Synthesis, Identification of Co(II), Cu(II) and Ni(II) Complexes with A Schiff Base–Azo Ligand Derived from Imidazol Derivatives, 4- Aminoacetophenon and 4- Chloroaniline and Study Their Physical Properties and Their Thermodynamic Stabilities

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Abstract

The complexes of Co(II), Cu(II) and Ni(II) were synthesized by using schiff base – azo as a ligand, which were prepared under this study by the reaction between the Schiff base diazonium salt and the imidazole derevitive. They were characterized by element analysis, FTIR spectroscopy and UV.VIS. spectroscopy. Their electric conductivity and magnetic features were determined. Their stepwise and overall stability constants and their thermodynamic data (ΔG^{O}, ΔS^{O} and ΔH^{O}) were determined. The results showed that all the complexes have paramagnetic features and all of them have good conductivity. The formula of the complexes under this paper were suggested by using the mole ratio method which lead to the formation of (1 : 2) metal : ligand formula for all the complexes. In all the complexes the coordinated sites was through N atoms of the azo groups and N atom of the imidazol ring. The suggested geometrical shapes of the complexes was the octahedral shape due to the (d^2sp^3) hybridization. Their stepwise stability constants were determined, it was found that for all the complexes they were increased toward the addition of ligand that because of the chelate effect. Their overall stability constants were determined, it was found that for all the complexes were high that because of the chelate effect. Their thermodynamic functions (ΔG^{O}, ΔS^{O} and ΔH^{O}) were had negative value, that refer to good stability for the complexes and these results were satisfied with the spontaneous reaction and high stability complexes.

Keywords : schiff base – azo ligand, stepwise stability constant, overall stability constant, metal complexes, coupling reaction.

1 – Introduction

In 1885 Peter Griess had been showed that the aromatic amines rapidly react with nitrose acid under cooling to give easy – water solubility salts, which called diazonium salts[1], these salts have electrophilic properties so it can coupling with the high electronic density compounds such as the aromatic compounds with - NH_2 , - NR_2 , - OH , - OR , groups to obtain the azo compounds[2]. Aromatic azo compounds are widely used and very important in different areas of life[3]. There are two types of aromatic azo compounds, the first one is homogeneous azo compounds which composed of two homogeneous aromatic rings laying at the two sides of the azo group, the second type is non – homogeneous azo compounds which contain a non – homogeneous aromatic ring on one of sides of the azo group[4].Our ligand under this study belongs to the second type, the compounds of this type are more uses and important than the first one because it has active atom (N, O, S) which shares building the aromatic ring and it can form the coordination bonds with metallic ions viaits non – bonding pairs of electron[5].

The high molecular weight of a coordination complexes have a wide importance in field of clinical and analytical chemistry in recent days that because of their high stability and their wide use[6-8]. The organic reagent which have the chelating properties, have been used as a photometric reagents in analytical chemistry due to their visibly complexes with transition ions[9,10]. The coordination of these compounds with metal ions depends upon the nature of the metal, its valence, the number of the donor atoms, the type of the chelating rings and the pH of the reaction medium[11].

The ability to coordinate and the probability to produce stable complexes increased if the ligand contains rather than one donor atom which localized on suitable position within the ligand molecule[12]. Complexes are compounds containing a central atom or ion which usually a metal with vacant orbitals (Lewis acid) surrounded by several electron donor items (Lewis bases) that are recognized as ligands[13]. The coordination of a polydentate ligand to an ion leads to the formation of a chelating complex so as do a saturated diamines such as 1,2-ethandiamine (en) which forms more flexible five chelate ring[14]. From 20 amino acids present in proteins, glycine is one of these has a relatively potential metal ligands, [15]. The metal ion in aqueous solution is hydrated for example the ion ($[M(H_2O)_6]^{Z+}$), by the addition of neutral ligand to its solution that lead to the formation of a series of complexes:$[M(H_2O)_5L]^{z+}$, $[M(H_2O)_4L_2]^{Z+}$…………$[M L_6]^{Z+}$[16]. The chelate effect enhanced the stability of the chelating complex system as compared to a similar non – chelating complex, so to understand the chelate effect properly we must study the thermodynamic stability of the complexes[17]. The oxidation state and the ionic size of the central atom are an important factor which effects on the complex stability, the high oxidation state leads to high stability and the high ionic size lead to low stability[18].

