Synthesis of Co(II) and Cu(II) Complexes with NO and N_2O_2 Ligands derived from Salicylaldehyde

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Abstract

Salicylaldehyde has been reacted with aniline and 1,2 phenylendiamine to give the NO and N_2O_2 Schiff Base type ligands named 2-[(pheneylimino) methyl] phenol **(LH)** and N,N'-bis(salicylidene)-1,2-phenylenediamine **(L''H₂)**. The structures of the ligands were elucidated by FT-IR, ^{1}H-NMR, ^{13}C-NMR and UV-Vis electronic spectra. The coordination behavior of the **(LH)** and **(L''H_2)** towards Cu(II) and Co(II) ions has been investigated The reaction of the Schiff base ligands **(LH)**, **(L''H_2)** with cobalt (II) and copper (II) ions in 1:1 molar ratio afforded mononuclear metal complexes. Whereas, the reaction of the Schiff base ligand **(L''H_2)** with cobalt (II) and copper (II) ions in 1:2 molar ratio gave binuclear metal complexes. The changes in the selected vibration bands in FT-IR indicate that Schiff bases behave as (NO) bidentate and N_2O_2 tetradentate ligands and coordinate to metal ions from phenolic oxygen atoms and azomethine nitrogen atoms. Characterization and structure elucidation of the prepared complexes were achieved by FT-IR, UV-Vis electronic spectra. The metal complexes exhibited different geometrical arrangements such as square planner, tetrahedral and octahedral arrangements.

Keywords: Salicylaldehyde, Schiff base, mononuclear and binuclear complexes, bidentate and tetradentate ligands

1. Introduction

The preparation of organic metal complexes is one of the most effective methods in the field of materials science and scientific research, because it offers great achievements of different applications and interesting, whether in the field of electrical conductivity and magnetism, or in structural chemistry or in mediation [1-2]. The metal chelating complexes of Schiff bases are one of the main types of metal complexes because their important role in the study of the stereochemistry of some elements of the main groups and transition metals because of the ease of preparation, diversity and its changing structure [3-6]. Goal is the synthesis of a new Schiff bases and mineral complexes in obtaining new compounds of industrial importance. Because they play an important role in the field of pharmaceuticals, dyes and plastics industries, as it owns the group Emin (-CH=N-) [7-8] in the structure, used its complexes in vital areas as anti-bacterial and fungi [9-10] and some types of tumors [11]. Bidentate ligands of Schiff bases (form NO) and tetradentate of Schiff bases (form N_2O_2) showed that it is widely ligands with a good many of the mineral ions and that is what brought her a lot of attention [12-13]. Especially those bidentate ligands of Schiff bases derived from Salicylaldehyde and aniline reaction and tetradentate ligands derived from Salicylaldehyde and 1,2-phenylenediamine reaction, which was the focus of attention of many researchers [14-15] As shown their complexes of diverse applications vital [16], clinically [17] and analytical [18].

2. Experimental:

2.1. Apparatus and chemicals:

(Salicylaldehyde for synthesis by MERCK), cobalt(II)-chloride 6-hydrate 97% (by SCP), copper(II)-chloride 97% (by BDH), absolute ethanol(by CHEMLAB), absolute methanol(by CHEMLAB), aniline 99.5% (by MERCK), 1,2-phenylenediamine 98% (by MERK), diethylether 95% (by PS).

UV/Vis spectroscopy (model: HITACHI U-1900), spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company, optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco, rotar evaporator 4.91 model from the German company Normschiff, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the Germa company Merck.

2.2. Experimental Procedure:

2.2.1. Synthesis of the ligand (LH):

The Schiff base, LH was prepared by the condensation of salicylaldehyde (0.025mol, 3.05gr) and aniline (0.025mol,2.33gr) in methanol (15mL) achieved by boiling the mixture under reflux for 3h. The precipitated LH was filtered and recrystallized from methanol and dried in vacuum desiccators. Ligand as yellow crystals was obtained with a yield of (81%).

2.2.2. Synthesis of the ligand (L″H_2):

The title compound was synthesized by adding salicylaldehyde (0.49gr,4mmol) to a solution of 1,2-phenylenediamine (0.22gr,2mmol) in ethanol 95% (30ml). The mixture was refluxed with stirring for 3h. The precipitated L″H_2 was filtered and recrystallized from methanol and dried in vacuum desiccators. Ligand as orange crystals was obtained with a yield of (71%).

2.2.3. Synthesis of metal complexes:

The hot ethanolic solution (30mL) of corresponding metal salts (Metal:LH = (1:1) for Co(II) and Cu(II), and Metal:L″H_2= (1:1) and (2:1) for Co(II) and Cu(II)) was mixed with hot ethanolic solution of the respective ligands and refluxed by using a water bath. By cooling the contents, the colored complex separated out in each case. The same was filtered, washed with ethanol and washed several times with diethylether.

3. Results and Discussion:

3.1. Elemental analysis and characterization for ligands and their complexes:

The bidentate Schiff base (LH) was prepared by the condensation of salicylaldehyde and aniline in their 1:1 molar ratio. Another tetradentate Schiff base (L″H_2) was prepared by the condensation of salicylaldehyde with 1,2-phenylenediamine in their 2:1 molar ratio. Both ligands were obtained after reflux and then on cooling as yellow and orange precipitates. The Schiff bases were subjected to elemental analyses. The results of elemental analyses (C, H, N) colors,yield and the melting points are presented in Table 1.

Table 1. Elemental analysis, molecular weight and melting point of the ligands.

Compounds	Mol. Weight	Color	Yield (%)	M.P. (°C)	Elemental Analysis % Found (% Calc.)		
					C	N	O
LH	197.23	Yellow	81	60	79.16 (78.99)	7.10 (6.94)	8.11 (8.02)
L″H_2	316.36	Orange	71	150-152	75.93 (76.64)	8.86 (8.90)	10.11 (9.56)

Table 2. Molecular weight and melting point of the different complexes.

Complexes	Mol. Weight	Color	Yield (%)	M.P. (°C)
$[LCoCl_2]$	326.07	Green	87	180-182
$[LCuCl_2]$	330.68	Brown	90	165-167
$[L''CoCl_2]$	444.18	Greenish brown	84	>300
$[L''Cu]$	377.89	Reddish brown	89	>300
$[L''Co_2Cl_4]$	574.02	Greenish brown	80	>300
$[L''Cu_2Cl_4]$	583.25	Reddish brown	86	210-211

3.2. Infrared Spectra

The infrared spectra for the present compounds taken in the range 400-4000 cm^{-1} help to indicate regions of absorption vibrations. The main stretching modes are for ν(C=N) and ν(C-O). The IR data of the spectra of Schiff base ligands (LH and L″H_2) and their complexes are presented in Table3. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation.

