Synthesis and Characterization of Co (II), Ni (II) and Cu (II) Complexes via Schiff Base Derived from Dithiooxamide and Salicylaldehyde

Hayder H. AL-Hmedawi   Rawaa Abdulkhaleq
Dept. of Chemistry, College of Science, University of Kerbala

ABSTRACT

The first part of this work was to optimize the synthesis of a Schiff base(N,N'-bis (2-hydroxybenzlidene) dithiooxamide (LH)) derived from the reaction between the dithiooxamide with salicyldehyde. The reaction was reflexed for 6 hours at 70 ºC. Three types of complexes were synthesized using metal of ions cobalt (II), nickel (II) and copper (II).The second part was to characterization of prepared compounds and study the properties of these compounds. Infrared spectroscopy (FT-IR) ,NMR-spectroscopy, UV- Visible spectroscopy and Atomic absorbtion were used to identify the structure of the compounds. The magnetic susceptibility was measured; magnetic moment of cobalt (II) complex was 2.82 B.M, magnetic moment of nickel (II) complex was dimagnatic and copper (II) complex was 1.67 B.M. Conductivity of complexes were measured using DMSO as a solvent where conductivities of complexes were ionic in ratio (1:1) of Co(II) complex while non-ionic of Ni(II) and Cu(II) complexes. Lastly, CHNS elemental analysis technique was used to identify and determine the amount of elements that are present in a ligand.

الخلاصة:

ينقسم العمل في هذا البحث الى جزئين ,الجزء الأول هو تحضيرالليكند (قاعدة شيف) من تفاعل الأمين(الدايثايواوكسمايد) مع الألديهايد(سللسلديهايد) بعملية تصعيد حوالي 6 ساعات, ثلاثة انواع من المعقدات حضرت باستعمال املاح الكوبلت الثنائي والنيكل الثنائي والنحاس الثنائي. اما الجزء الثاني في هذا البحث هو تحليل ودراسة خواص المركبات التي حضرت بتقنيات مختلفة مثل المطيافية تحت الحمراء ,تقنية الطيف الرنين النووي المغناطيسي ,تقنية الامتصاص الدري وتقنية المطيافية الفوق البنفسجية –المرئية لمعرفة المجاميع الفعالة والأنتقالات الالكترونيه على التوالي, استخدم قياس الحساسية المغناطيسية لمعرفة الخواص المغناطيسية للمعقدات التي حضرت حيث وجد ان العزم المغناطيسي لمعقد الكوبلت كان 2.82 مغناطون بور ومعقد النيكل كان دايامغناطيسي اما العزم المغناطيسي لمعقد النحاس كان 1.67 مغناطون بور.درست التوصيلية الكهربائية للمعقدات حيث وجد ان معقد الكوبلت موصل بنسبة(1:1) اما معقدي النيكل والنحاس فكانا غير موصلين, استخدمت تقنية تحليل العناصر(CHNS) لتشخيص وتقدير كمية العناصر هذه في الليكند .

1. INTRODUCTION

Schiff bases named after Hugo Schiff described the condensation between an aldehyde and an amine. Schiff base ligands are able to coordinate metals through imine nitrogen and another group have usually liked to aldehyde [1] . In fact, Schiff bases are able to stabilize many different metals in various oxidation states [2]. Schiff bases are very important in development of coordination chemistry. These compounds have a lot of uses. For example, dye industries, plastic, agriculture, physiology and providing liquid crystal [3]. Not only have they played a seminal role in the development of modern coordination chemistry, but they can also be found at key points in the development of inorganic biochemistry[4]. Schiff base ligands containing various donor atoms (like N, O, S etc.) show broad biological activity and of special interest because of the Varity of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compound may enhance their activities [5]. Various metal complexes with bi- and tridentate Schiff bases containing nitrogen and oxygen donor atoms play important role in biological system and represent interesting models for metalloenzymes which efficiently catalyze the reduction of dinitrogen and dioxygen [6]. Generally Schiff base metal complexes are prepared by producing a reaction between the Schiff base and available metal salt in ethanolic medium. This

approach is clearly simple and suitable .Essentially; five different synthetic routes can be identified for the preparation of Schiff base metal complexes (schem 1.0).
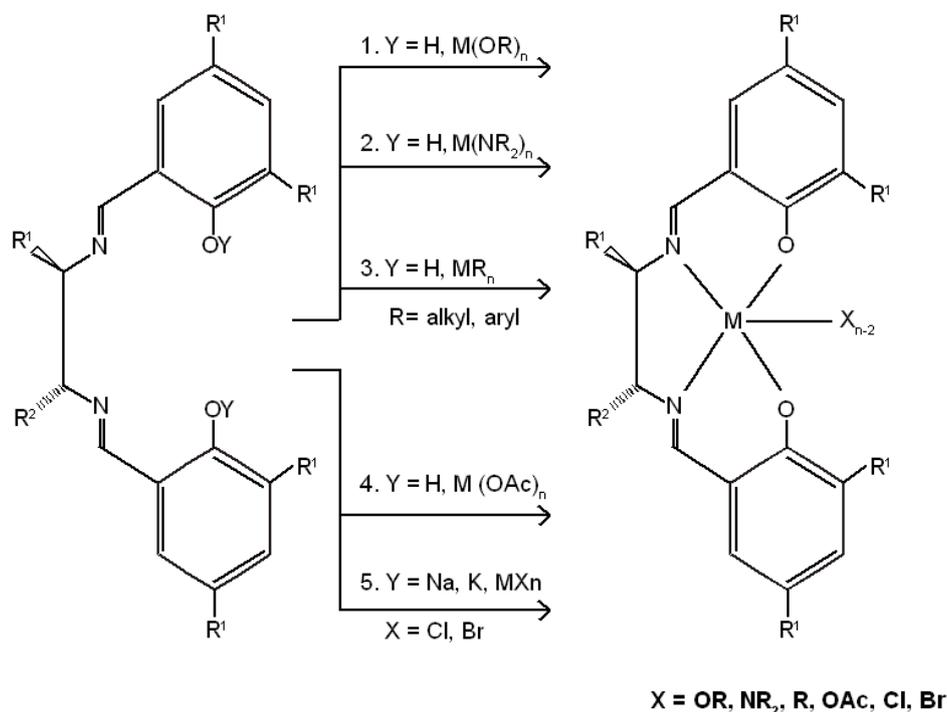
Scheme 1.0: General methods of preparation of Schiff base complexes

