

Synthesis and Characterization of Some Cobalt (II) and Copper (II) Complexes with N₂O₂ Ligands Derived from 2-Hydroxybenzaldehyde

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Abstract

2-Hydroxybenzaldehyde has been reacted with 1,4-phenylenediamine and 1,2-phenylenediamine to give the N₂O₂ Schiff Base type ligands named N,N'-bis(salicylidene)-1,4-phenylenediamine (**L'H₂**) and N,N'-bis(salicylidene)-1,2-phenylenediamine (**L''H₂**). The structures of the ligands were elucidated by FT-IR, ¹H-NMR, ¹³C-NMR and UV-Vis electronic spectra. The coordination behavior of the (**L'H₂**) and (**L''H₂**) towards Cu(II) and Co(II) ions has been investigated. The reaction of the Schiff base ligands (**L'H₂**), (**L''H₂**) with cobalt (II) and copper (II) ions in 1:2 molar ratio afforded binuclear metal complexes. The changes in the selected vibration bands in FT-IR indicate that Schiff bases behave as N₂O₂ 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 planar and tetrahedral arrangements.

Keywords: 2-Hydroxybenzaldehyde, Schiff base, binuclear complexes, tetradentate ligands.

1. Introduction

Schiff bases are considered as a very important class of organic compounds because of their ability to form complexes with transition metal ions [1-3] and of their pharmacological properties. 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 imine (or Azomethine) (-CH=N-) [4-5] in the structure, used its complexes in vital areas as anti-bacterial and fungi [6-7] and some types of tumors [8]. Previous studies on reaction of transition metal ions with Schiff bases derived from 2-Hydroxybenzaldehyde and diamines showed complexes with the Schiff base coordinates to metal ions as a tetradentate ligand via the two imine nitrogen atoms and the two phenolic oxygen atoms [2].

Tetradentate ligands of Schiff bases (form N₂O₂) showed that it is widely ligands with a good many of the mineral ions and that is what brought her a lot of attention [9-10]. Especially those tetradentate ligands of Schiff bases derived from 2-Hydroxybenzaldehyde and 1,4-phenylenediamine or 1,2-phenylenediamine reaction, which was the focus of attention of many researchers [11-12].

2. Experimental:

2.1. Apparatus and chemicals:

(2-Hydroxybenzaldehyde 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), 1,4-phenylenediamine 98% (by MERK), 1,2-phenylenediamine 98% (by MERK), diethylether 95% (by PS), triethylamine 99.5% (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 (**L'H₂**) and (**L''H₂**):

The title compound was synthesized by adding 2-Hydroxybenzaldehyde (0.49gr,4mmol) to a solution of 1,4-phenylenediamine or 1,2-phenylenediamine (0.22gr,2mmol) in ethanol 95% (30ml). The mixture was refluxed with stirring for 3h. The precipitated L'H₂ and L''H₂ were filtered and recrystallized from methanol and dried in vacuum desiccators. Ligands as orange crystals was obtained with a yield of (79%) and (71%) ,respectively.

2.2.2. Synthesis of metal complexes:

The title compound was synthesized by adding the ligand in ethanol 95% (30 ml). The hot ethanolic solution

(30mL) of corresponding metal salts (Metal:L'H₂ = (2:1) and Metal:L''H₂= (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, followed by triethylamine (0.36gr, 3.6mmol).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 tetradentate Schiff base (L'H₂) was prepared by the condensation of 2-Hydroxybenzaldehyde and 1,4-phenylenediamine in their 2:1 molar ratio. Another tetradentate Schiff base (L''H₂) was prepared by the condensation of 2-Hydroxybenzaldehyde with 1,2-phenylenediamine in their 2:1 molar ratio. Both ligands were obtained after reflux and then on cooling as 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
L'H ₂	316.36	Orange	79	210	75.93 (76.57)	8.86 (8.68)	10.11 (9.75)
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)
[L'Co ₂ Cl ₄]	574.02	Greenish brown	82	>300
[L'Cu ₂ Cl ₄]	583.25	Black	96	270-272
[L''Co ₂ Cl ₄]	574.02	Greenish brown	80	>300
[L''Cu ₂ Cl 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 (L'H₂ and L''H₂) 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 L'H₂ ligand shows a medium band at (1610cm⁻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 (L'H₂) changed after complexation with Co(II) from (1610cm⁻¹) to (1605cm⁻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 (N₂O₂) tetradentate ligands and coordinate to metal ions from phenolic oxygen atoms and azomethine nitrogen atoms.