Spectrum of the LH ligand shows a medium band at (1617cm^{-1}) du to ν(C=N) Azomethine group which has shifted to lower frequency in the complexes indicating its participation in chelation through azomethine nitrogen. The lowering of band is du to the reduction of electron density in the azomethine link. Azomethine group in the Schiff base (LH) changed after complexation with Co(II) from (1617cm^{-1}) to (1609cm^{-1}) this indicate that involvement of Azomethine group in complexation. The changes in the selected vibration bands in FT-IR indicate that Schiff bases behave as (NO) bidentate and (N_2O_2) tetradentate ligands and coordinate to metal ions from phenolic oxygen atoms and azomethine nitrogen atoms.

IR spectrum of L″H_2 ligand shows a band at (1614cm^{-1}) du to ν(C=N) Azomethine group, which shifts down by (1606cm^{-1}) in Cu(II) complex this suggests coordination through Azomethine group.

Table 3. Characteristic infrared absorption frequencies (cm^{-1}) of the ligand and complexes.

Compounds	ν(C=N) cm^{-1}	ν(C-O) cm^{-1}
LH	1617	1277
[$LCoCl_2$]	1609	1238
[$LCuCl_2$]	1611	1236
$L''H_2$	1614	1275
[$L''CoCl_2$]	1610	1249
[L''Cu]	1606	1240
[$L''Co_2Cl_4$]	1608	1255
[$L''Cu_2Cl_4$]	1606	1257

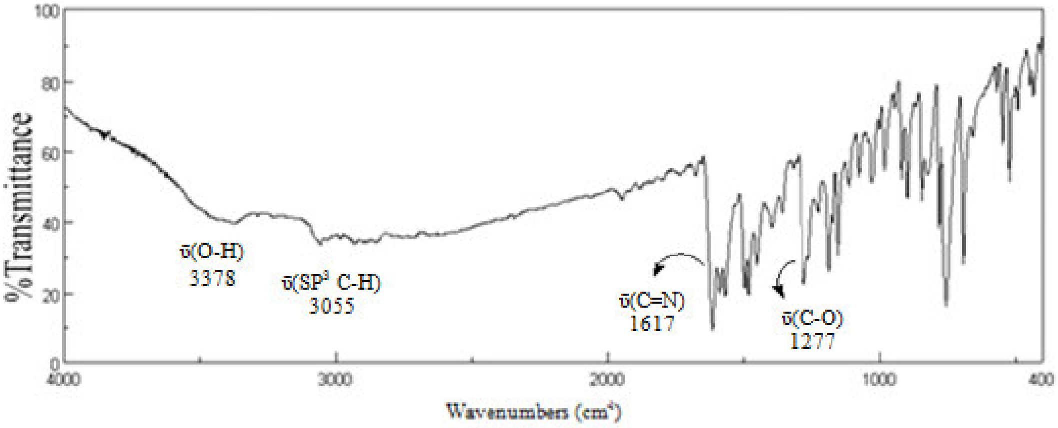


Figure 1. IR absorption spectra of ligand (LH)

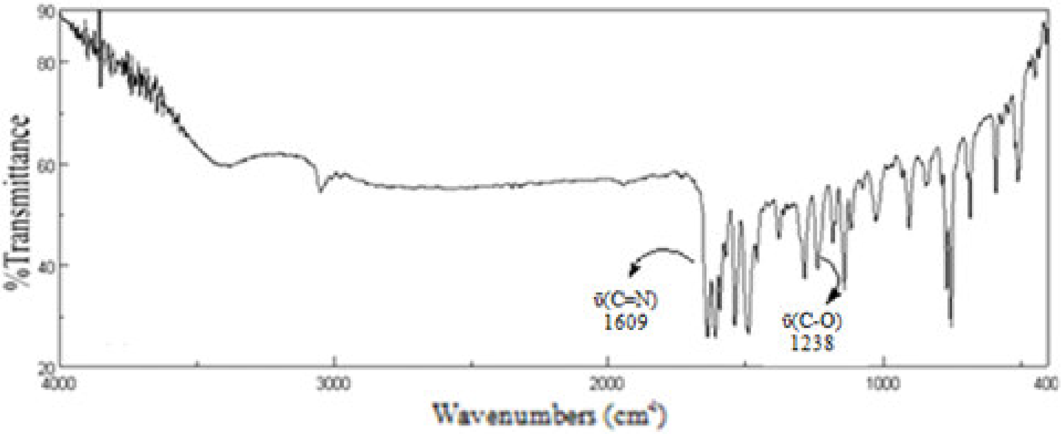


Figure 2. IR absorption spectra of [$LCoCl_2$]

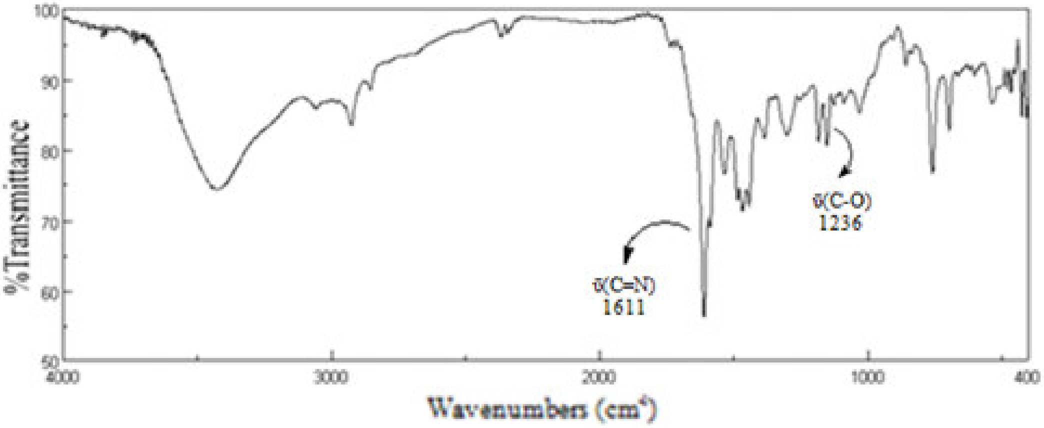


Figure 3. IR absorption spectra of [$LCuCl_2$]