 Common oxidation states of cobalt include +2, +3 as for all metals molecular compound of cobalt are classified as coordination complexes, that is molecules or ion that contain cobalt linked to several ligands, the principle of electronagtivity and hardness – softness of the sires of ligands can be used to explain the usual oxidation state of the cobalt. The cobalt (II) ion has ($3d^7$) and give in octahedral high spin complexes (t_2g^5 eg^2) that have ground state (^4T_1g) in addition to low spin complexes (t_2g^6 eg^1) that have ground state (^2Eg).Complexes formed from Schiff basses and metals such as cobalt have been studied as " oxygen carriers" [7]. Cobalt is an essential trace element for all animals as the active center of coenzymes called cobalamins. These include vitamin B_{12} which is essential for mammals. Cobalt is also an active nutrient for bacteria, algae and fungi [8].

   The nickel ion in nickel (II)-complexes exists in the coordination number of 4, 5 and 6. Its octahedral, trigonal-bipyramidal, -pyramidal and tetrahedral complexes are paramagnetic and have in the majority of cases a green or blue colour [9]. The quadratic-planar nickel complexes are diamagnetic and mostly have a yellow, red or brown colour. The bonding between the centered atom and the ligand in metal complexes are the result of electron donor and acceptor interactions. The centered metal atom represents a Lewis acid and the ligand a Lewis base. From the negative charged ligand acts a repulsing force on the electron orbitals of the centered atom. On the other hand the positive charge of the centered atom affects an attracting force on the ligand. As well as the repulsing force of the negative charged ligand has no energetic effect on the spherical-symmetrical s-orbital of the centered metal ion, it has an energetic effect on the d-orbitals.

    Copper forms a rich variety of compounds with oxidation states +1 and +2, which are often called *cuprous* and *cupric*, respectively. Copper, like all metals, forms coordination complexes with ligands, this make it to use in several fields especially in an industry. Copper is essential to all living organisms as a trace dietary mineral because it is a key constituent of the respiratory enzyme complex cytochrome oxidase. Cooper is the important key for the making of the metalloenzymes that contribute to melanin formation, and it is very important in the process of hemopiosis and maintains the structure of the vessels , arteries and muscles. Also, copper plays an important role in the action of nervous system[10]. Copper complexes are used in biological activities, especially

against *Bacillus subtluse*. Copper is an important trace element for plants and animals and is involved in mixed ligand complex formation in a number of biological processes. Copper complexes containing Schiff base ligands are of great interest since they exhibit numerous biological activities, such as anti tumor, axnticandida [11] ,antimicrobial activities, etc.

In the present study the complexes of Co(II), Ni(II) and Cu(II) with Schiff base derived from salicylaldehyde and dithiooxamide have been prepared and characterized in different techniques. Co(II) found that coordination takes place through two phenolic oxygen, two azomethine N atom, aqua molecule and chloro Cl atom gives octahedral geometry of the complex [12].Ni (II) complex found that coordinate with tetradentate Schiff base via two nitrogen atoms and two oxygen atomsd [13].Cu (II) complex suggests coordination through tow azomethine N atom and tow phenolic oxygen after deprotonation [14].

2.EXPERIMENTAL
Chemicals and Instruments

Salicyladehyde 99% (Fluka), dithiooxamide 99% (BDH), ethanol absolute (Fluka), $CoCl_2$. $6H_2O$ (BDH), $NiCl_2$. $6H_2O$ (BDH), $CuCl_2$. $2H_2O$ BDH) and methanol 99% (Fluka). While the techniques that were used in this work are : FT-IR 8000s (Shimadzu), Uv-Vis. (Shimadzu), elemental analysis (EuroEA Elemental Analyser) in university of kufa , ^{1}H-NMR, was measured by BRUKER in university of Iran, melting point of compounds produced was measured by using Gallen kamp melting point, the molar conductivity for complexses was measured using WTW balance. The magnetic susceptibility of prepared complexes were measured by using magnetic sufcetitility balance.

3. Synthesis
3.1 Synthesis of N,N'-bis (2-hydroxybenzlidene) dithiooxamide(LH)

The ligand was synthesized by desolivong (10mmole) of dithiooxamide in 20 ml of a hot absolute ethanol and then (20 mmole) of salicyldehyde was added after that 2-3 drop of triethylamine was added to the mixture. The reaction was stirred and relaxed for 6 hours. The precipitate was filtered and washed with cold ethanol several times and then dried at 45 ºC for 5 hours. Physical properties of the ligand is shown in Table(2.0). Figure 1.0 shows structure of ligand.
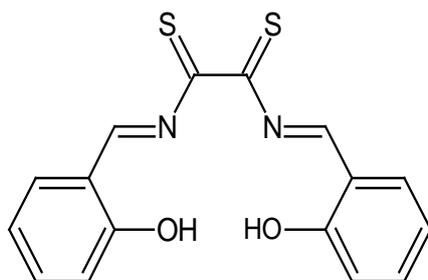

Figure (1.0) structure of ligand

Elemental analysis technique is used to identify and determine the amount of elements that are present in a sample. This method is used as a qualitative and quantitative method, as it can be employed to identify the types of elements in the sample and it can be used to determine the ratio of elements in the sample material. For example the ratio of carbon, hydrogen, nitrogen and sulfur can be measured using this method [15].In this work the elemental analysis technique is used to study ratio of elements for ligand that was prepared . The instrument was (EuroEA Elemental Analyser), in university of kufi . Theoretical and practical values of elements of ligand show in table 1.0 .