2-Practical Part

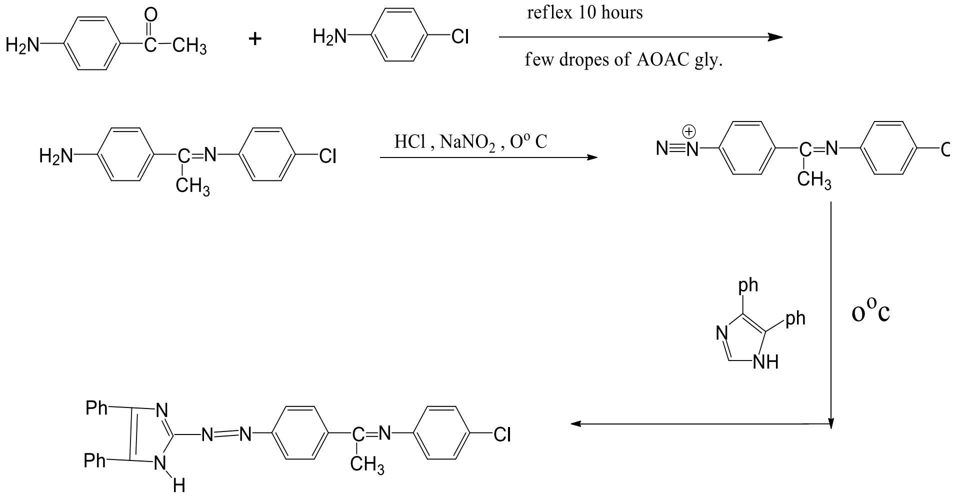
Materials:

All the materials which were used in this paper were so sensitive to moisture that they had been kept in dry containers. The water used was double distilled water. Metal ion solutions (0.01 M) were prepared from theirs chloride salts ($NiCl_2$ 99%, $COCl_2$ 98%, $CuCl_2$99%) All the reagents were of high purity (99%) , they had been get from BDH and FULKA companies. Ammonium nitrate (2M) was used as a background electrolytic solution. The commercial name of the ligand is schiff base – azo ligand.

Preparation the ligand:

1 - Preparation of schiff base: 1.35 g (0.01 mol)of p - amino acetophenone was dissolved in 25 ml of absolute ethanol, 1.72 gm (0.01 mol) of p - chloroaniline was dissolved in 25 ml of absolute ethanol, the two solutions were mixed and refluxed for 10 hours at 70^{O} C with few drops of glacial acetic acid. by the time a yellow to orange crystals of Schiff base was formed.

2 – preparation of azo – Schiff base ligand:2.445 gm (0.01 mol) of Schiff base was dissolved in 20 ml of 5 M HCl at 0^{O} C, 0.07 gm (0.01 mol) of sodium nitrite was dissolved in 10 ml of distilled water and added slowly by stirring at this temperature for 15 minute to obtain the diazonium salt. 2.2 gm (0,01 mol) of 4,5 – diphenyl imidazole, was dissolved in 50 ml of 10 % NaOH, was added slowly to the diazonium salt solution under cooling with stirrer, soon an orange solution was formed. by adjusted the pH to 7, a large amount of orange precipitate was formed. The scheme (1) show these reactions.



Preparation the complexes:

Specific weight of the metal salt [metal (Ni, Cu, Co) chloride] dissolved in D.W. and specific amount of the ligand dissolved in ethanol then the two solutions mixed together and refluxed to 70 C^{0} for 30 minutes, a precipitate of the complexes were formed, separated, washed by D.W. and dried.

