L1 and L2 were compared with that of cobalt (II) mixed ligand, which was show peak at (460 nm) has been recognized to the electron transition , $\nu 3 = {}^4T_1g\ (F) \rightarrow {}^4T_1g\ (P)$ This fact is consistent with the literature on the appearance of this band in octahedral cobalt(II) complexes [25].

The UV-visible spectrum of nickel (II) mixed ligand complex solution recorded an absorption peak at (465 nm) has been attributed to the electron transition $v3={}^3A_2g(F) \rightarrow {}^3T_1g\ (P)$ and this is consistent with what was mentioned in the literature regarding octahedral nickel(II) complexes[25,26].

The UV-visible of mixed ligand complex L1 and L2 solution with Copper (II) spectrum showed peak at (459nm) due to the to the Charge Transfer type (L-M) and This is similar to previous research's [27]. The spectra of the free ligands is red-shifted in complexes, suggesting an octahedral geometry around metal (II) in the complexes as showed in Fig.(12, 13 and 14) . The spectra of the ligands L3 and L2 were compared with that of cobalt (II) mixed ligand complex solution , which showed a peak at (560 nm) has been recognized to the electron transition , $\nu 3 = {}^4T_1g\ (F) \rightarrow {}^4T_1g\ (P)$ This fact is consistent with the literature on the appearance of this band in octahedral cobalt(II) complexes (28). The UV-visible spectrum of nickel (II) mixed ligand complex solution recorded an absorption peak at (559 nm) has been attributed to the electron transition $v3={}^3A_2g(F) \rightarrow {}^3T_1g\ (P)$ and this is consistent with what was declared in the collected works as regards of octahedral shape in Nickel(II) complexes [29-32].

The free ligands spectra were red-shift in complexes, proposing an octahedral geometry around metallic complexes as showed in Fig.(15) and (16) . All these data

were listed in Table (5) shows the transition of electronic spectra for the ligands **L1,L2,L3** and their metallic mixed ligand complexes in DMSO solvent.

Table (5) The ligands L1, L2 Electronic Spectra and their metallic mixed ligand complexes in DMSO solvent.

Compounds	Absorption band nm	Assignment	Proposed Geometrical
L1= $C_{23}H_{23}N_7SO_3$	**240nm** **284nm** **441nm**	**$\pi \longrightarrow \pi^*$** **$\pi \longrightarrow \pi^*$** **$n \longrightarrow \pi^*$**	---
L2= $C_{19}H_{16}N_4O_2$	**315 nm** **449 nm**	**$\pi \longrightarrow \pi^*$** **$n \longrightarrow \pi^*$**	**...**
[CO (L_1) (L_2)Cl_2]	**460nm**	**$^4T_1g(F) \longrightarrow {}^4T_1g(P)$**	**Oh**
[Ni (L_1) (L_2) Cl_2]	**465nm**	**$^3A_2g(F) \longrightarrow {}^3T_1g(F)$**	**Oh**
[Cu(L_1) (L_2) Cl_2]	**456 nm**	**C.T**	**Oh**
L3= $C_{25}H_{22}N_6O$	**295nm** **435nm**	**$\pi \longrightarrow \pi^*$** **$n \longrightarrow \pi^*$**	---
[Co(L3)(L2)]Cl_2	**560nm**	**$^4T_1g(F) \longrightarrow {}^4A_2g$**	oh

$[Ni(L3)(L2)]Cl_2$	559nm	$^3A_2g(F) \longrightarrow {}^3Tig(F)$	Oh

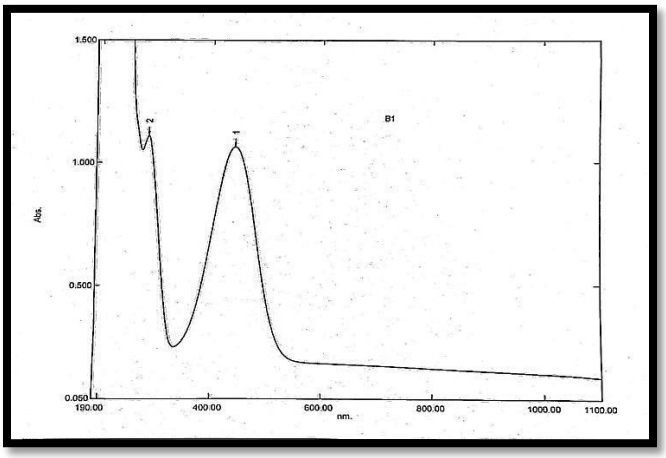


Fig. (9): UV-Vis. spectra of the Ligand (L1)