Table 1.0 Theoretical and practical values of elements of ligand

Ligand	% C	% H	% N	% S
Theory value	58.500	3.600	8.500	19.500
Experiment value	57.698	3.357	10.500	19.992

3.2 Synthesise of Cobalt (II), Nickel (II) and Copper (II) Complexes

   10 mmmole of ligand (LH) was dissolved in 30 ml of methanol and 10 mmole of cobalt salt ($CoCl_2.6H_2O$) was dissolved in 10 ml of methanol. Ligand solution and cobalt salt solution were mixed and reflexed for 2.0 hours. Idealism condition of complex is (pH = 7, λmax = 491 nm and the concentration 0.009 M).The final product was filtered and washed with cold methanol several times and lastly dried at 45 ºC for 5.0 hours. Both of Nickel and copper complex were synthesized using the same method that was used to synthesis cobalt complex, but the idealism conditions were at pH = 10 and λmax= 390 nm, 478 nm respectively and the concentration 0.008 M. Physical properties of the synthesis complexes are shown in Table (2.0).

 Table (2.0) shows color, melting point, yield and purification solvent for ligand and its complexes.

Compound	Color	Melting Point ºC	Yield %	Suitable Solvent
LH	Orange	256- 259	82 %	DMF
LH(Co)	Deep brown	280	86%	DMSO
LH(Ni)	Deep orange	265- 270	64%	DMSO
LH(Cu)	Black- Brown	289	75%	DMSO

4.RESULTS AND DISCUSSION
4.1Infrared Spectroscopy

   Figure (2.0) shows FT-IR spectrum of the ligand. It is clear from the figure that there is a peak at 1610 cm^{-1} this represents the azomethine starching band υ(C=N). The peak at 1213 cm^{-1} is due the thio carbonyl band υ (C=S). There is a peak at 1180 cm^{-1} which corresponds to υ (C-O-H) symmetric, while the peak at 1276 cm^{-1} corresponds to υ (C-O-H) asymmetric [16,17].
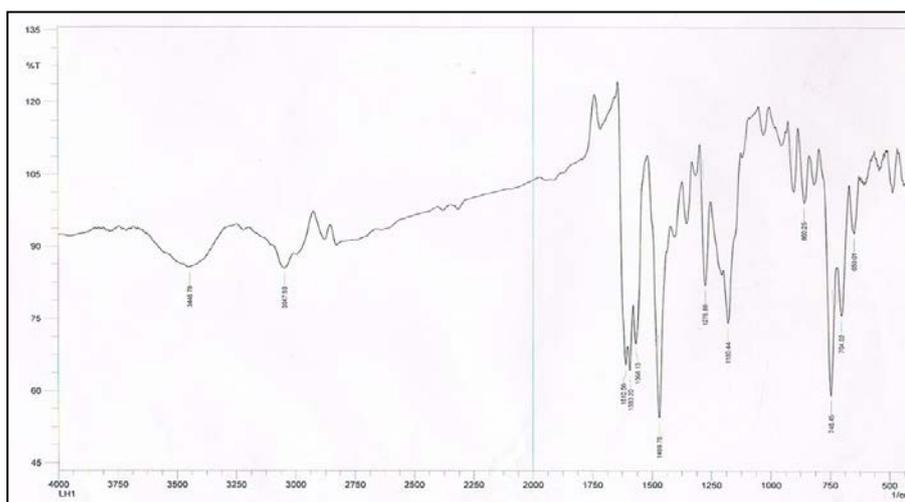

Figure (2.0): FT-IR spectrum of ligand(LH)

Cobalt (II) complex spectrum is shown in figure (3.0). There is a peak at 1597 cm^{-1} can be assigned to azomethine starching band υ (C=N) which is shifting from 1610 to 1597cm^{-1}. The peak at 1215 cm^{-1} relates to the thio carbonyl band υ (C=S). There is a strong peak at 1182 cm^{-1} which may represent to υ (C-O-H) symmetric, whilst the peak at at 1276 cm^{-1} relates to υ (C-O-H) asymmetric.

In addition, there is a peak at 554 cm^{-1} corresponds to υ (Co-N). Lastly, the peak at 3051 cm^{-1} can be belong to υ (O-H) of the lattice water [17].
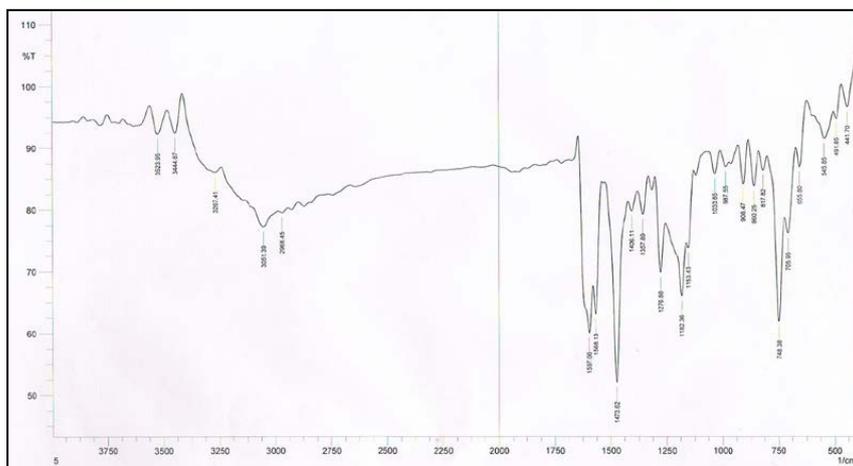