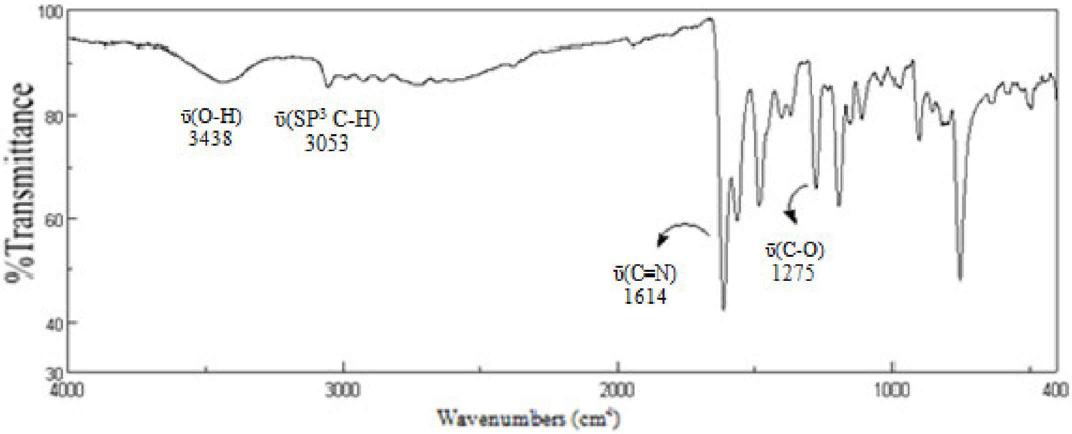


Figure 4. IR absorption spectra of L″H_2

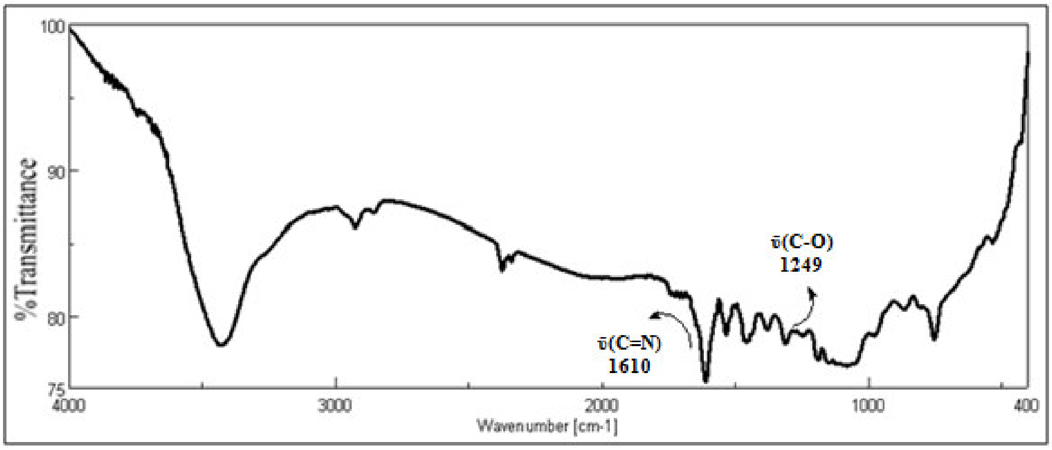


Figure 5. IR absorption spectra of [L"$CoCl_2$]

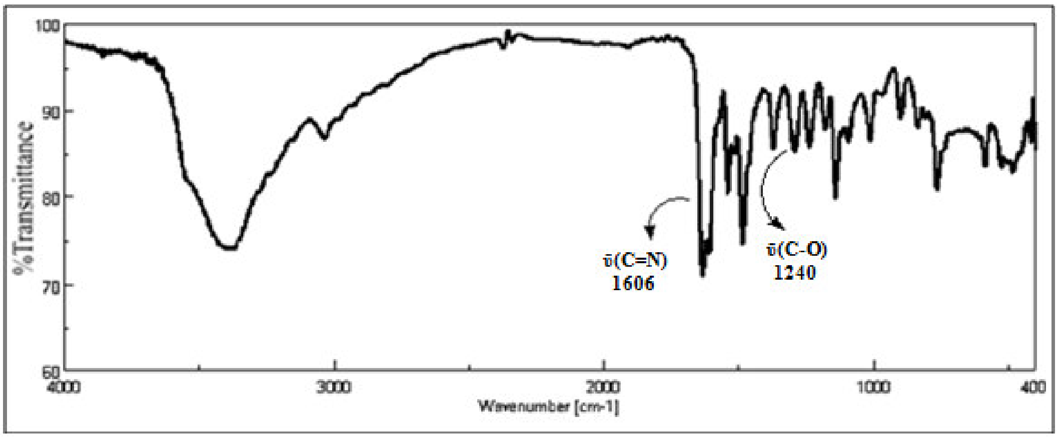


Figure 6. IR absorption spectra of [L"Cu]

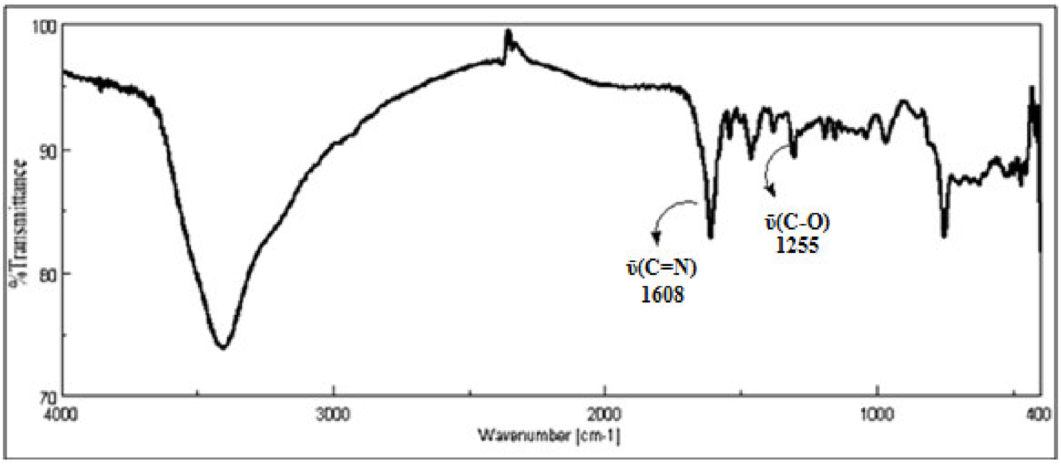


Figure 7. IR absorption spectra of [L''Co_2Cl_4]

