

Synthesis and Characterization of Co (II) And Cu (II) Complexes Of Some Aroylhydrazone Ligands

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Abstract:

Aroylhydrazones which are compounds formed by the reaction of carbonyl compounds (ketones or aldehydes) with hydrazine or its derivatives, are among the important Schiff bases. They form coordination compounds with almost all transition elements, forming various geometries. The present work focuses on the synthesis and characterization of Co (II) and Cu (II) complexes of some aroylhydrazone ligands. For this purpose three (3) different aroylhydrazone ligands were synthesized, by reacting different types of hydrazine derivatives with carbonyl compounds (ketones or aldehydes). Each of these ligands were used to form complexes with Co (II) and Cu (II), using their hexahydrated metal salts. The complexes were characterized using; IR spectroscopy, UV-Visible spectroscopy, elemental analysis, conductivity measurement and magnetic susceptibility measurement.

Keywords — Aroylhydrazone, complexes and Schiff base.

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1.0 INTRODUCTION.

Coordination compounds are composed of a metal atom or ion and one or more and one or more **ligands** (atoms, ions, or molecules) that donate electrons to the metal. This definition includes compounds with metal-carbon bonds, or organometallic compounds. *Coordination compound* comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another. In coordination compounds the donors are usually the ligands, and the acceptors are the metals. Coordination compounds are examples of acid-base adducts frequently called **complexes** or, if charged, **complex ion**.

Although the formal study of coordination compounds really begins with Alfred Werner (1866–1919), coordination compounds have been used as pigments and dyes since antiquity. Examples include Prussian blue ($\text{KFe}[\text{Fe}(\text{CN})_6]$), aureolin yellow, ($\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot 6\text{H}_2\text{O}$), and alizarin red dye (the calcium aluminum salt of 1,2-dihydroxy-9,10-anthraquinone). The tetraamminecopper (II) ion, actually $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ in solution, which has a striking royal blue color—was known in prehistoric times. The formulas of these compounds were deduced in the late nineteenth century, providing background for the development of bonding theories [12].

The research interest in inorganic chemistry has progressively increased over hundreds of years and has been flourished by the versatile development in the area of coordination chemistry. Widespread interest in the chemistry

of coordination compounds is associated with their broad spectrum of applications in different areas such as catalysis, molecular sensors, nonlinear optics, bioinorganic, magnetic and medicinal chemistry. Coordination chemistry has greatly contributed to the rational design of new classes of host molecules. For instance, crystal structure of a copper complex which resembles a wheel and axle' may belong to a new category of host molecules [6].

Molecules with this shape is not suitable for close packing but tend to accommodate other molecules thus serving as adsorbents, sensors and catalysts. The architectural beauty of coordination compounds is due to the interesting ligand systems containing different donor sites Smagnetism, supra molecular chemistry, non-silicon based devices, precursors for various phase deposition and single molecule— based photonic devices and sensors[2].

1.4 COBALT

Humans have been using compounds of cobalt since at least 1400 B.C. The compounds were used to color glass and glazes blue. In 1735, Swedish chemist Georg Brandt analyzed a dark blue pigment found in copper ore. Brandt demonstrated that the pigment contained a new element, later named cobalt.

Cobalt is a transition metal, one of several elements found in Row 4 through 7 between Groups 2 and 13 in the periodic table. Cobalt is located between iron and nickel and shares many chemical and physical properties with these two elements.