IR spectrum of L''H₂ 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
L'H ₂	1610	1281
[L'Co ₂ Cl ₄]	1605	1241
[L'Cu ₂ Cl ₄]	1606	1240
L''H ₂	1614	1275
[L''Co ₂ Cl ₄]	1608	1255
[L''Cu ₂ Cl ₄]	1606	1257

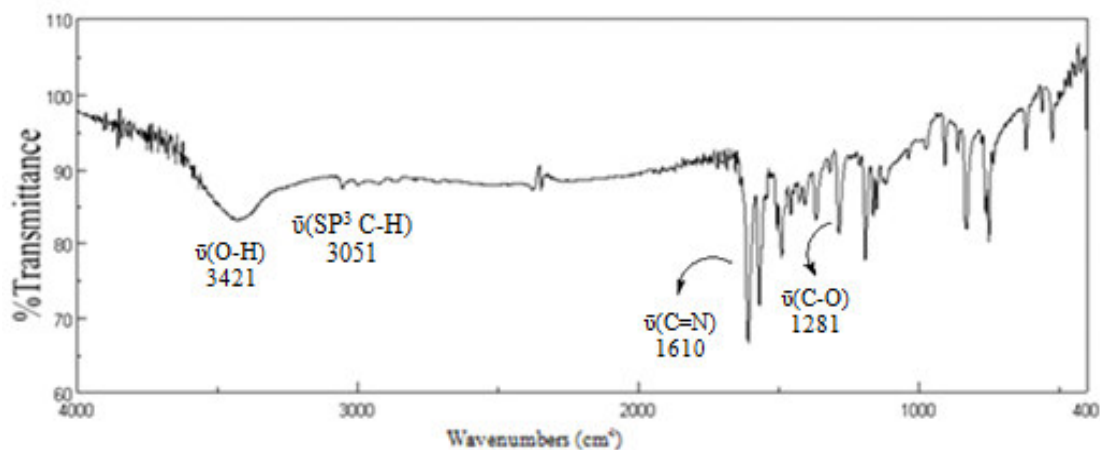


Figure 1. IR absorption spectra of ligand (L/H₂)

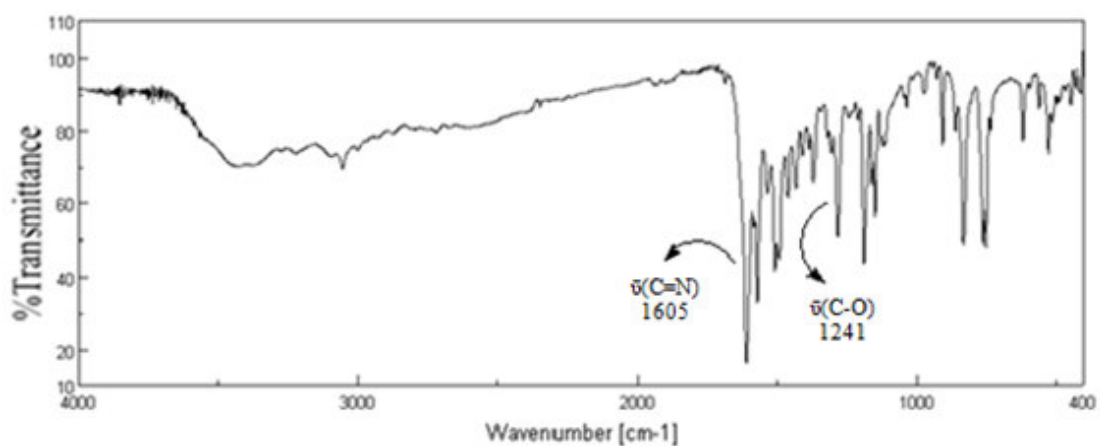


Figure 2. IR absorption spectra of [L/Co₂Cl₄]