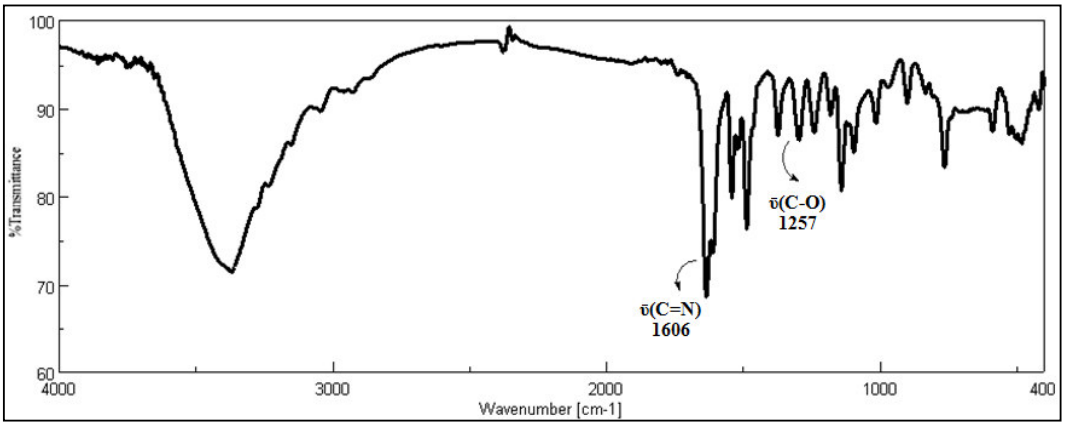


Figure 8. IR absorption spectra of [L''Cu_2Cl_4]

3.3. Electronic spectral data:

The data of the electronic spectra of the ligand and its complexes are given in Table 4. The spectrum of Schiff base (LH) presented three bands in the UV interval at 267nm assigned to (n→ π*), 305nm and 335nm assigned to (π→ π*) transitions respectively.

The electronic spectra of the [LCoCl_2] in DMF has two bands at (605, 670)nm. These bands may be assigned to the transitions $^4T_{1g}(P)\rightarrow{}^4A_{2g}(F)$, and $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ respectively. The position of these bands suggests an square planner structure [19] (Fig 9):

Table 4. Electronic spectral data and geometries of ligand and complexes.

Compounds	Electronic spectra nm	Assignments	Geometry
LH	267 305,335	n→ π* π→ π*	
[LCoCl₂]	605 670	$^4T_{1g}(P)\rightarrow{}^4A_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$	Square planner
[LCuCl₂]	545	$(^2B_{1g}\rightarrow{}^2A_{1g})$	Square planner
L''H₂	275 335,370	n→ π* π→ π*	
[L''CoCl₂]	465 600 680	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$	Octahedral
[L''Cu]	435	$(^2B_{1g}\rightarrow{}^2A_{1g})$	Square planner
[L''Co₂Cl₄]	435 465	$^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$	Tetrahedral
[L''Cu₂Cl₄]	430	$(^2B_{1g}\rightarrow{}^2A_{1g})$	Square planner

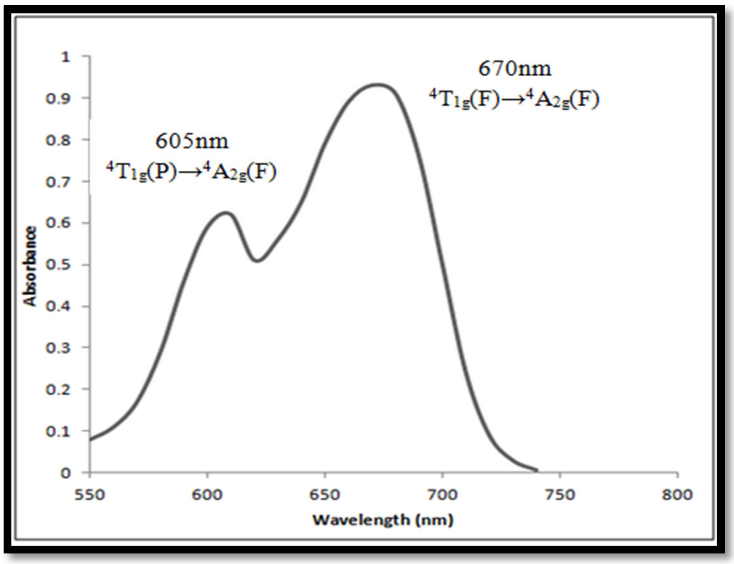


Figure 9. UV absorption spectra of [$LCoCl_2$]

The electronic spectra of the [$LCuCl_2$] in DMF has one band at (545nm). This band may be assigned to the transitions ($^2B_{1g}\rightarrow{}^2A_{1g}$) ,The position of this band suggests a square planner structure [20] (Fig 10):

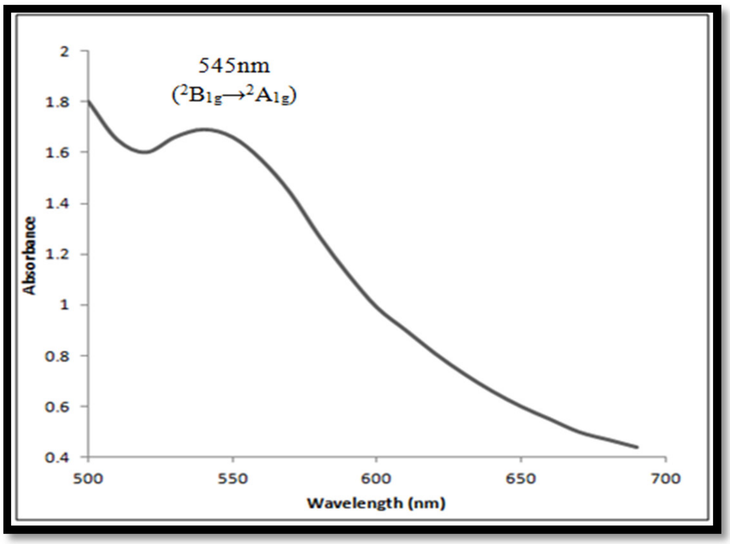


Figure 10. UV absorption spectra of [$LCuCl_2$]