FTIR Spectra:

FTIR spectrum for the ligand and their complexes were recorded by using FTIR–84005 shimadzu spectroscopy with KBr discs in the range 400 – 4000 cm-1. Figures (1– 4) shows these spectra. Table (1) shows the important absorption bands for the functional groups of the ligand and the complexes

Determination λmax of the ligand and its complexes:

Maximum wave length (λmax) of the ligand and for each its complexes solution (10^{-3} M) were obtained by using UV. VIS. Spectroscopy scanning (UV–1650 PC shimadzu spectroscopy with quartz cells). The figures (5– 8) shows the electronic spectra for the ligand and the complexes.

Table (1): Important FTIR absorption bands for the ligand and the complexes:

assignment	ligand	Co^{2+} + L	Cu^{2+} + L	Ni^{2+} + L
N – H	3441	3444	3429	3338
C – H (st.)	3387	3200	3182	3300
C – H (ben.)	1149	1111	1116	1107
N = N	1578	1512	1516	1539
C = N	1666	1627	1600	1627
C – N	1396	1361	1361	1361
C - Cl	648	663	559	667

Determination the formula of complexes:

The formula of each complex was determined by using the continuous variation method. The formula (1 : 2) metal : ligand ratio, for all complexes under this research, was found.

Elemental Analysis:

Element analysis in solid complexes were measured by using EURO element analyzer and shimadzu –AA–160 atomic absorption – flame emission spectrophotometer. Table (2) shows the results of the elemental analysis.

Table (2): The results of the elemental analysis for the prepared complexes

M. F.	Azo- schiff L	Co^{2+} + Sch. Bas. L	Cu^{2+} + Sch. Bas. L	Ni^{2+} + Sch. Bas. L
C	73.26(73.21)	66.60(66.32)	66.60(66.43)	66.59(66.18)
N	14.74(14.57)	13.39(13.04)	13.40(13.11)	13.39(13.06)
H	4.63(4.21)	4.59(4.32)	4.59(4.01)	4.59(4.30)
Cl	7.36(7.12)	6.69(6.37)	6.70(6.16)	6.69(6.40)
M		5.64(5.12)	5.67(5.29)	5.65(5.19)

Molar conductivity study:

Molar conductivity for the aqueous solutions of the complexes (10^{-3} M) at 25 ^{o}C were measured by using INOIL AB 740 potentiometer. Table (3) shows the results of this study.

Magnetic properties study:

Magnetic susceptibility of the complexes were established due to Gouy Balance Method by using MSB – MKI magnetic susceptibility measurement balance. The effective magnetic momentum (μeff) at 25^{o}C was calculated and the results are shown in table (3).

Table (3): Physical properties of the prepared complexes

Item	complex	Co ion + comp.	Cu ion + comp.	Ni ion + comp.
M. W.	475	1045	1049	1044
Am (ms/cm)		4.55	3.21	3.01
μ_{eff} (BM)		1.1	1.2	3.2
λ_{max} (nm)	434	452	509	500

3 - Theoretical calculations

Thermodynamic stability studies [15 - 17]:

To calculate the concentration of the metal ion, the experiment had been done by using ion selective electrode technique in 2 M NH_4NO_3 aqueous solution and the concentrations of the metal salt and the ligand (bidentate ligand) were 0.01 M. The stability constant (K), for the formation of the complex obtains as follow:

$$[M(H_2O)_6]^{2+} + L \leftrightarrow [M(H_2O)_4L]^{2+} + 2(H_2O)$$

$$K = \frac{[M(H_2O)_4L]^{2+}}{[M(H_2O)_6]^{2+}[L]}$$

$[M(H_2O)_6]$ can be obtain from the electric cell (ion selective electrode) and K can be obtain from the above equation, ΔG^O can be obtain from the relation :

At equilibrium:

$$[M(H_2O)_4L] + [(H_2O)_6] = 0.01 \; and \; [M(H_2O)_6] + [L]$$

$$\Delta G^O = -RT\ln K$$

ΔH^O can be obtaining by using thermometric titration SO: $K = \frac{0.01-[M(H_2O)_6]}{[M(H_2O)_6]^2}$ calorimetric method, in which the ligand adds slowly to the metal and the temperature record as the addition proceeds.