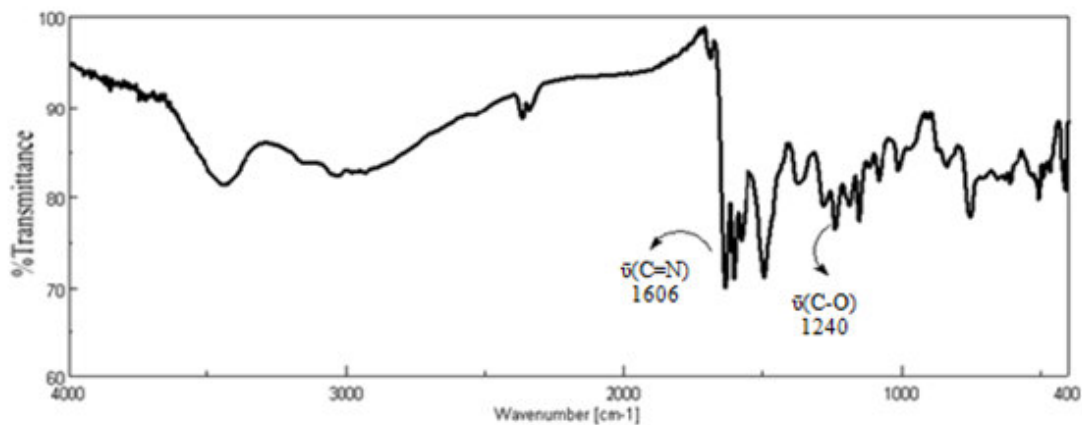


Figure 3. IR absorption spectra of [L/Cu₂Cl₄]

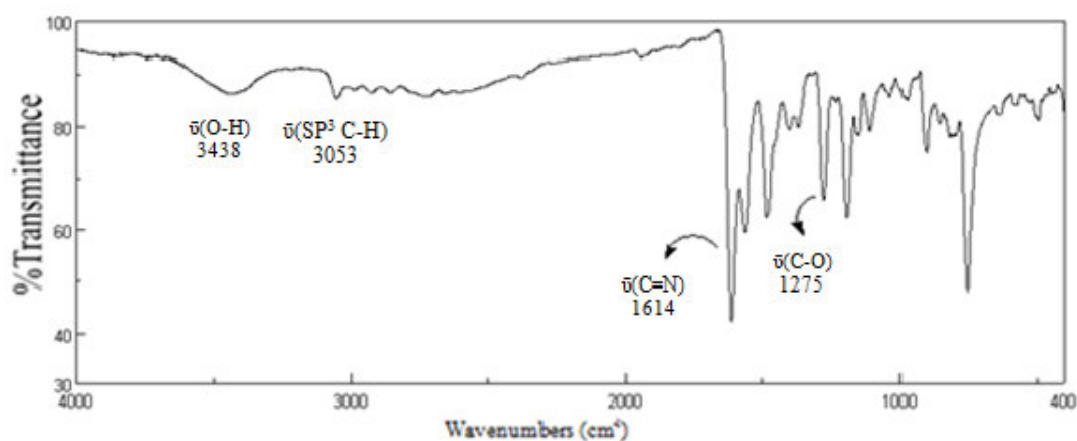


Figure 4. IR absorption spectra of L'H₂

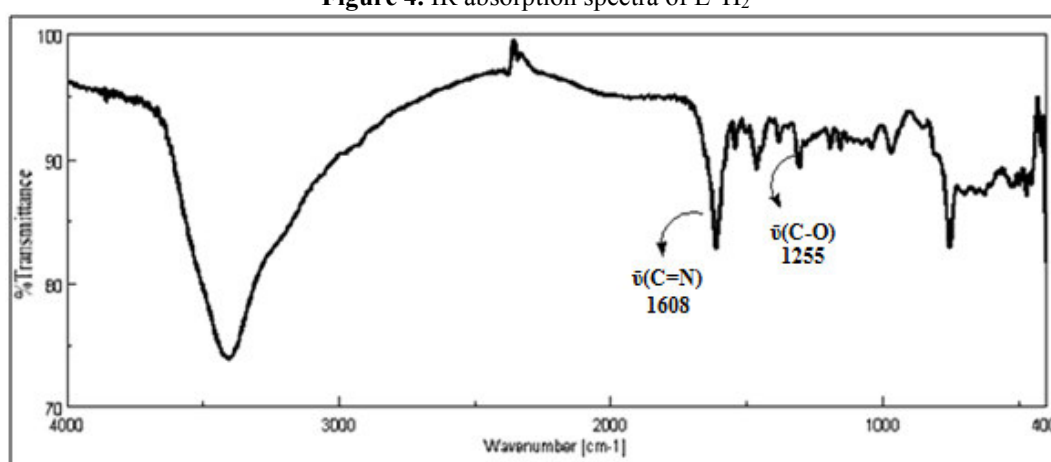


Figure 5. IR absorption spectra of [L'Co₂Cl₄]