The spectrum of Schiff base ($L''H_2$) presented three bands in the UV interval at (275nm) assigned to ($n\rightarrow\pi^*$) ,(335nm) and (370nm) assigned to ($\pi\rightarrow\pi^*$) transitions, respectively. The electronic spectra of the [$L''CoCl_2$] in DMF has three bands at (465, 600,680)nm.These bands may be assigned to the transitions $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$,$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$,$^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$ respectively. The position of these bands suggests an octahedral structure [21] (Fig 11):

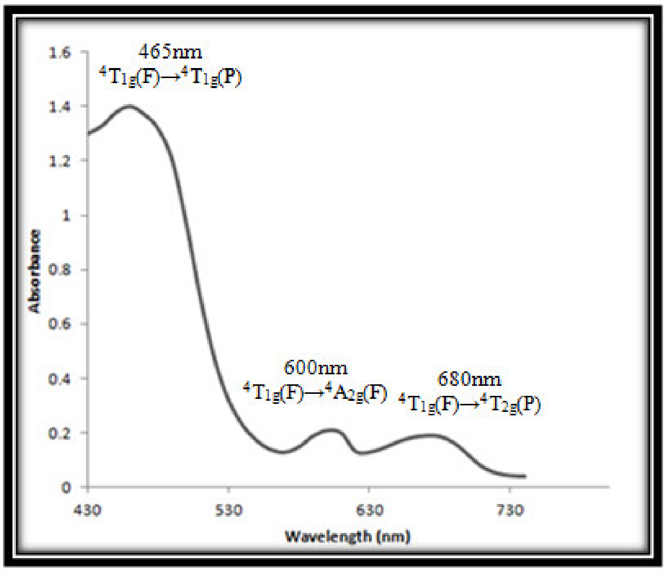


Figure 11. UV absorption spectra of [L"$CoCl_2$]

The electronic spectra of the [L"Cu] in DMF has one band at (435nm).This band may be assigned to the transitions ($^2B_{1g}\rightarrow{}^2A_{1g}$).The position of this band suggests a square planner structure [20] (Fig 12):

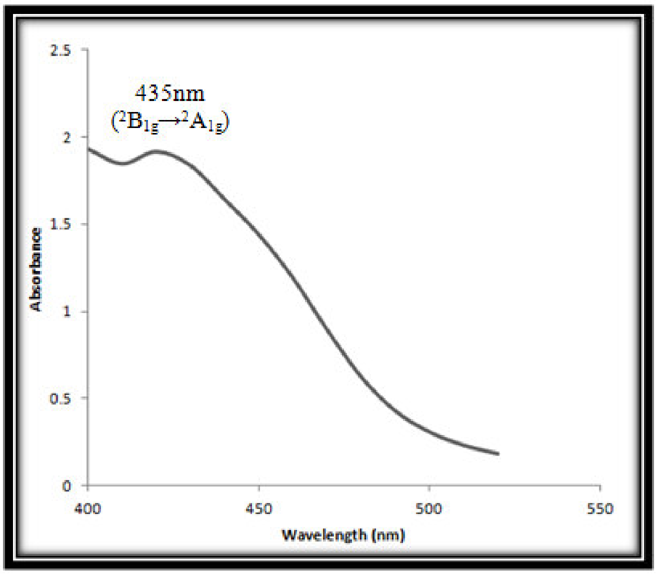


Figure 12. UV absorption spectra of [L"Cu]

The electronic spectra of the [L"Co_2Cl_4] in DMF has two bands at (435, 465nm).These bands may be assigned to the transitions $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$,$^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$, respectively. The position of these bands suggests an tetrahedral structure [22] (Fig 13):

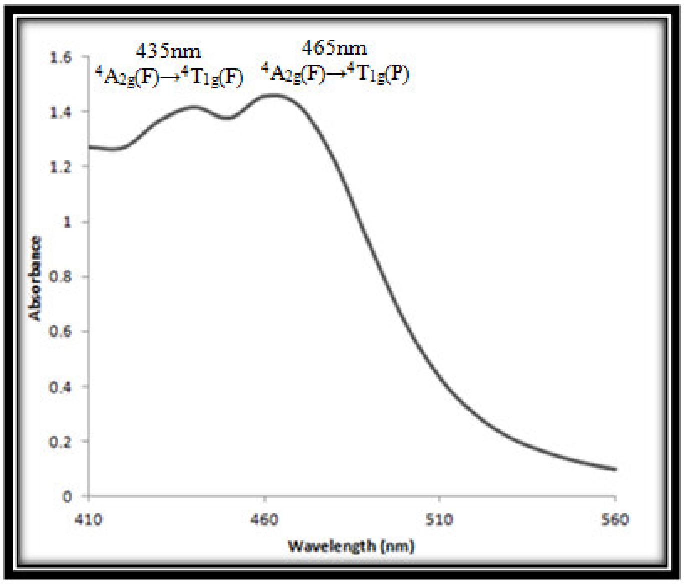


Figure 13. UV absorption spectra of [L"Co_2Cl_4]

The electronic spectra of the [L"Cu_2Cl_4]in DMF has one band at (430nm).This band may be assigned to the transitions ($^2B_{1g}\rightarrow{}^2A_{1g}$).The position of this band suggests square planner structure [20] (Fig 14):

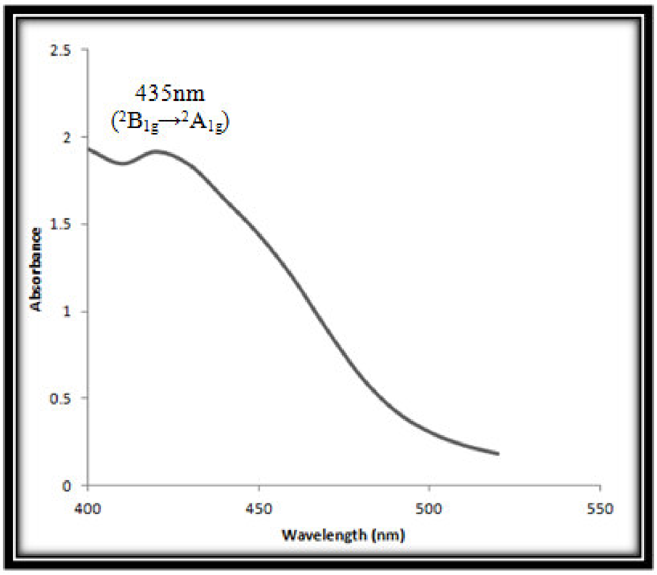
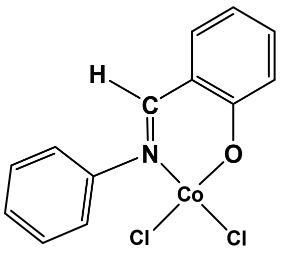
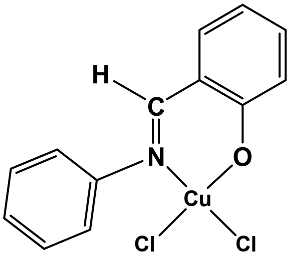