The word cobalt may have been first used near the end of the fifteenth century. In German, the word Kobold means "goblin" or "evil spirit." The term was used by miners to describe a mineral that was very difficult to mine and was damaging to their health. When the mineral was heated, it gave off an offensive gas that caused illness. The gas that affected the miners was arsenic trioxide (As_2O_3), which often occurs with cobalt in nature. At first, chemists were skeptical about Brandt's claims of a new element, but he continued his research on the mineral. He showed that its compounds were a much deeper blue than copper compounds. Eventually, Brandt was given credit for the discovery of the element. The name chosen was a version of the original German term, Kobold. Cobalt is an important element in the formation of cobalamin or vitamin B12. It is easily assimilated in the body and it is stored in the red blood cells, liver, spleen, kidney and pancreas. Cobalt in small amount is essential to many life forms including humans. Cobalt compounds are widely used to make coloring materials. The following compounds are used to color glass, glazes, cosmetics, paints, rubber, inks, and pottery: cobalt oxide, or cobalt black (Co_3O_4); cobalt potassium nitrite, or cobalt yellow ($CoK_3(NO_2)_6$); cobalt aluminates, or cobalt blue ($Co(AlO_2)_2$); and cobalt ammonium phosphate, or cobalt violet ($CoNH_4PO_4$) [6]. Another important use of cobalt compounds is as catalysts. Cobalt molybdate ($CoMoO_4$) is used in the petroleum industry to convert crude oil to gasoline and other petroleum products. It is also used to remove sulfur from crude oil [18].

1.5 COPPER

Copper is reddish brown metal which melt at 1083C. It is malleable and ductile and can be drawn in to wire of small diameter as 0.03mm. It is excellent conductor of heat and electricity, the best conductor next to silver. The presence of other metals even in small quantities appreciably lower the conductivity. Copper has +1 and +2 oxidation states in its complexes, and out of these most stable +2 oxidation state predominates over less stable +1 oxidation state. A wide variety of coordination compounds are formed by the combination of different types of ligands with Cu (II) cation. Normally the copper complexes are having square planar, tetrahedral and octahedral stereochemistry.

In Cu (II) complexes, the $3d^9$ outer electronic configuration lacks cubic symmetry and hence there are distortions from basic stereochemistries and Jahn-Teller effect plays a major role in deciding the distortion effect of stereochemistries of Cu(II) complexes. Copper is essential constituent of many metalloproteinase and enzymes. The copper containing

enzymes play important role in pigmentation of skin, functioning of brain and in ion metabolism in the body. The chemistry of aqueous copper (II) oxidation state is similar to that of +2 ions of other transition elements. Although most of anhydrous copper (II) salts are colourless, they are blue when hydrated. This is due to the presence of the hydrated ion $[Cu(H_2O)_4]^{+2}$ which is blue. Solution of copper (II) salts are acidic due to hydrolysis, the level of hydrolysis however is quite small [19].

1.6 Aroylhydrazones

Hydrazones which belong to a class of azomethines having the group $C=N-N-$ are interesting ligands in coordination chemistry. Introduction of a $C=O$ group in the hydrazide part increases the electron delocalization and denticity of the hydrazones and the resulting compound is known as an *aroylhydrazone*.

Aroyl hydrazones and their metal derivatives often possess biological activity and can inhibit enzymatic reactions in the cell. N-aroylhydrazones are usually obtained by condensation of aldehydes or ketones with aroylhydrazines, in the presence of an acid catalyst, with reaction times varying from 30 minutes to several hours [42,43]. Their purification can be accomplished by simple recrystallization and they are stable at ambient temperature. Recently variety of N-aroylhydrazones were synthesized by another method i.e., under microwave irradiation within 2.5-10 minutes, starting from benzosalicyloyl and Isonicotinic hydrazides. The protocol developed employs microwave irradiation in the absence of solvents and catalysts, leading to high yields [2].

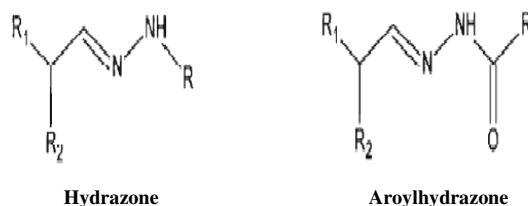


Figure 1 hydrazone and aroylhydrazone structure

1.6.1 Mode of bonding of aroylhydrazone ligands with transition metals

The bonding of hydrazone ligands with transition metals may proceed according to one of the following paths;