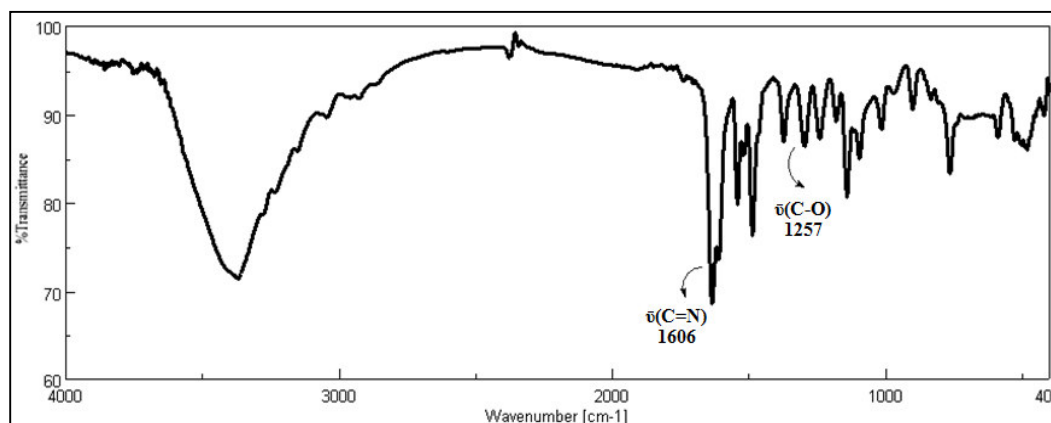


Figure 6. IR absorption spectra of [L'Cu₂Cl₄]

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 (L'H₂) presented two bands in the UV interval at 261nm assigned to ($\pi \rightarrow \pi^*$), 372nm assigned to ($n \rightarrow \pi^*$) transitions respectively.

The electronic spectra of the [L'Co₂Cl₄] in DMF has two bands at (600, 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 planar structure [13] (Fig 7):

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

Compounds	Electronic spectra nm	Assignments	Geometry
$L'H_2$	261 372	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	
$[L'Co_2Cl_4]$	600 670	${}^4T_{1g}(P) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	Square planner
$[L'Cu_2Cl_4]$	530	$({}^2B_{1g} \rightarrow {}^2A_{1g})$	Square planner
$L''H_2$	275,335 370	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	
$[L''Co_2Cl_4]$	435 465	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	Tetrahedral
$[L''Cu_2Cl_4]$	430	$({}^2B_{1g} \rightarrow {}^2A_{1g})$	Square planner

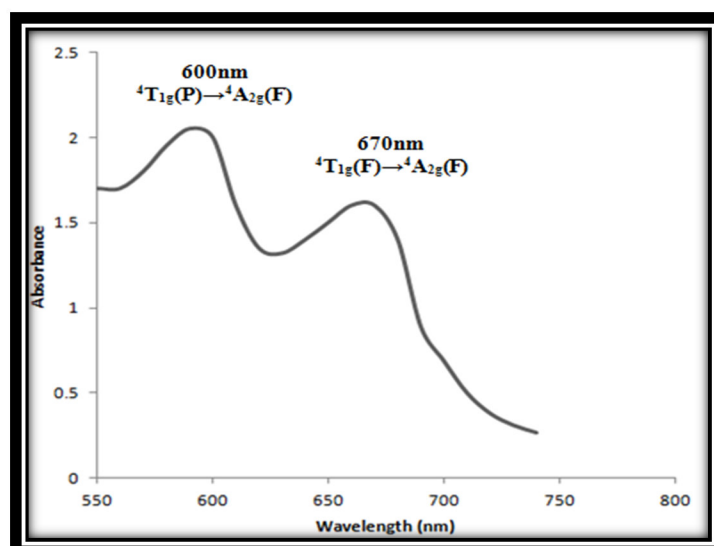


Figure 7. UV absorption spectra of $[L'Co_2Cl_4]$

The electronic spectra of the $[L'Cu_2Cl_4]$ in DMF has one band at (530nm). This band may be assigned to the transitions $({}^2B_{1g} \rightarrow {}^2A_{1g})$, The position of this band suggests a square planner structure [14] (Fig 8):