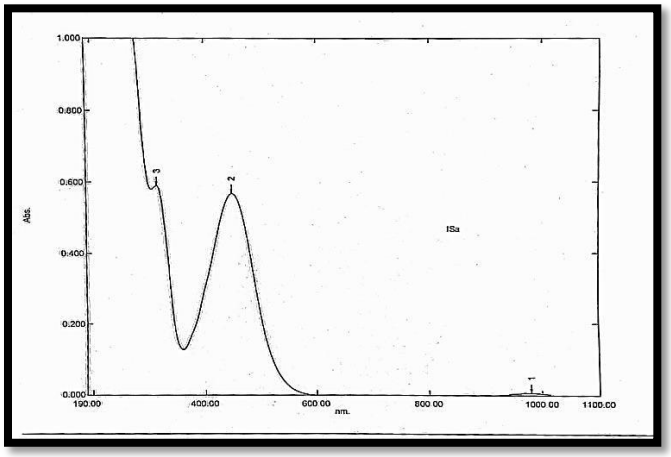


Fig. (10): UV-Vis. spectra of the Ligand (L2)

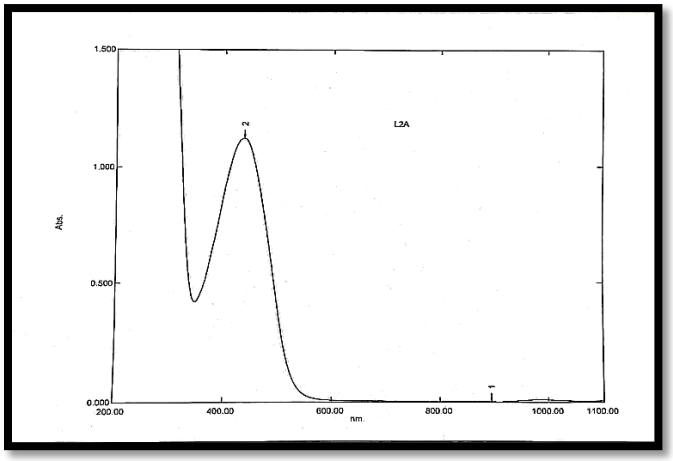


Fig. (11): UV-Vis. spectra of the Ligand (L3)

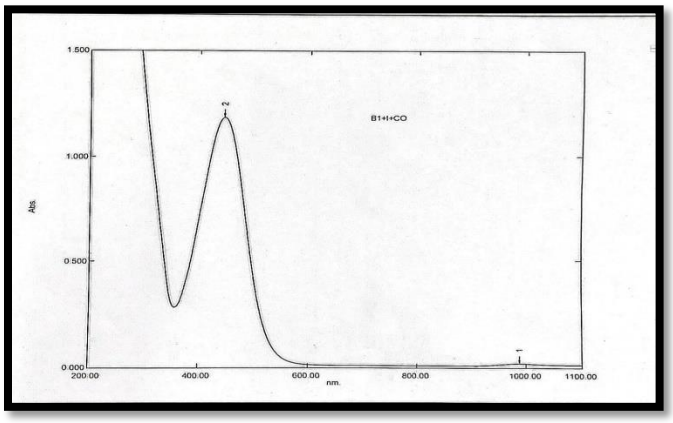


Fig. (12): UV-Vis. spectra of the mixed Ligand L1and L2 complex of Co(II)

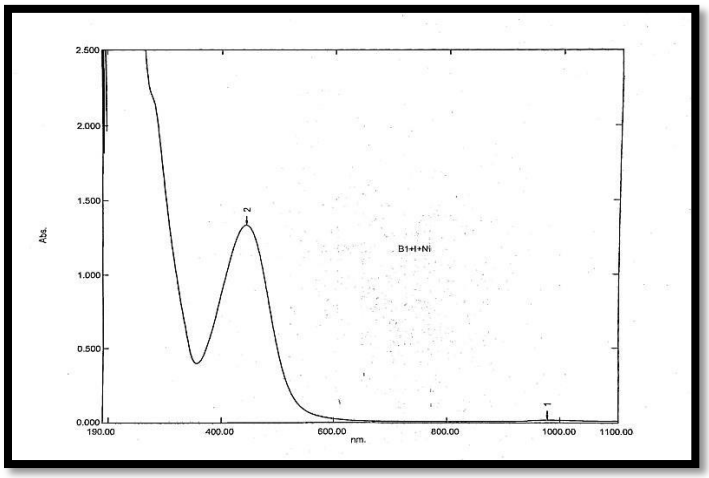


Fig. (13): UV-Vis. spectra of the mixed Ligand L1and L2 complex of Ni(II)