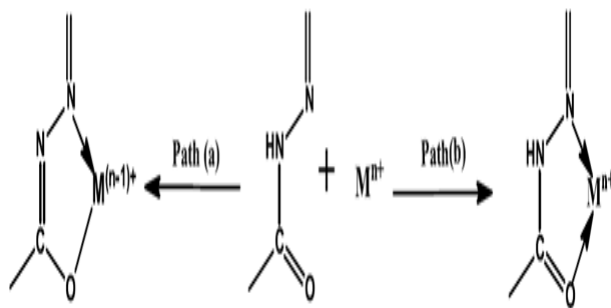


Fig.2 Mode of bonding of aroylhydrazone ligands with transition metals. The first one leads to formation of complexes in which the hydrazone react with transition metal in the ketonic form:(Fig. 2 (a)) Whereas the second one hydrazones react in the enolic form (Fig. 2(b)) leading to the formation of two types of complexes. The mode of bonding of hydrazone and molecular structure of the resulted complexes depends on the nature of the metal ion, anion of the salt and alkalinity of the reaction medium.

2.0 MATERIALS AND METHODS

2.1 Equipments:

Heating mantles
Electronic weighing machine
Melting point apparatus
Perkin-Elmer 240 analyzer for elemental analysis
IR spectrophotometer
UV/VIS spectrophotometer
Magnetometer
Magnetic stirrer

2.2 Apparatus:

Reflux condensers
Round bottom flasks
Beakers
Conical flasks
Filter papers
Stirrer
Measuring cylinder

2.3 Reagents:

Methyl anthranilate
Hydrazine hydride
Ethanol
Methanol
Diethyl ether
Calcium chloride (fused)
Methyl benzoate
Methyl salicylate

Acetophenone
Benzaldehyde
 $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$
 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

2.4 EXPERIMENTAL:

2.4.1 Physical measurements:

C, H, and N analyses were performed by perkin-elmer 2400 instrument. FTIR spectra ($4000\text{--}600\text{ cm}^{-1}$) as KBr discs of the samples were recorded on a jasco-460 plus spectrophotometer. Electronic spectra were obtained using a cecil ce7400, 7000 series, uv/vis spectrophotometer. Magnetic susceptibility was measured with a sherwood scientific msbm1 sample magnetometer with $\text{Hg}[\text{SCN}_4]$ as calibrant.

2.4.2 Chemicals and solvents:

Chemicals used are of high purity and were used without further purification. Hydrazine hydride, diethyl ether, calcium chloride, methyl benzoate, methyl salicylate, benzaldehyde, triethyl mine and acetophenone were obtained from loba chemie laboratory reagents and fine chemicals. Methyl anthranilate, cobalt chloride (hexahydrate) and cupric chloride (hexahydrate) were obtained from ASES chemical works (laboratory chemical division), jodhpur (india). Methanol and ethanol were used as solvents and were obtained from sigma-aldrich.

2.5 Syntheses of ligands:

The synthesis of final ligand consists of two steps.

2.5.1 Synthesis of acid hydrazides

2.5.1.1 the precursor ligand benzoylhydrazide was prepared by reacting methyl benzoate (6.26 gm / 50 mmol) and hydrazine hydride (3.64 gm / 75 mmol) under reflux condition for 3 hr. The resulting white compound was filtered, washed thrice with ethanol and diethyl ether, it was dried over fused CaCl_2 .

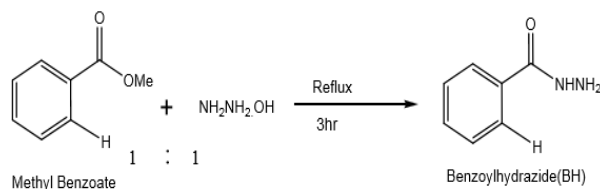


Figure 3 synthesis of (BH) precursor

2.5.1.2 The precursor ligand 2-aminobenzoylhydrazide was prepared by reacting methyl anthranilate (6.5 gm / 50 mmol) and hydrazine hydride (3.64 gm / 75 mmol) under reflux condition for 3 hr. The resulting white compound was filtered, washed thrice with ethanol and diethyl ether which was dried over fused CaCl_2 .