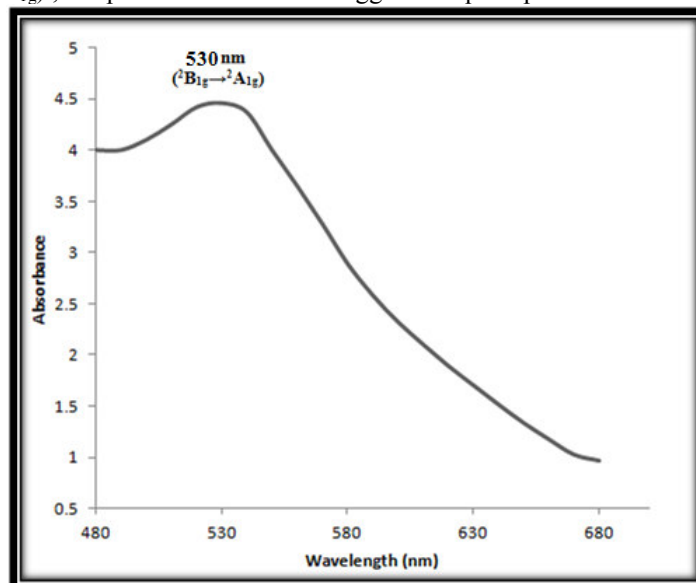


Figure 8. UV absorption spectra of $[L'Cu_2Cl_4]$

The spectrum of Schiff base ($L''H_2$) presented three bands in the UV interval at (275nm) and (335nm) assigned to $(\pi \rightarrow \pi^*)$, (370nm) assigned to $(n \rightarrow \pi^*)$ transitions, respectively. The electronic spectra of the $[L''Co_2Cl_4]$ in DMF has two bands at (435, 465)nm. 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 a tetrahedral structure [15] (Fig 9):

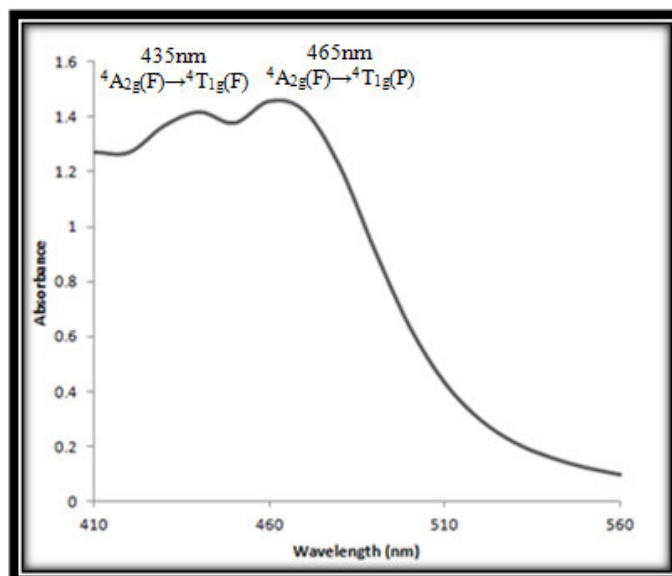


Figure 9. UV absorption spectra of [L''Co₂Cl₄]

The electronic spectra of the [L''Cu₂Cl₄] 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 planer structure [14] (Fig 10):