Figure 14. UV absorption spectra of [L"Cu_2Cl_4]

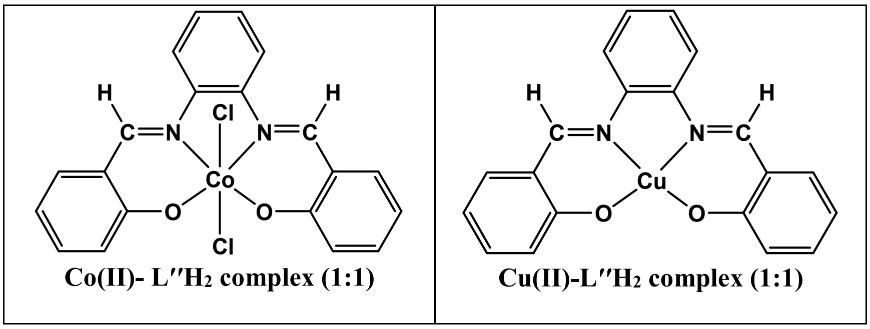


Co(II)- LH complex



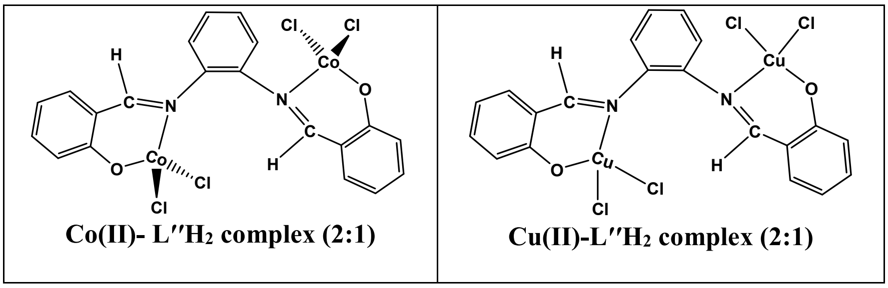
Cu(II)-LH complex

Figure 15. Suggested structures for the LH complexes



Co(II)- $L''H_2$ complex (1:1) **Cu(II)-$L''H_2$ complex (1:1)**

Figure 16. Suggested structures for the $L''H_2$ complexes (1:1)



Co(II)- $L''H_2$ complex (2:1) **Cu(II)-$L''H_2$ complex (2:1)**

Figure 17. Suggested structures for the $L''H_2$ complexes (2:1)

3.4. ^{13}C and ^{1}HNMR spectroscopic measurements:

(^{1}H-NMR) spectra of the Schiff base ligand *LH* revealed its formation by the presence of (HC=N) proton signal at (δ=8.72ppm) and proton signal for hydroxyl at (δ=13.03ppm) . The (^{13}C-NMR) of the *LH* ligand exhibits signal at (δ=163.72ppm). This signal assigned to carbon Azomethine group.

The (^{13}C and ^{1}HNMR) spectroscopic measurements of *LH,*$L''H_2$ Schiff bases are given in Table 5.

Table 5. The (^{13}C and ^{1}HNMR) spectroscopic measurements of *LH,*$L''H_2$ Schiff bases.

Compounds	**^{1}H-NMR(δ ppm)**	**^{13}C-NMR(δ ppm)**
LH	13.03 (s, 1H, OH) 8.72 (s, 1H, HC=N) 7.45-7.43 (d, 1H, H_6) 7.34-7.24 (m, 5H, b, f, H_3, H_4, H_5) 7.2-7.14 (dd, 1H, d) 6.79-6.85 (dd, 2H, c, e)	116.68(C_6) ,119.08(C_4) ,119.41(C_2), 121.28(b,f) ,126.93(d) ,129.45(c,e) 132.85(C_3) ,133.15(C_5) ,148.54(j) 161.20(C_7) ,163.72(a)
$L''H_2$	8.91 (s, 2H, HC=N) 7.77-7.65 (m, 4H, b, b`, $H_3$, $H_{3`}$) 7.57-7.49 (m, 6H, c, c`, $H_4$, $H_{4`}$, H_6, $H_{6`}$ ) 7.32-7.18 (m, 2H, $H_5$, $H_{5`}$) 5.71 (s, 2H, OH)	117.45(C_6,$C_{6`}$), 119.29($C_2$,$C_{2`}$), 120.10(C_4,$C_{4`}$), 128.00(c,c`), 128.17(d,d`), 133.00($C_3$,$C_{3`}$), 133.59(C_5,$C_{5`}$) 137.13(b,b`) ,161.12($C_7$,$C_{7`}$) ,164.94(a,a`)

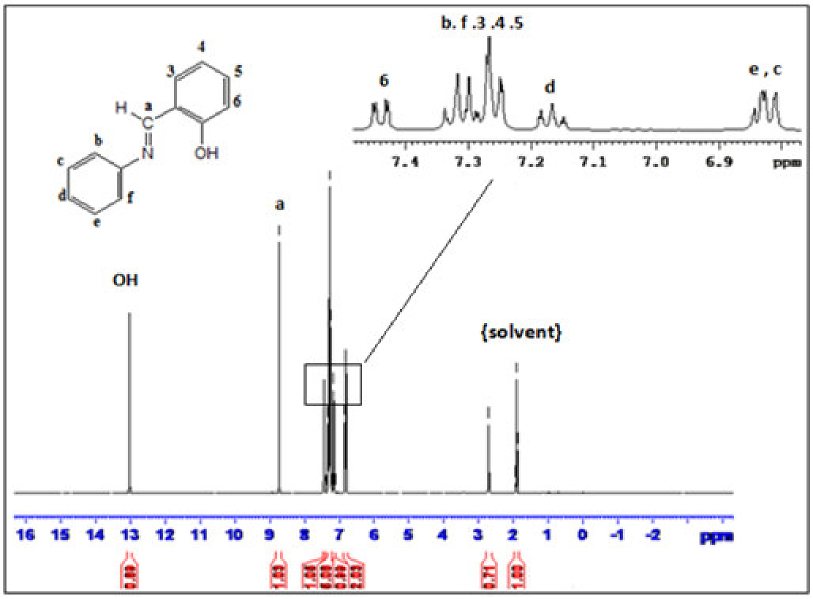


Figure 18. ^{1}H-NMR spectrum of LH.