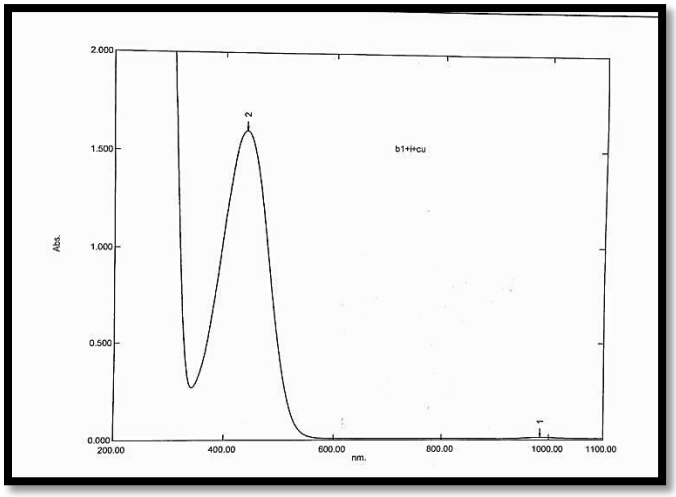


Fig. (14): UV-Vis. spectra of the mixed Ligand L1and L2 complex of Cu(II)

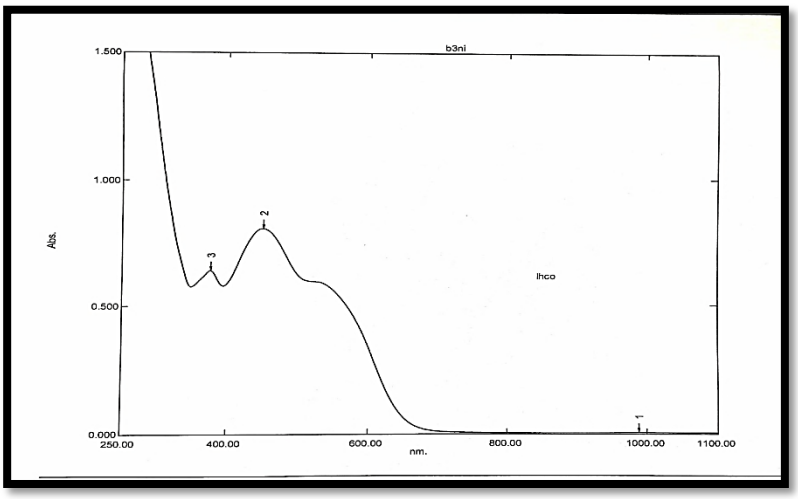


Fig. (15): UV-Vis. spectra of the mixed Ligand L3and L2 complex of Co(II)

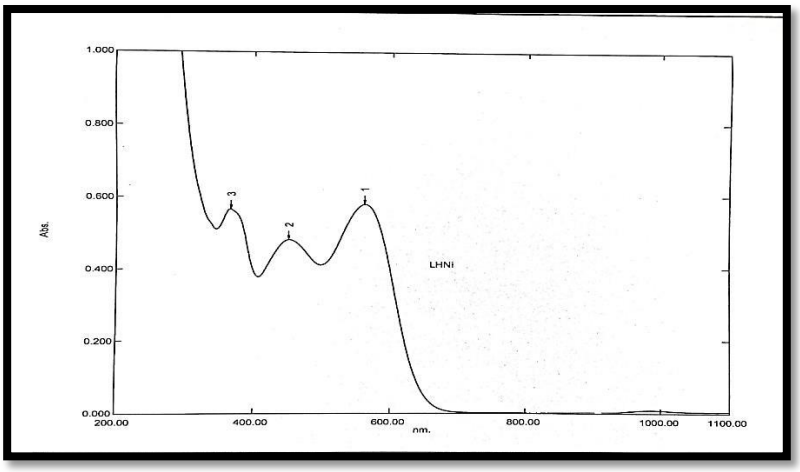


Fig. (16): UV-Vis. spectra of the mixed Ligand L3and L2 complex of Ni(II)