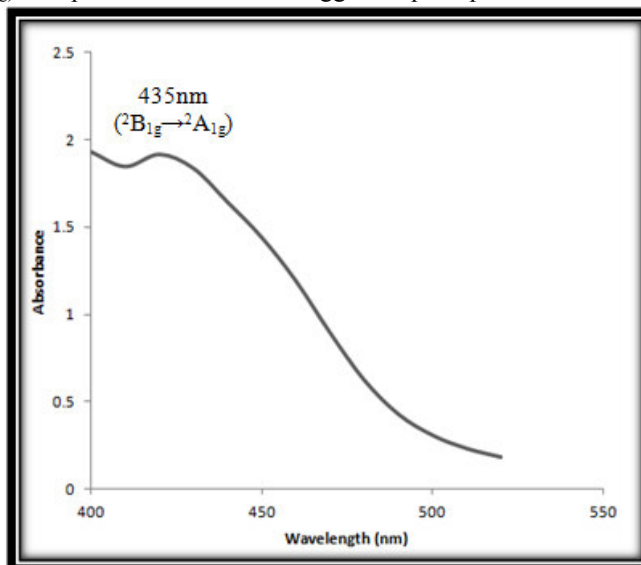


Figure 10. UV absorption spectra of [L''Cu₂Cl₄]

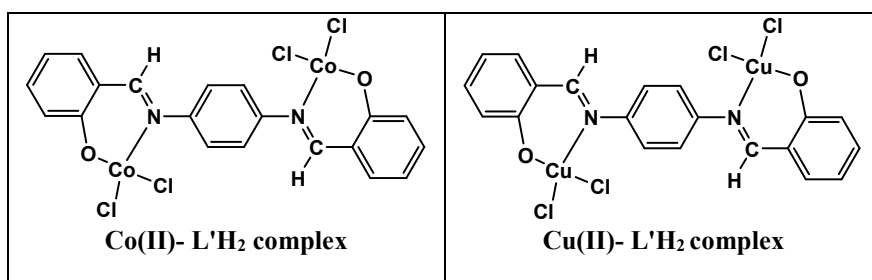


Figure 11. Suggested structures for the L'H₂ complexes

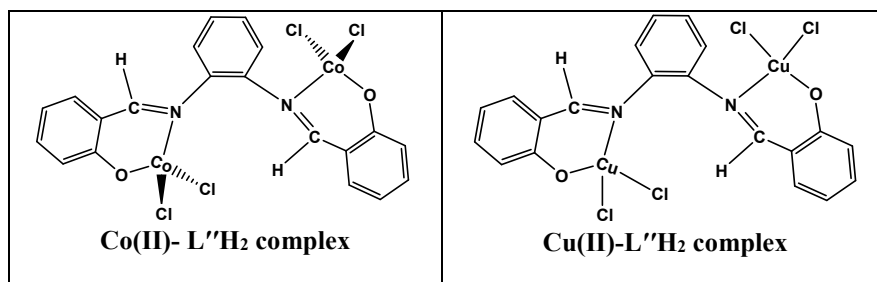


Figure 12. Suggested structures for the $L'H_2$ complexes

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

(1H -NMR) spectra of the Schiff base ligand $L'H_2$ revealed its formation by the presence of (HC=N) proton signal at ($\delta=8.84$ ppm) and proton signal for hydroxyl at ($\delta=13.01$ ppm). The (^{13}C -NMR) of the $L'H_2$ ligand exhibits signal at ($\delta=164.47$ ppm). This signal assigned to carbon Azomethine group.

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

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

Compounds	1H -NMR(δ ppm)	^{13}C -NMR(δ ppm)
$L'H_2$	13.01 (s, 2H, OH) 8.84 (s, 2H, HC=N) 7.50-7.48 (d, 2H, H ₆ , H _{6'}) 7.47-7.43 (d, 4H, b, b', c, c') 7.32-7.28 (dd, 2H, H ₅ , H _{5'}) 6.88-6.83 (m, 4H, H ₃ , H _{3'} , H ₄ , H _{4'})	117.69(C ₆ ,C _{6'}), 119.95(C ₂ ,C _{2'}), 120.35(C ₄ ,C _{4'}), 123.39(d,d',c,c'), 133.84(C ₃ ,C _{3'}), 134.14(C ₅ ,C _{5'}) 148.12(b,b'), 162.13(C ₇ ,C _{7'}), 164.47(a,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')