Figure (3.0):FT-IR spectrum of cobalt(II) complex

Figure(4.0) illustrates peaks of nickel (II) complex. The peak at 1622 cm^{-1} corresponds to azomethine starching band υ (C=N) . There is peak at 1205 cm^{-1} belongs to thio carbonyl υ (C=S). The peak at 1180 cm^{-1} can be related to υ (C-O-H) symmetric, while the peak at 1278 cm^{-1} represents to υ (C-O-H) asymmetric. There is peak at 489 cm^{-1} is due υ (Ni- N). Finally, the peak at 3053 cm^{-1} which can be assigned to υ (O-H) of the lattice water [17].
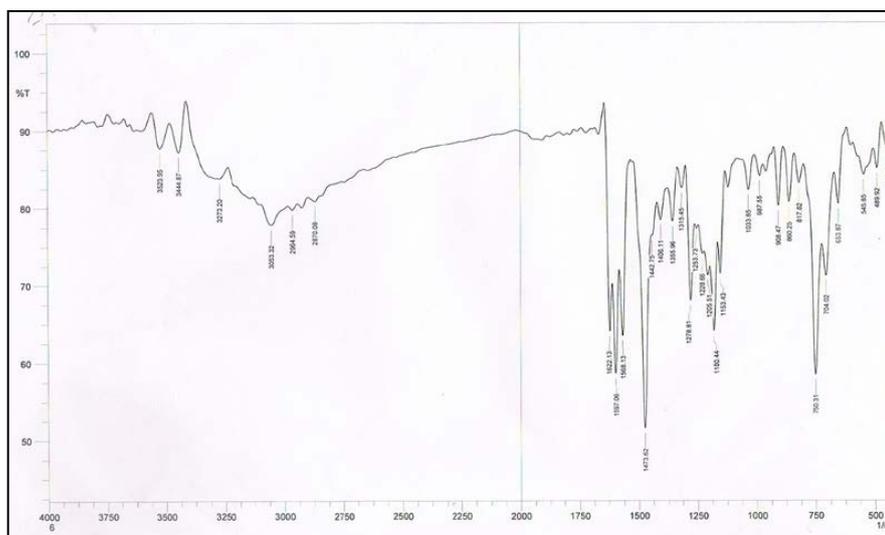

Figure (4.0): FT-IR spectrum of Nickel (II) complex

Figure (5.0) show peaks of Copper (II) complex. It is clear from figure there is peak at 1598 cm^{-1} assigns to azomethine starching band υ (C=N). There is peak at 1217 cm^{-1} which relates to thio carbonyl υ (C=S). The peak at 1157 cm^{-1} corresponds to υ (C-O-H) symmetric. The peak at 1292 cm^{-1} is due υ (C-O-H) asymmetric. The small peak at 559 cm^{-1} can be related to υ (Cu-N), while the peak at 3051cm^{-1} can be assigned to υ (O-H) of the lattice water[17].
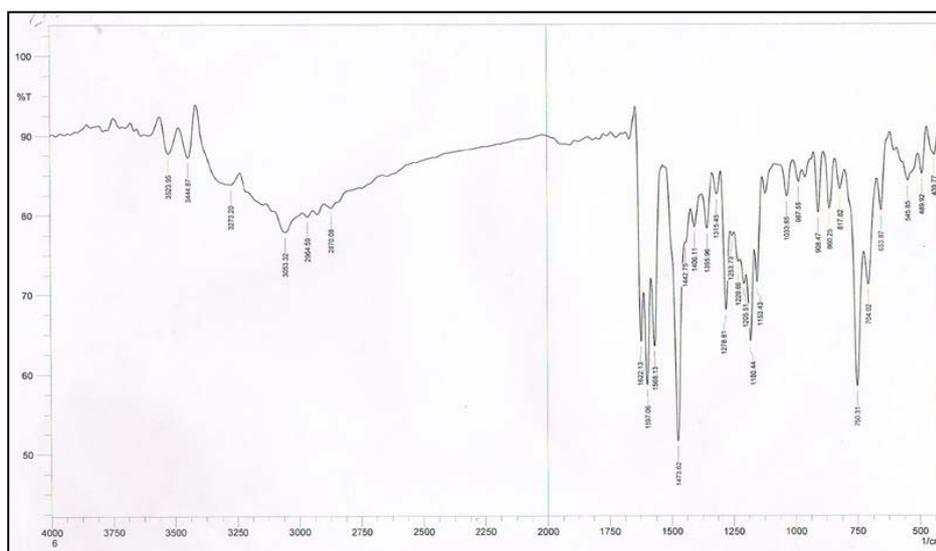
Figure (5.0): FT-IR spectrum of copper (II) complex

4.2 Electronic spectra and magnetic properties

The spectrum of ligand Fig.(6.0)show the first absorption band in 283 nm (35335 cm^{-1}) which can be attributed to (π - π*) transition for the aromatic nucleus. The second band appearing in 374 nm (26737 cm^{-1}) is attributed to (π - π*) transition in all molecules. The third band which appeared in 393 nm (25445 cm^{-1}) was attributed to (n- π*) transition in imino group (C=N) [18].
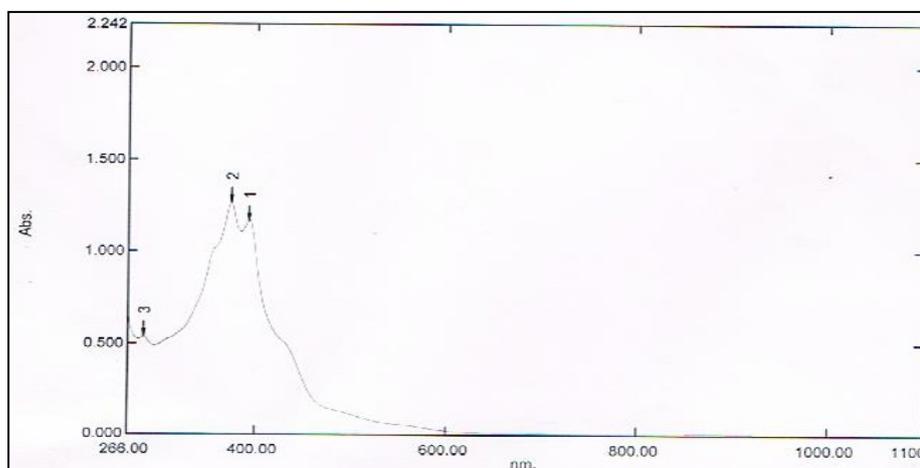