ΔSO can be obtaining from the relation:

$$\Delta G^O = \Delta H^O - T\Delta S^O$$

The stepwise stability constants(Kn) and the overall stability constant (β) for the formation of the complex $[ML_3]^{2+}$ are:

$$[M(H_2O)_4L] + [(H_2O)_6] = 0.01 \; and \; [M(H_2O)_6] + [L]$$

$$K_1 = \frac{[M(H_2\,O)_4L]^{2+}}{[M(H_2\,O)_6]^{2+}\,[L]}$$

$$[M(H_2)_4L]^{2+} + L \leftrightarrow [M(H_2O)_2L_2]^{2+} + 2H_2O$$

$$K_2 = \frac{[M(H_2\,O)_2\,L_2]^{2+}}{[M(H_2\,O)_4L]^{2+}\,[L]}$$

$$[M(H_2O)_2L_2]^{2+} + L \leftrightarrow [ML_3]^{2+} + 2H_2O$$

$$[M(H_2O)_6]^{Z+} + L_3 \leftrightarrow [ML_3]^{Z+} + 6(H_2O)$$

$$K_3 = \frac{[ML_3]^{2+}}{[M(H_2\,O)_2L_2]^{2+}\,[L]}$$

The overall stability constant (β) is:

$$[M(H_2O)_6]^{Z+} + L_3 \leftrightarrow [ML_3]^{Z+} + 6(H_2O)$$

$\beta = K_1\,K_2\,K_3$

$\log \beta = \log K_1 + \log K_2 + \log K_3$

$$[M(H_2O)_6]^{Z+} + L_3 \leftrightarrow [ML_3]^{Z+} + 6(H_2O)$$

$$\beta = \frac{[ML_3]^{Z+}}{[M(H_2O)_6]^{Z+}[L]^3}$$

Table (4): The results of the stepwise and overall stability constants

ion	Moles of L	Con of ion (M)	Stepwise stab. const. (K)	Log K	Log β	Overall stab. Const. (β)
Co ion	1	0.0034	K1=570.9	2.76	log β_1=2.76	2 * 10^9
Co ion	2	0.0025	K2=1209.6	3.12	log β_2=5.88	
Co ion	3	0.0017	K3=2862.1	3.45	log β_3=9.30	
Cu ion	1	0.0036	K1=493.8	2.69	log β_1=2.67	8 * 10^8
Cu ion	2	0.0030	K2=777.7	2.89	log β_2=5.55	
Cu ion	3	0.0025	K3=1200.0	3.08	log β_3=8.90	
Ni ion	1	0.0062	K1=100.0	2.00	log β_1=2.00	4 * 10^6
Ni ion	2	0.0052	K2=200.0	2.30	log β_2=4.30	
Ni ion	3	0.0041	K3=347.0	2.54	log β_3=6.60	

Table (5): The results of the thermodynamic functions

complex	ΔH^O (kj/mol)	ΔG^O (kj/mol)	ΔS^O (kj/mol)
Co ion + comp.	-67.9	-53.8	-0.04
Cu ion + comp.	-70.9	-51.5	-0.063
Ni ion + comp.	-41.3	-38.8	-0.013