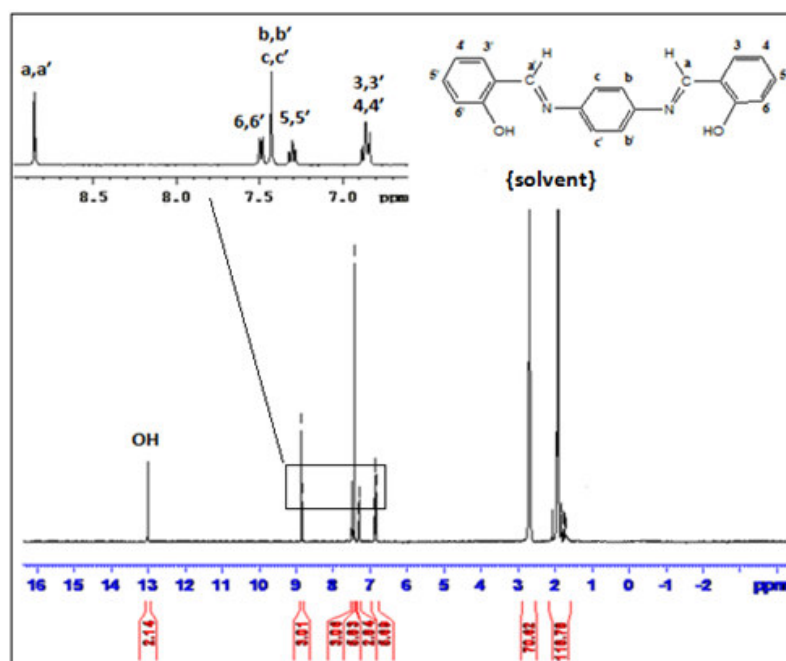


Figure 13. 1H -NMR spectrum of $L'H_2$.

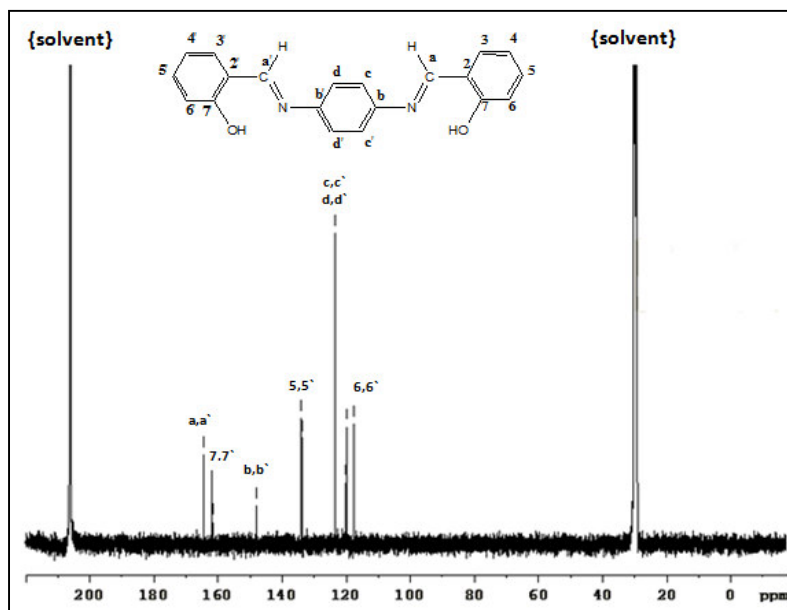


Figure 14. ^{13}C -NMR spectrum of $L'H_2$.

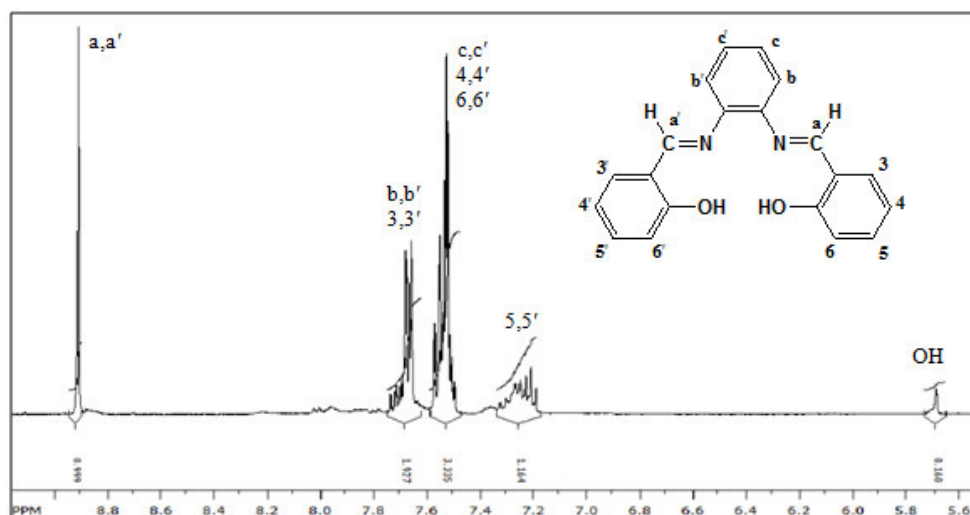


Figure 15. ^1H -NMR spectrum of $L''H_2$.