Figure (6.0): UV-Vis- spectrum of ligand

Electronic spectrum for cobalt (II) complex Fig.(7.0) was measured and it was found one absorption band which is d-d in 456nm (21929 cm^{-1}) where this band can be assigned to electronic transation $^2Eg \rightarrow ^2T_1g$ in Co(II) complexes which have octahedral low spin[19], The magnetic susceptibility (2.82 B.M)and molar conductivity measurement in DMSO and was 43 µs/cm in type 1:1 that indicate the complex is paramagnetic and electrolyte[22], from these results , an octahedral geometry a round Co(II) can be suggested, Fig.(7.0) .
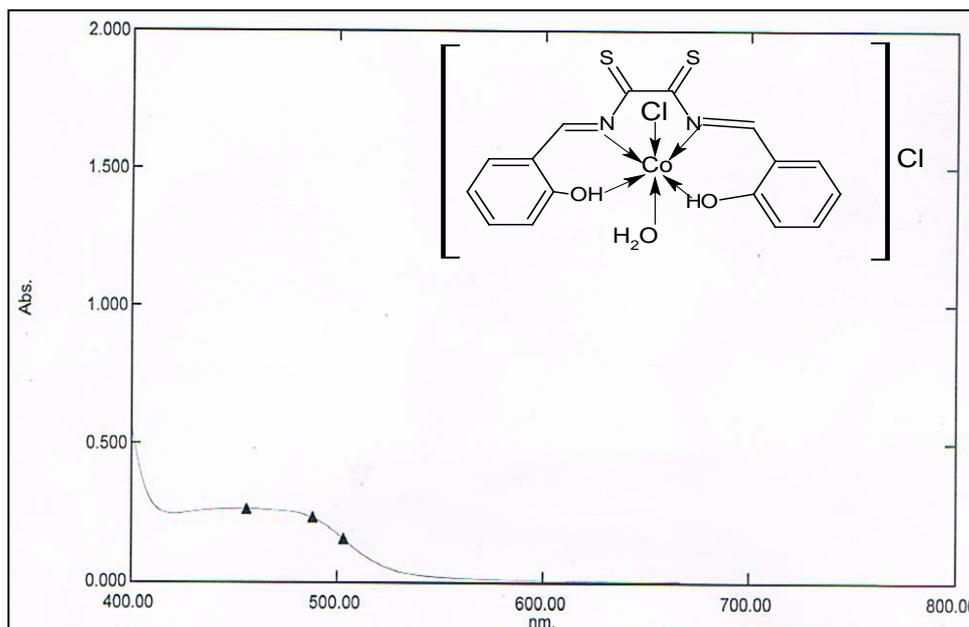
Figure 7.0: UV-Vis-Spectrum and Proposed structure of the Complex CoLH

The nickel (II) can be formed complexes with a square planer shape, the electronic spectra for this complexes appear two band of absorption belong to $^1A_1g \rightarrow ^1A_2g$, $^1A_1g \rightarrow ^1B_1g$ respectively [20].Spectrum of the Ni(II) complex Fig.(8.0) shows two band of absorption, one of them strong (15000 – 23000 cm^{-1}) this belong to $^1A_1g \rightarrow ^1A_2g$. while the second band (23000- 27000 cm^{-1}) this belong to $^1A_1g \rightarrow ^1B_1g$, where this can be conformed this complex may to take a square planer shape where this agree with the magnetic susceptibility (μ=0 B.M) and conductivity measurement in DMSO was 18 μs/cm that indicate the complexe was (non electrolyte)[22]. According to these data and those obtained from I.R spectra, an squar planar geometry around Ni(II) can be suggested as illustrated in Fig.(8.0)

Fig.(8.0) Uv-Vis spectrum and Proposed structure of the complex NiLH

The spectrum of (CuLH) Fig. 9.0 have a broad band at 493nm (18939- 20263) cm^{-1} due to a combination of two transitions, $^2B_1g{\rightarrow}^2Eg$ and $^2B_1g{\rightarrow}^2A_1g$ respectively. These transitions refer to square planar geometry around Cu (II) ion [21]. The value of magnetic moment that have been measured at R.T was 1.67 B.M. This value came within the rang of to square planar [22]. Molar conductivity measurement in DMSO was 12 µs/cm that show the complex was non-electrolyte. According to these data, an to square planar geometry around Cu (II) ion can be suggested, Fig.9.0.
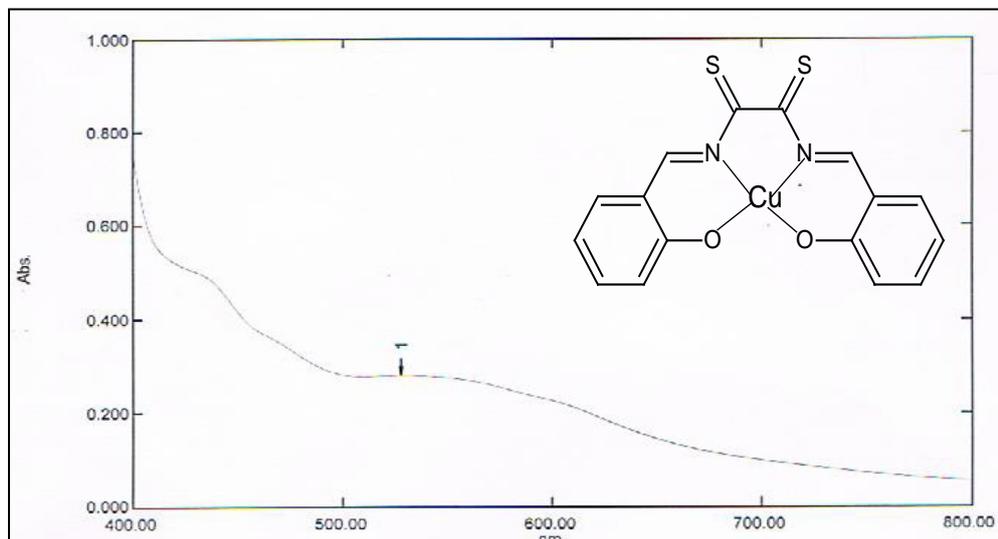