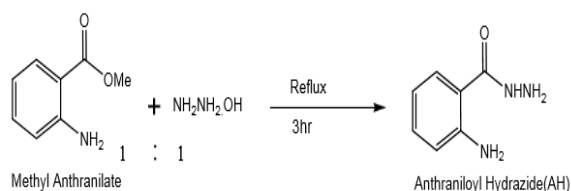
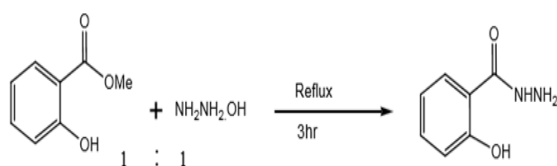


Fig.4 synthesis (AH) precursor

2.5.1.3 The precursor ligand 2-hydroxybenzoylhydrazide was prepared by reacting methyl salicylate (6.5 gm / 50 mmol) and hydrazine hydride (3.64 gm / 75 mmol) under reflux condition for 3 hr. The resulting white compound was filtered, washed thrice with ethanol and diethyl ether, it was then dried over fused CaCl_2 .



Methyl salicylate (SH) Fig.5

synthesis of (SH) precursor

2.5.2 Synthesis of ligands

2.5.2.1 acetophenone anthranoylhydrazone ligand ($\text{L}_1^{\text{A}}\text{H}_1$)

The ligand Acetophenone anthranoylhydrazone ($\text{L}_1^{\text{A}}\text{H}_1$) was prepared by reacting 2-aminobenzoylhydrazide (1.51 gm / 10 mmol) and acetophenone (1.19 gm / 10 mmol) in 25mL of absolute EtOH. Three drops of conc. HCl were added and the resulting solution was refluxed for 3 h. The compound precipitated upon cooling to room temperature, was collected by filtration and recrystallized from EtOH and dried over fused CaCl_2 .

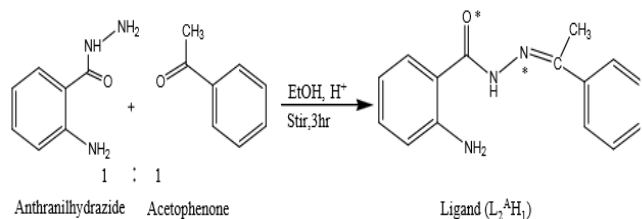
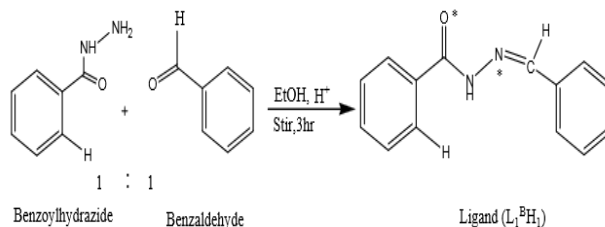


Fig.6 synthesis of ligand ($\text{L}_1^{\text{A}}\text{H}_1$)

2.5.2.2 Benzaldehyde Benzoylhydrazone Ligand ($\text{L}_2^{\text{B}}\text{H}_1$)

The ligand Benzaldehyde Benzoylhydrazone ($\text{L}_2^{\text{B}}\text{H}_1$) was prepared by reacting benzoylhydrazide (1.36 gm / 10 mmol) and benzaldehyde (1.19 gm / 10 mmol) in 25mL of absolute

EtOH. Three drops of conc. HCl were added and the resulting solution was refluxed for 3 h. The compound precipitated upon cooling to room temperature, was collected by filtration and recrystallized from EtOH and dried over fused CaCl_2 .