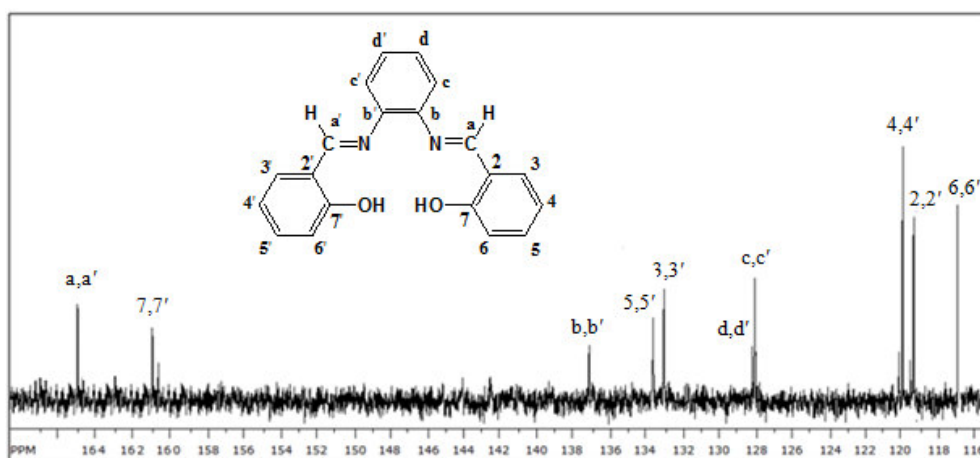


Figure 16. ^{13}C -NMR spectrum of $L''H_2$.

Conclusions

In this research the preparation, isolation, and characterization of a new tetradentate Schiff base derived from 2-Hydroxybenzaldehyde and its complexes with Co(II) and Cu(II) have been carried out. It has been proposed that the Schiff base ligand coordinates through the nitrogen of the azomethine group and the phenolic oxygen atom, forming a stable chelate complex.

In the light of the above discussion, square planar geometry has been proposed for Cu(II) complexes with both $L'H_2$ and $L''H_2$ ligands. Whereas Co(II) formed square planar with $L'H_2$ and with $L''H_2$ a tetrahedral structure, respectively.

References:

- [1]- Pichon.C, Dechambenoit.P & Cl rac.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.
- [2]- Abdallah.S.M, Mohamed.G.G, Zayed.M.A & Abou El-Ela.M.S. (2009) . Spectroscopic study of molecular structures of novel Schiff base derived from o-phthaldehyde and 2-aminophenol and its coordination compounds together with their biological activity, *Spectrochim. Acta A*,V73, pp.833–840.
- [3]- Chattopadhyay.S, Drew.M.G.B & Ghosh.A. (2008).Methylene Spacer-Regulated Structural Variation in Cobalt (II/III) Complexes with Bridging Acetate and Salen-Type Schiff Base Ligands, *Eur. J. Inorg. Chem*, V2008, pp.1693–1701.
- [4]- 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.
- [5]- 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.
- [6]- 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.
- [7]- 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.
- [8]- Datta.A, Karan.N.K, Mitra.S & Rosair.G. (2002).Synthesis and Structural Characterization of $[Cu(NH_2CH_2C_6H_4N=CHC_3H_5N)Cl_2]$, *Z.Naturforsch*, V57b, pp.999-1002.
- [9]- 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.
- [10]-  enol.C, Hayvali.Z, Dal.H & H kelek.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.
- [11]- 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.
- [12]- Shebl.M. (2008).Synthesis and spectroscopic studies of binuclear metal complexes of a tetradentate N₂O₂ Schiff base ligand derived from 4,6-diacetylresorcinol and benzylamine, *Spectrochimica Acta Part A*, V70, pp.850-859.
- [13]- 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'-diaminobenzidine, 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.
- [14]- 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.
- [15]- 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.