5.6 Detection of chloride ions: -

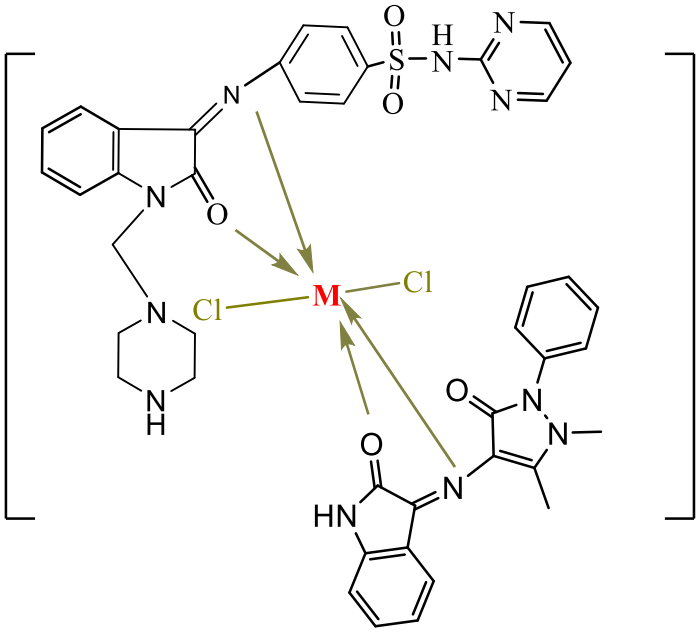
In order to verify the presence of chloride ions outside the coordination sphere or not for all the coordination mixed ligand complexes prepared, the detection process was carried out in light of the interaction of each metal complex dissolved in an alcohol solution with an aqueous solution of silver nitrate [27-29], which led to the absence of turbidity or the appearance of a white precipitate of Silver chloride, AgCl, in solutions, which is a clear indication of the absence of chloride ions outside the coordination ball, which supports the validity of the proposed structures of the mixed ligand L1 and L2 complexes under study. While the mixed ligand complexes of L3 and L2 showed the presence of a chloride ion outside the coordination sphere, by observing the precipitation of a white precipitate of silver chloride and the turbidity of the solution when conducting this detection.

6. Proposed structural formula of mixed ligands

Depending on the results of measurements and detection of the absence of chloride ion outside the coordination sphere of the chelated complexes prepared in our study and the data of infrared and ultraviolet-visible , CHNS elemental analysis and atomic absorption techniques, and compared with what was reported in the literature (14,20,27) about the coordination sites available in the Schiff Mannich base ligand L1 and Schiff base ligands L2 and L3 with the selected metal ions in this study .We can conclude that the two ligands L1 as primary ligand and L2 as Co-ligand behaved as neutral bi-chelated ligands with cobalt (II), nickel (II) and copper (II) ions to form two five-sided metallic hetero-rings with these ligands, as the binding of the two bi-chelated ligand molecules with The metal ion provides four coordination bonds with the presence of a di negatively charged of chloride ions to offset the positive charge of the central metal ion to form the octahedral structure.

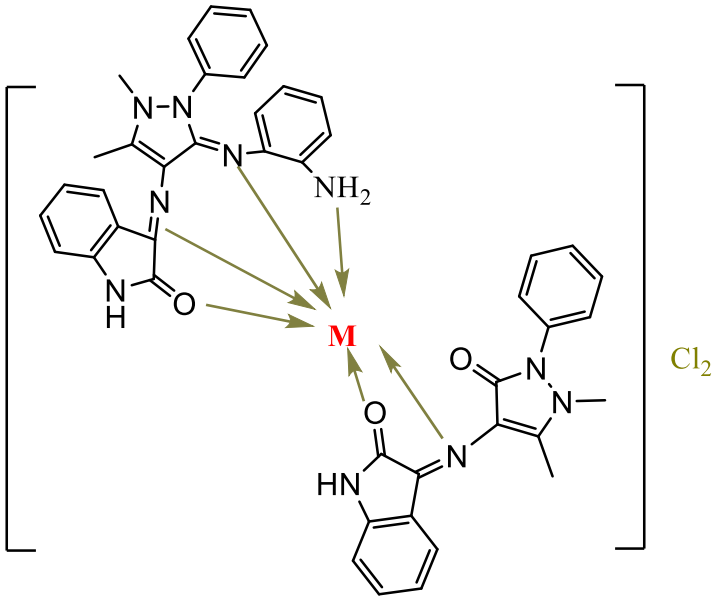
With regard to the L2 and L3 mixed ligand complexes, the L3 ligand behave as neutral tetra- chelated ligand and L2 behaved as neutral bi-chelated ligand. The octahedral structure was proposed for the prepared complexes of cobalt (II) and nickel (II) ions with the mix of ligands L3 as primary ligand and L2 as Co-ligand . As well as detecting the presence of chloride ions outside the coordination sphere. The magnetic susceptibility of the mixed ligand complexes at room temperature were consistent with the octahedral geometry, as is the magnetic susceptibility around the center of the surrounding metal ions. The mixed ligand complexes with L1 and L2 showed low conductivity values. This prove that the complexes were non-electrolytic in nature . while the mixed ligand complexes with L3 and L2 showed high conductivity values. This prove that the complexes were electrolytic characters. After the results reached it is possible to

suggested the octahedral structure of all metallic mixed ligand complexes with the two ligands L1 and L2.and the ligands L3 and L2 . The Suggested Structural of metallic complexes can be demonstrated in the Figures (17 and 18) .



M= Co (II) , Ni(II) and Cu(II)

Fig.(17): Proposed Structural of the mixed ligand complexes with L1 and L2



M= Co (II) , Ni(II)

Fig.(18): Proposed Structural of the mixed ligand complexes with L3 and L2

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