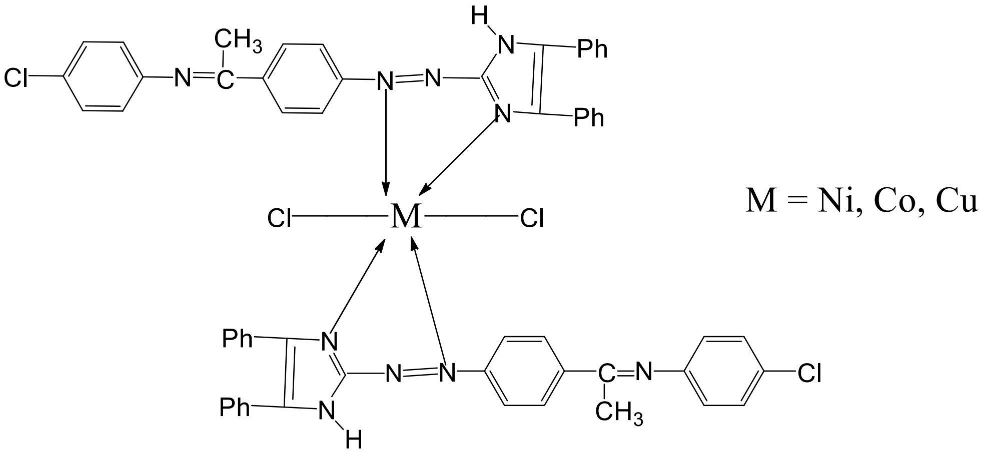
4 - Results and Discussion

The results of the stepwise stability constants (Kn) and overall stability constant (β) for the complexes are shown in table (4), and the results of the thermodynamic functions (ΔG^O, ΔS^O and ΔH^O) are shown in table (5). Figures (8, 9 and 10) show the relation between the number of ligand moles and log K for the complexes. All the measurements established at 303 o K.The FTIR spectra of the ligand and the complexes show the most important absorption bands within the range (4000 – 400) cm-1. The important stretching bands in the ligand spectrum belongs to C-H, N-H, C=N, N=N,C-N, C=C, C-Cl and C-C bands. The shifting observed in the absorption bands, after the coordination with the metal ions under this research, supports that the coordination had been occurred between the metal ion and the ligands via the N imidazol atoms and N=N group.

The ligand electronic spectrum shows that there is a principle band,434 nm which belongs to the charge transfer band[18]. Clear displacement of the principal band of the ligand (434 nm) had occurred after the formation of the complexes, that refer to that the electronic environment of the coordinated atom had been changed. This result agree with the published papers which used like this ligand [19,20].

The results of the molar conductivity measurements indicate that the complexes have good conductivities due to the positive charge on the coordination core and the negative on the neighbor ion. The magnetic properties indicate that all the complexes have paramagnetic properties, [21].

Schem 2 showed the proposed shape of the complexes.