Benzaldehyde benzoylhydrazone Fig. 7 synthesis of ligand ($\text{L}_2^{\text{B}}\text{H}_1$)

2.5.2.3 Benzaldehyde salicyloylhydrazone Ligand ($\text{L}_3^{\text{S}}\text{H}_1$)

The ligand Benzaldehyde salicyloylhydrazone ($\text{L}_3^{\text{S}}\text{H}_1$) was prepared by reacting 2-hydroxybenzoylhydrazide (1.52 gm / 10 mmol) and benzaldehyde (1.06 gm / 10 mmol) in 30mL of absolute EtOH. Three drops of conc. HCl were added and the resulting solution was refluxed for 3 h. The compound precipitated upon cooling to room temperature, was collected by filtration and recrystallized from EtOH and dried over fused CaCl_2 .

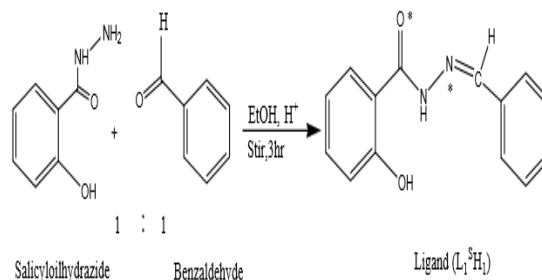


Fig.8 synthesis ligand $\text{L}_3^{\text{S}}\text{H}_1$

2.6 SYNTHESIS OF THE METAL COMPLEXES

2.6.1 Complex 1, $[\text{Co}^{2+}(\text{L}_2^{\text{B}}\text{A})_2]$:

(0.506 gm / 2.00-mmol) sample of ligand $\text{L}_2^{\text{A}}\text{H}_1$ was dissolved in 30 ml of methanol and (0.238gm/1.00-mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the solution. Color of the solution slowly changed to wine red. After 3 hr of refluxing, the remaining product was filtered, washed with methanol and dried over Calcium chloride (CaCl_2), in which red colored crystals were produced.

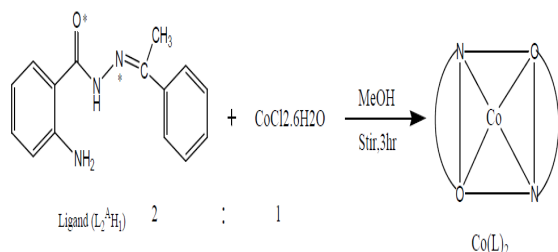


Fig.9 formation of Co complex with ($L_2^A H_1$) 2 Yield~75%. Anal. Calc for $C_{30}H_{28}N_6O_2Co$: C, 63.83; H, 4.93; N, 14.89. Found: C, 61.54; H, 5.02; N, 13.34.

2.6.2 Complex 2, [$Cu^{2+}(L_2^A H_1)_2$]

(0.506 gm / 2.00-mmol) sample of ligand $L_2^A H_1$ was dissolved in 30 ml of methanol and (0.238gm/1.00-mmol) of $CuCl_2.6H_2O$ was added to the solution. Color of the solution slowly changed to light green. After 3 hr of refluxing, the remaining product was filtered, washed with methanol, followed by ether and dried over $CaCl_2$, in which green colored crystals were produced.

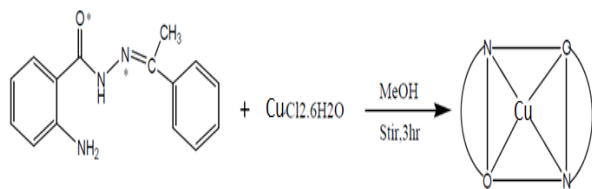


Fig.10 formation of Cu complex with ($L_2^A H_1$) 2 Yield~75%. Anal. Calc for $C_{30}H_{28}N_6O_2Cu$: C, 63.94; H, 4.65; N, 14.96. Found: C, 62.54; H, 3.72; N, 14.34.