Figure (9.0): UV-Vis spectrum and proposed structure of copper (II) complex

5 NMR Spectroscopy

Nuclear magnetic resonance (nmr) is probably the chemists most valuable tool for determining the structures of compounds in liquid and dissolved states. Fig(10) shows NMR-Spectrum of ligand.Its clear that there is chemical shifts at 2.3-2.7 ppm this belong to benzylic hydrogens [23]..Also in this figure shows chemical shifts at 6.5-8.0ppm this belong to hydrogen attached to an aromatic (benzenoid) ring have a large chemical shift, usually near 7.0 ppm[24]. The –OH hydrogen is usually split by hydrogen on the adjacent carbon (-CH-OH) because rapid exchange decouples this interaction. There is chemical shift at 11-12 ppm belong to the ArOH.
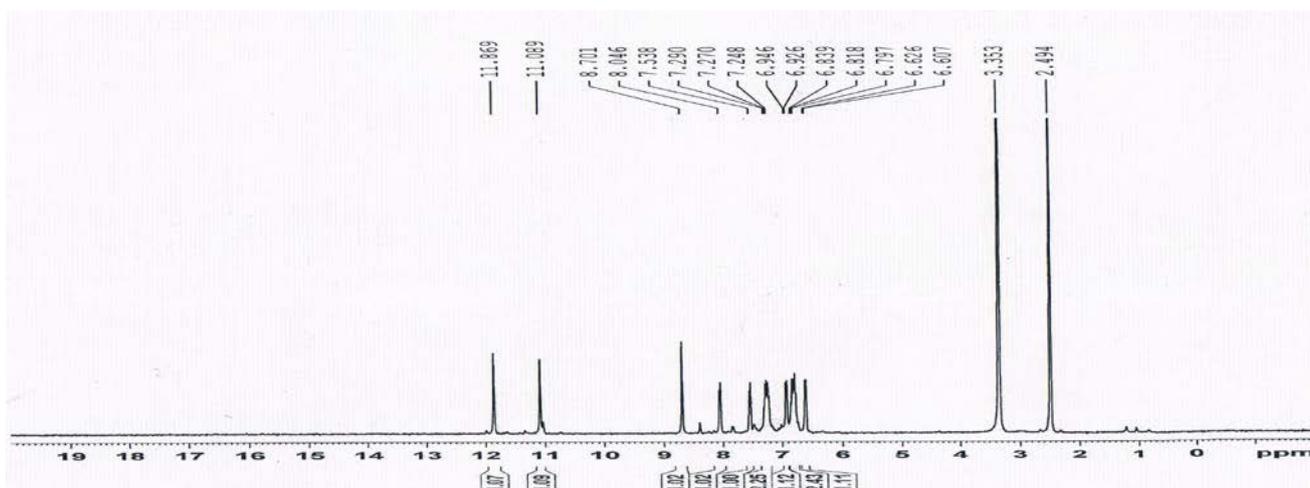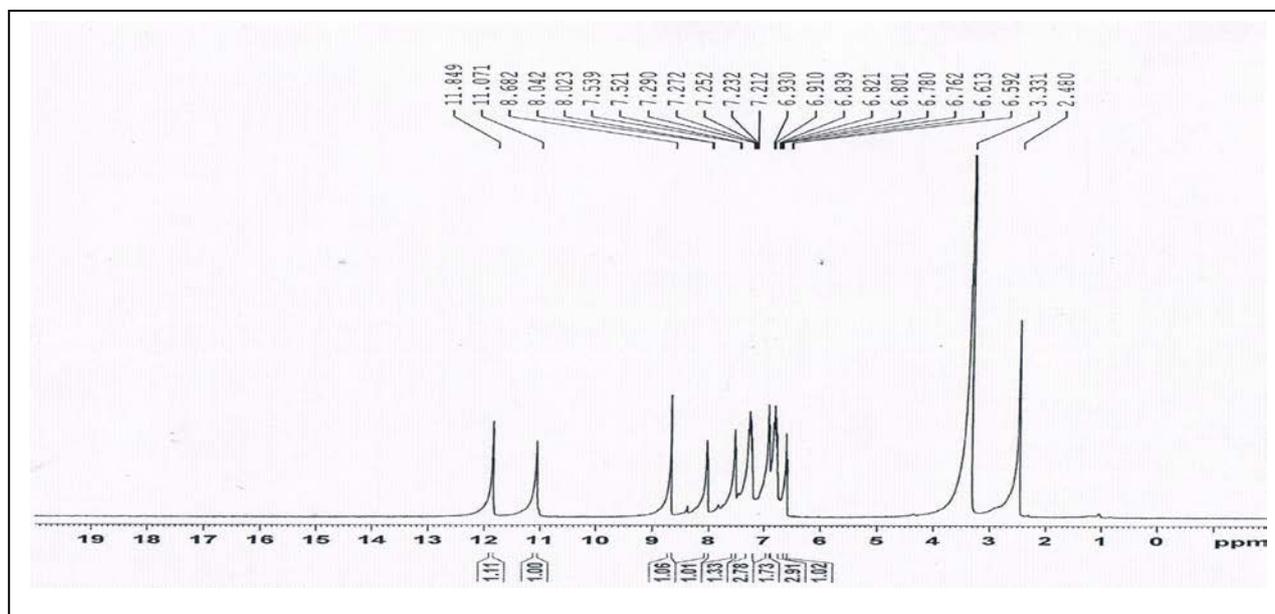