M = Ni, Co, Cu

Schem 2: the proposed shape of the complexes

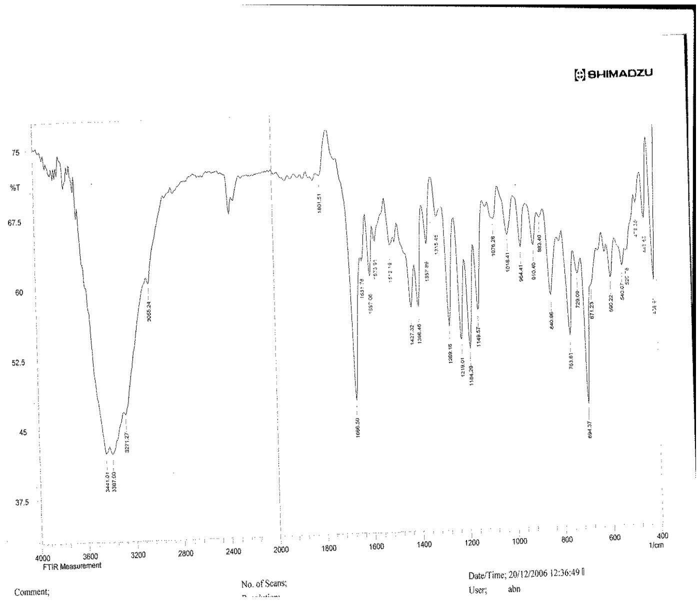


Figure (1): FTIR spectra for the ligand

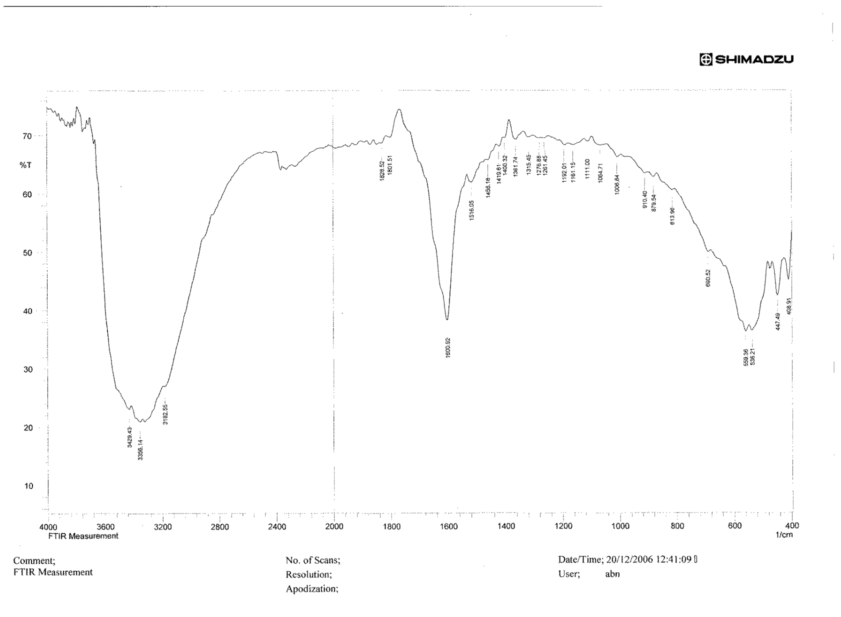


Figure (2): FTIR spectra for the Co ion + ligand

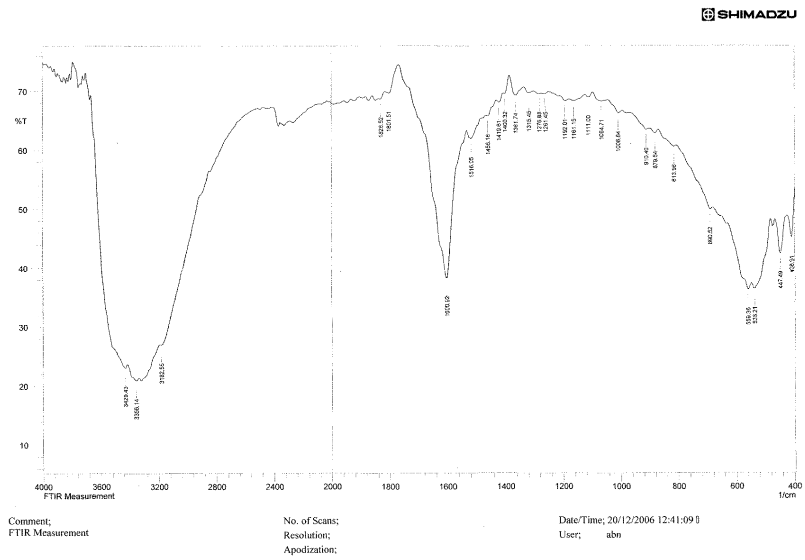


Figure (3): FTIR spectra for the Cu ion + ligand

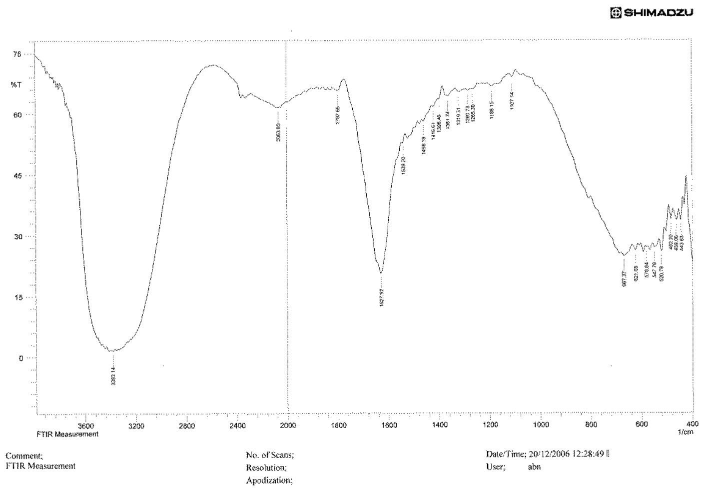


Figure (4): FTIR spectra for the Ni ion + ligand

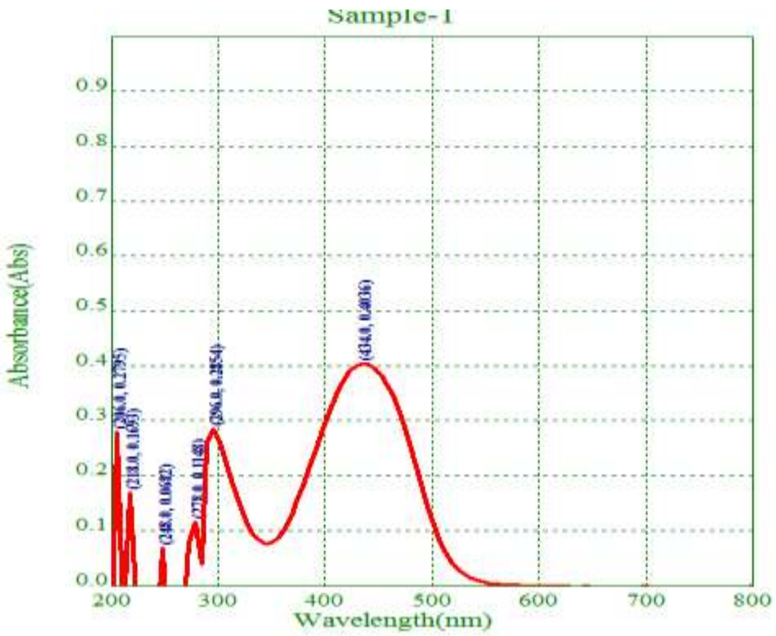


Figure (5): The electronic spectra for the ligand

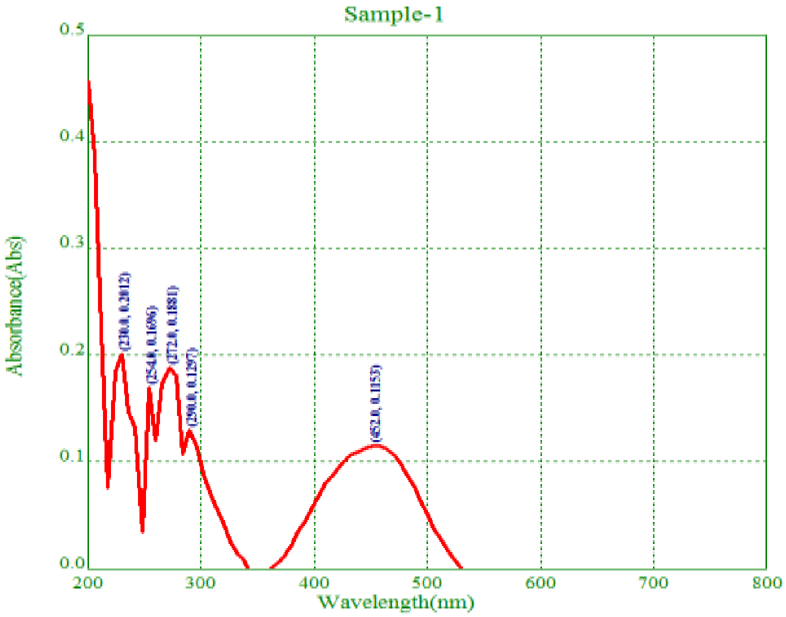


Figure (6): The electronic spectra for the Co ion + ligand