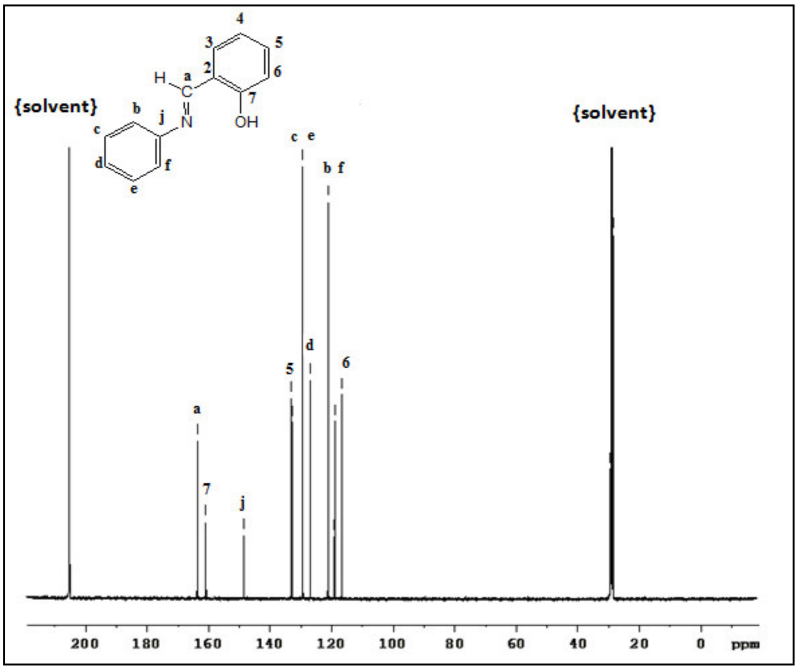


Figure 19. ^{13}C-NMR spectrum of LH.

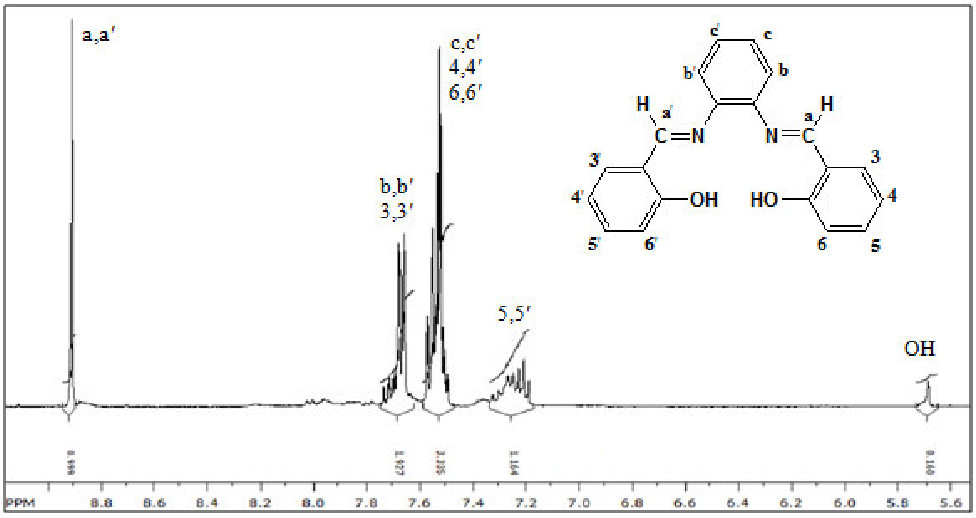


Figure 20. ^{1}H-NMR spectrum of L''H_2.

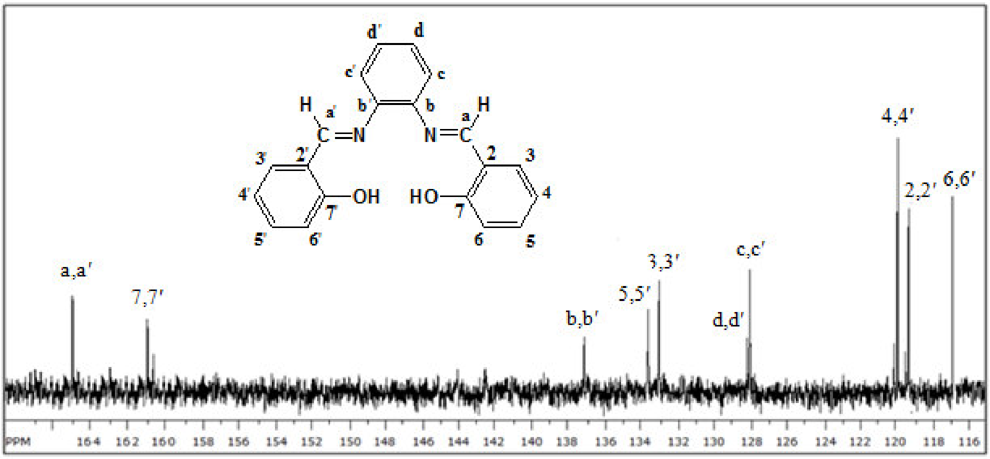


Figure 21. ^{13}C-NMR spectrum of L''H_2.

Conclusions

In this research the preparation, isolation, and characterization of a new bidentate and tetradentate Schiff base derived from Salicylaldehyde and its complexes with Co(II) and Cu(II) have been carried out. It have been proposed that the Schiff base ligand coordinates through the nitrogen of the azomethine group and the phenolic oxygen atom, forming a stable chelate complexes.

In the light of the above discussion, square planner geometry have been proposed for Cu(II) complexes with both **LH** and **L''H_2** ligands. Whereas Co(II) formed square planner with **LH** in (1:1) molar ratio and with **L''H_2** an octahedral , tetrahedral structure for (1:1) and (1:2) molar ratio, respectively.

References

[1]- Chen.C.T & Suslick.K.S. (1993).One-dimensional coordination polymers: Applications to material science, *Coord. Chem. Rev,* V128, pp.293-322.