**Fig(10): NMR-Spectrum of ligand(LH1)**
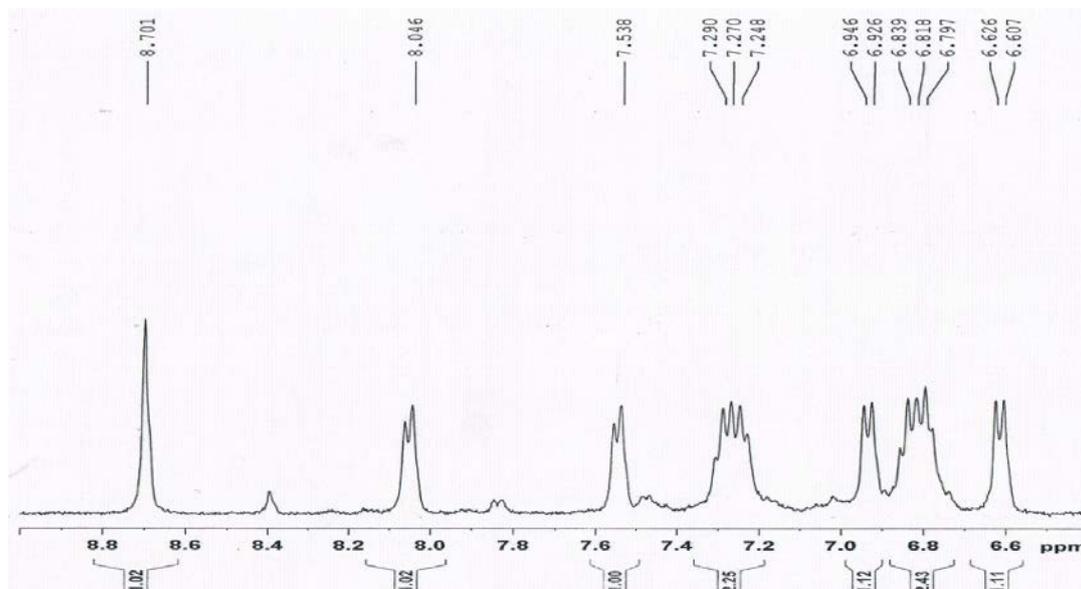
NMR-Expansion of Ligand(LH1)

While NMR-Spectrum of CoLH Figure(11) Shows chemical shifts at 2.3-2.7 ppm this belong to benzylic hydrogens. The hydrogen attached to aromatic rings are easily identified. They are found in region of their own (6.5-8.0ppm) in which few other types of hydrogen show absorption. Also in this figure shows chemical shifts at 6.5-8.0ppm this belong to hydrogen attached to an aromatic (benzenoid) ring have a large chemical shift, usually near 7.0 ppm. There is chemical shift at 11-12 ppm belong to the ArOH.

Figure(11):NMR Spectrum of CoLH
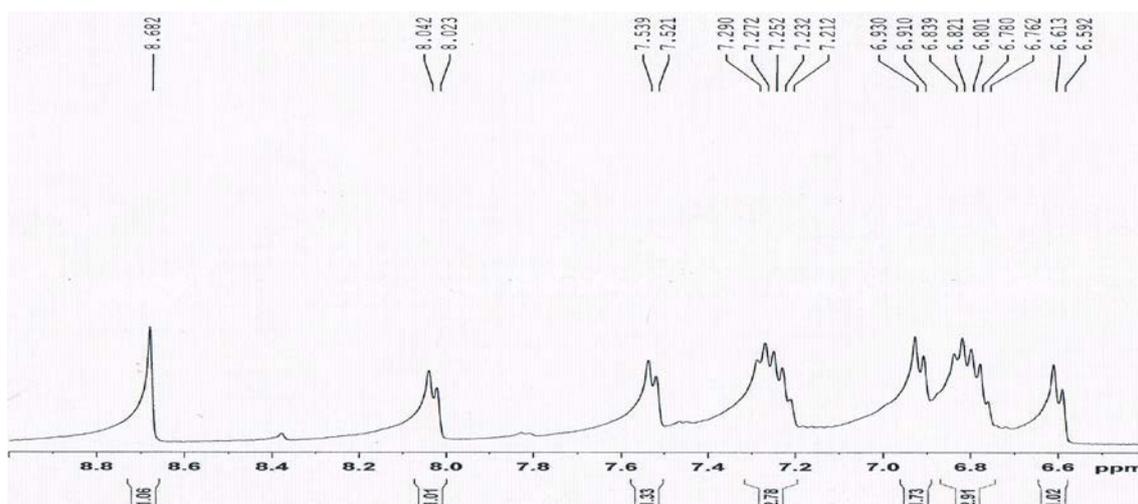
NMR-Expansion of CoLH

Table(3.0):^{1}H NMR (DMSO-d^6) ppm of the Compounds

Compound	^{1}H NMR (DMSO-d^6) ppm
Ligand(LH)	2.5(s,1H,CH=N), 3.7(s,1H,CH =N) 6.6(m,1H,ph), 6.8(m,1H,ph) 6.9(m,1H,ph), 7.3(m,1H,ph) 7.5(m,1H,ph), 7.9(m,1H,ph), 8.1(m,1H,ph), 8.7(m,1H,ph), 11.1(s,1H,ph-OH), 11.9(s,1H,ph-OH)
CoLH	2.7(s,1H,CH=N),3.4(s,1H,CH=N), 6.6(m,1H,ph), 6.9(m,1H,ph), 7(m,1H,ph), 7.3(m,1H,ph), 7.6(m,1H,ph), 7.8(m,1H,ph), 8.0(m,1H,ph), 8.7(m,1H,ph), 11.0(s,1H,ph-OH), 11.8(s,1H,ph-OH)

6 Atomic absorption

Atomic Absorption Spectrometry (AAS) is a technique for measuring quantities of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest[25]. Theoretical values of metals of complexes can be calculated and found The experiment value approximately to theory value This shows in table 4.0

Table(4.0) Shows the analytical data of compound

Compound	% of metal	
	Theory value	Experiment value
CoLH1	12.3	12.1
NiLH1	15.25	15.1
CuLH1	16.3	15.8

REFERENCES

[1] Seitz M., Kaiser A., Stempfhuber S., Zabel M., Reiser O., (2004) Helical, nonracemic inorganic-organic hybrid polymers of cadmium halides with pentadentate bis (oxazoline) ligands, J. Am. Chems. Soc. 126 (37): 11426.