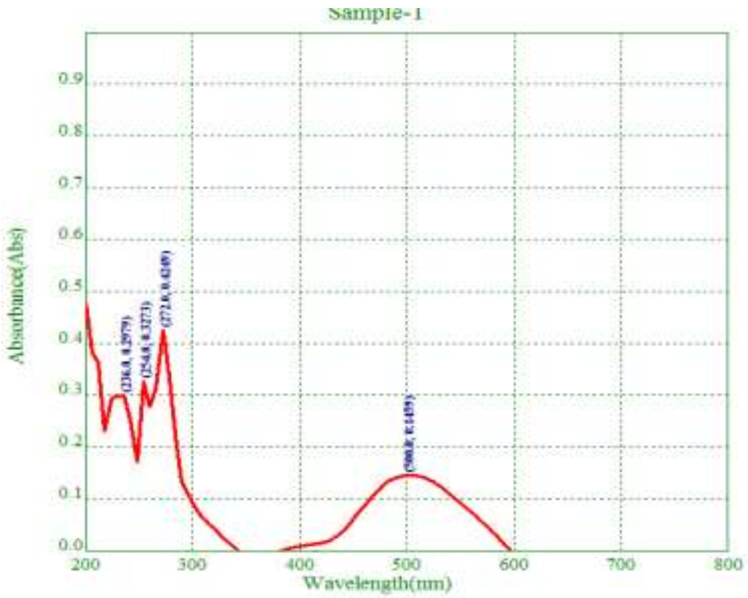


Figure (7): The electronic spectra for the Cu ion + ligand

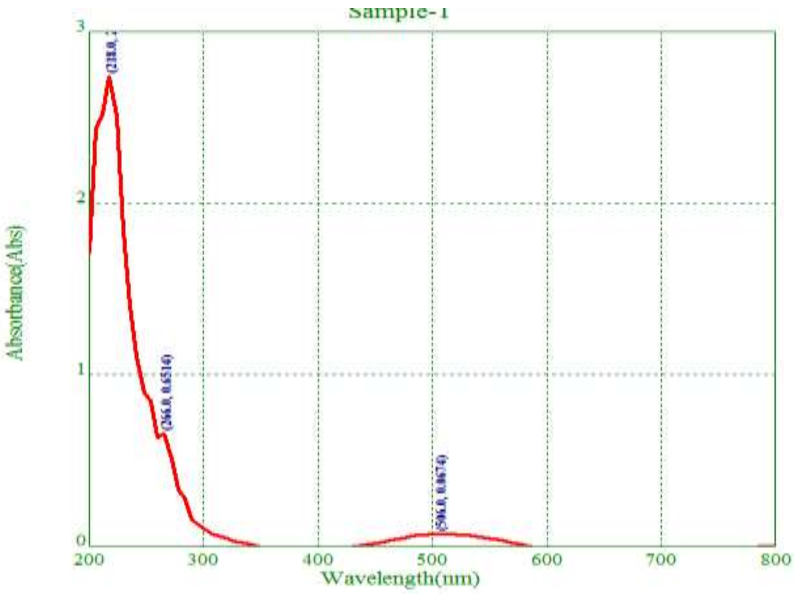


Figure (8): The electronic spectra for the Ni ion + ligand

Conflict of Interests.

There are non-conflicts of interest .

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الخلاصة

حضرت معقدات الكوبالت الثنائي والنحاس الثنائي والنيكل الثنائي باستخدام ليكاند آزو- قاعدة شف والتي حضرت في هذه الدراسة من تفاعل ملح الدايوزونيوم لقاعدة شف مع مشتق الايميدازول . شخصت هذه المعقدات بواسطة عدة تقنيات CHN وتقنية تحليل العناصر FTIR ومطيافية الاشعة تحت الحمراء .UV.VISBمطيافية الاشعة المرئية-البنفسجية وعينت الصفات المغناطيسية والكهربائية لهذه المعقدات كما عينت ثوابت الاستفرارية الكلية والمرحلية والخواص الثرموديناميكية وقد وجد ان كل المعقدات لها خواص بارامغناطيسية ولها توصيلية كهربائية جيدة. استخدمت طريقة النسب المولية لتعيين صيغة المعقدات وبينت النتائج انها تمتلك التركيب (1:3) ليكاند: فلز في كل المعقدات. ان التناسق كان عبر ذرة النتروجين لمجموعة الآزو وذرة النتروجين لحلقة الايميدازول وان الشكل الهندسي لهذه المعقدات d^2sp^3 هو ثمانية السطوح. ان ثوابت الاستقرارية المرحلية والكلية تزداد باضافة الليكاند والسبب يعود الى التأثير الكليتي لليكاند وان قيم الدوال الثرموديناميكية كانت سالبة مما يدل على ان التفاعل تلقائي والمعقدات ذات استقرارية عالية.