[2]- Yaghi.O.M, Li.G & Li.H. (1995).Selective binding and removal of guests in a microporous metal-organic framework, *Nature,* V378, pp.703-706.

[3]- Pichon.C, Dechambenoit.P & Clérac.R. (2013).A cyanido-bridged two-dimensional network based on a Ru^{III} schiff base complex and Mn^{II} ions: Synthesis, crystal structure and magnetic properties, *Polyhedron* , V52, pp.476-481.

[4]- Fan.Y.H, Wang.A.D, Bi.C.F, Xiao.Y, Bi.S.Y, Zhang.X & Wang.Q. (2011).Synthesis, crystal structure and anticancer activity of 2D-coordination polymer of cerium(III) with chiral Schiff base trans - N,N′- bis -(2-hydroxy-1-naphthalidehydene) - (1R , 2R)- cyclohexane diamine, *Synthetic Metals*, V161, pp.1552-1556.

[5]- Da Silva.C.M, Da Silva.D.L, Modolo.L.V, Alves.R.B, De Resende.M.A, Martins.C.V.B & De Fátima.Â. (2011).Schiff bases: A short review of their antimicrobial activities, *Journal of Advanced Research*, V2, pp.1-8.

[6]- Matar.S.A, Talib.W.H, and Mustafa.M.S, Mubarak.M.S & AlDamen.M.A. (2015).Synthesis, characterization, and antimicrobial activity of Schiff bases derived from benzaldehydes and 3,3′-diaminodipropylamine, *Arabian Journal of Chemistry*, V8, 850-857.

[7]- Omar.M.M, Mohamed.G.G & Hindy.A.M. (2006).Transition metal complexes of heterocyclic Schiff base, *J.Therm. Anal. Calorim*, V86, pp.315-325.

[8]- Balasubramanian.K.P, Parameswari.K, Chinnusamy.V, Prabhakaran.R & Natarajan.K. (2006).Synthesis, characterization, electro chemistry, catalytic and biological activities of ruthenium(III) complexes with bidentate N, O/S donor ligands, *Spectrochimica. Acta. Part A*, V65, pp.678-683.

[9]- Karthikeyan.M.S, Prasad.D.J, Poojary.B, Bhat.K.S, Holla.B.S & Kumari.N.S. (2006).Synthesis and biological activity of Schiff and Mannich bases bearing 2,4-dichloro-5-fluorophenyl moiety, *Bioorg. Med. Chem*, V14, pp.7482-7489.

[10]- Singh.K, Barwa.M.S & Tyagi.P. (2006).Synthesis, characterization and biological studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with bidentate Schiff bases derived by heterocyclic ketone, *Eur. J. Med. Chem,* V41, pp.147-153.

[11]- Datta.A, Karan.N.K, Mitra.S & Rosair.G. (2002).Synthesis and Structural Characterization of [$Cu(NH_2CH_2C_6H_4N=CHC_5H_5N)Cl_2$], *Z.Naturforsch,* V57b, pp.999-1002.

[12]- Vimal Kumar.P.M & Radhakrishnan.P.K. (2011).Synthesis, spectral and X-ray structural studies of a NO donor Schiff base ligand and its Ni(II) complexes, *Inorganica Chimica Acta,* V375, pp.84-92.

[13]- Şenol.C, Hayvali.Z, Dal.H & Hökelek.T. (2011).Syntheses, characterizations and structures of NO donor Schiff base ligands and nickel(II) and copper(II) complexes, *Journal of Molecular Structure,* V997, pp.53-59.

[14]- Taha.Z.A, Ajlouni.A.M, Al Momani.W & Al-Ghzawi.A.A. (2011).Syntheses, characterization, biological activities and photophysical properties of lanthanides complexes with a tetradentate Schiff base ligand, *Spectrochimica Acta Part A,* V81, pp.570-577.

[15]- Shebl.M. (2008).Synthesis and spectroscopic studies of binuclear metal complexes of a tetradentate N2O2 Schiff base ligand derived from4,6-diacetylresorcinol and benzylamine, *Spectrochimica Acta Part A,* V70, pp.850-859.

[16]- Singh.B.K, Prakash.A, Rajour.H.K, Bhojak.N & Adhikari.D. (2010).Spectroscopic characterization and biological activity of Zn(II), Cd(II), Sn(II) and Pb(II) complexes with Schiff base derived from pyrrole-2-carboxaldehyde and 2-amino phenol, *Spectrochimica Acta Part A,* V76, pp.376-383.

[17]- Creaven.B.S, Duff.B, Egan.D.A, Kavanagh.K, Rosair.G, Thangella.V.R & Walsh.M. (2010).Anticancer and antifungal activity of copper(II) complexes of quinolin-2(1H)-one-derived Schiff bases, *Inorganica Chimica Acta,* V363, pp.4048-4058.

[18]- Fakhari.A.R, Khorrami.A.R & Naeimi.H. (2005).Synthesis and analytical application of a novel tetradentate N_2O_2 Schiff base as a chromogenic reagent for determination of nickel in some natural food samples, *Talanta,* V66, pp.813-817.

[19]- Shakir.M, Abbasi.A, Khan.A.U & Khan.S.N. (2011).Synthesis and spectroscopic studies on the Schiff base ligand derived from condensation of 2-furaldehyde and 3,3′-diaminobenzidene, L and its complexes with Co(II), Ni(II), Cu(II)and Zn(II): Comparative DNA binding studies of L and its Cu(II)and Zn(II)complexes, *Spectrochimica Acta Part A,* V78, pp.29-35.

[20]- Golchoubian.H, Nazari.O & Kariuki.B. (2010).A new copper(II) complex of unsymmetrical tetradentate ligand generated in situ: synthesis and molecular structure, *Inorganica Chimica Acta,* V363, pp.2673-2676.

[21]- Jadhav.S.M, Shelke.V.A, Shankarwar.S.G, Munde.A.S & Chondhekar.T.K. (2014).Synthesis,spectral, thermal, potentiometric and antimicrobial studies of transition metal complexes of tridentate ligand, *Journal of Saudi Chemical Society*, V18, pp.27-34.

[22]- Ahmadi.R.A, Hasanvand.F, Bruno.G, Rudbari.H.A & Amani.S. (2013).Synthesis, Spectroscopy, and Magnetic Characterization of Copper(II) and Cobalt(II) Complexes with 2-Amino-5-bromopyridine as Ligand, *ISRN Inorganic Chemistry*, pp.7.