[2] Bhendkar A K,Vijay K, Raut A W., (2004) Synthesis of some novel Schiff bases of 2-aminopyrimidine and their antimicrobial activity. Acta ciencia indica(chemistry)30:29.

[3] Lien E.J.,(2002) Synthesis Biological evaluation and quantitative structure-activity relationship analysis of New Schiff Bases,J.Med.Chem,45,410-419.

[4] Kilic A, Tas E, Deverec B, Yilmaz I. , (2007) Synthesis, electrochemical and insitu spectroelectrochemical studies of new transition metal complexes with tow new Schiff- bases containing N2O2/N2O4 donor groups polyhedron 26:4009.

[5] Mohamed G G. , (2006) Synthesis,characterization and biological activity of bis(phenylimine)Schiff base ligands and their metal complexes,Spectrochim.Acta A 64(1):188.

[6] Kasumov V T,Ozalp-Yaman S,TasE. , (2005) Synthesis,spectroscopy and electrochemical behaviors of nickel(II) complexes with tetradentate Schiff bases derived from 3,5-Bu(2)(t)-salicylaldehyde,Spectrochim.Acta 62(1-3):716.

[7] Calvin, M., R. H. Balles, and W. K. Wilmarth. , (1946) The oxygen-carrying synthetic chelate compounds. I. J. Amer. Chem. Soc. 68:2254-2258

[8] Omar M M, Mohamed G G, Hindy A M M. , (2006) Transition metal complexes of heterocyclic Schiff base, J Therm. Anal. Cal. 86(2):315.

[9] J. Ehrenmann ,J. Gonzalez. , (2009) Synthesis of nickel complexes.

[10] Tarafder M T H, Ali M A, Wee D J, Azahari K, Silong S, Crouse K A. , (2000) Complexes of a tridentate ONS Schiff base. Synthesis and biological properties, Trans.Met. Chem. 25(4):456.

[11] Saha D K, Sandbhor U, Shirisha K, Paddye S, Deobagkar D, Ansond C E, Powell A K. , (2004) A novel mixed-ligand antimycobacterial dimeric copper complex of ciprofloxacin and phenanthroline,Bioorg Med. Chem. Lett. 14(12):3027.

[12] Daneshwar N,Entezami A A, Khandar A A, Saghatforoush L A. , (2003) Synthesis and characterization of Copper(II) complexes with dissymmetric tetradentate Schiff base ligands derived from aminothioether pyridine. Crystal structures of [Cu(PYTISAL)]ClO4.0.5CH3OH AND [Cu(PYTAZOSAL)]ClO4,Polyhedron22(11):1437.

[13] Costes J P, Lamere J F, Lepetit C, Lacroix P G, Dahan F, Nakatani K. , (2005) Synthesis, crystal structures, and nonlinear optical(NLO) properties of new Schiff-base nickel(II) complexes. Toward a new type of molecular switch?,Chem.44:1973.

[14] Rigamanti L, Demartin F, Forni A, Righetto S, Pasini A. , (2006) Copper(II) Complexes of salen Analogues with Two Differently Substituted (Push-Pull) Salicylaldehyde Moieties. A Study on the Modulation of Electronic Asymmetry and Nonlinear Optical Properties, Inorg.Chem. 45(26):10976.

[15] Meguid S.A. , Refaat M.H. , (1997) Finite element analysis of the deep drawing process using variation inequalities. Elsevier Science.

[16] Bibhesh K. and Devjani A. , (2012) " Complexation behaviour of Schiff base ligands with transitions metal ions, Int.J. Chem. 2277-2073

[17] Sallomi I.J, AL-Saheen A.J. , (1994) "Complexes of hydrazide Schiff bases" , Transition, Met. Chem., 19,275.

[18] Al-Mukhtar S, Mustafa I.A. , (1988) "Inorganic and coordination chemistry" , Arabic Version , p 467, 611 , 613.

[19] Mahapatra B.B, Panda D, and Putari S.K. , (1983) "Complexes of cobalt(II), nickel(II) ,copper(II), zinc(II), cadmium(II) AND mercury(II) with chelating hydrazones" ,J. Indian, Chem. Soc., 60, 529.

[20] Lat K. and Geol S. , (1990) "Studies of metal complexes of Schiff bases derived from sulphadiazine and sulphadimidine with 5-substituted salicylaldehyde" ,Assian, J.Chem., 277.

[21] Purohit K.M and Raman D.V. , (1980) "Mixed chelate complexes of copper(II)" ,J. Indian , Chem. Soc. ,57 ,363.

[22] Ibrahim I.K.M., Bekheit M.M., Abu El-Reosh G.M and Mostafa M.M. ,

(1986) ["spectral thermal and magnatic studies of biacetyl monooximesonicotionylhydrazine complexes,"] polyhedron,5,1635.

[23] William L. Jolly. , (1970) "The Synthesis and Characterization of Inorganic Compounds" California, Berkeley.

[24] Donald L. Pavia, Gary M.,George S. and James R.Vyvyan. , (2008) "Introduction To Spectroscopy" Bellingham, Washington.

[25] Garcia R. and Baez A.P. , (2007) "Chemical Composition of rainwater Collected at a Southwest site of Mexico City, Mexico" Rrv . Atomspheric Research. 86:61-75.