2.6.3 Complex 3 [$Co^{2+}(L_1^S H_1)_2$]

A (0.480gm /2.00mmol) sample of ligand $L_1^S H_1$ was dissolved in 30 ml of methanol and (0.238gm /1.00-mmol) of $CoCl_2.6H_2O$ was added to the solution. Color of the solution slowly changed to wine red. After 3 hr of refluxing, the remaining product was filtered, washed with methanol, and dried over $CaCl_2$, in which red colored crystals were produced.

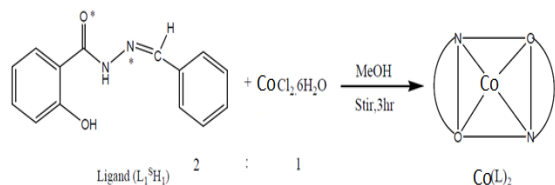


Fig.11 formation of Co complex with (L_1^S) 2 Yield~70%. Anal. Calc for $C_{28}H_{22}N_4O_4Co$: C, 62.87; H, 4.10; N, 10.10. Found: C, 57.77; H, 3.72; N, 9.64.

2.6.4 Complex 4 [$Cu^{2+}(L_1^S)_2$]

A (0.480gm /2.00mmol) sample of ligand $L_1^S H_1$ was dissolved in 30 ml of methanol and (0.238gm /1.00-mmol) of $CuCl_2.6H_2O$ was added to the solution. Color of the solution slowly changed to light green. After 3 hr of refluxing, the remaining product was filtered, washed with methanol, followed by ether and dried over $CaCl_2$, in which green colored crystals were produced.

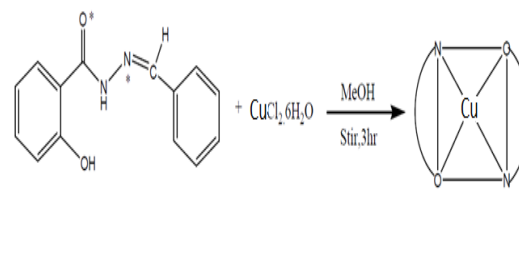
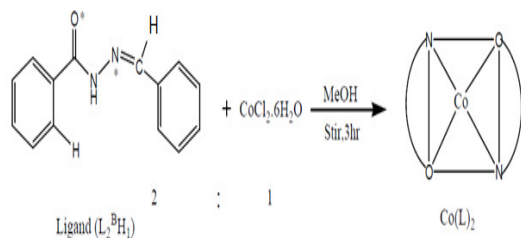


Figure 12 formation of Cu complex with (L_1^S) 2 Yield~76%. Anal. Calc for $C_{28}H_{22}N_4O_4Cu$: C, 62.45; H, 4.08; N, 10.41. Found: C, 63.77; H, 3.92; N, 3.94.

2.6.5 Complex 5, [$Co^{2+S}(L_1^B H_1)_2$]

A (0.448gm /2.00-mmol) sample of ligand $L_1^B H_1$ was dissolved in 30 ml of methanol and (0.238gm /1.00-mmol) of $CoCl_2.6H_2O$ was added to the solution, to this solution drop of Et_3N was added. Color of the solution slowly changed to dark pink. After 3 hr of refluxing, the remaining product was filtered, washed with methanol and dried over $CaCl_2$, in which red colored crystals were produced.

Fig.13 formation of Co complex with (L_1^B) 2



Yield~65%. Anal. Calc for $C_{30}H_{28}N_6O_2Co$: C, 66.54; H, 4.36; N, 11.09
Found: C, 66.54; H, 4.12; N, 11.04.

2.6.6 Complex 6, $[Cu(II)(L_1^B H_1)_2]$:

A (0.448gm /2.00-mmol) sample of ligand $L_1^B H_1$ was dissolved in 30 ml of methanol and (0.238gm /1.00-mmol) of $CuCl_2 \cdot 6H_2O$ was added to the solution, to this solution drop of Et3N was added. Color of the solution slowly changed to light green. After 3 hr of refluxing, the remaining product was filtered, washed with methanol, followed by ether and dried over $CaCl_2$, in which green colored crystals were produced.

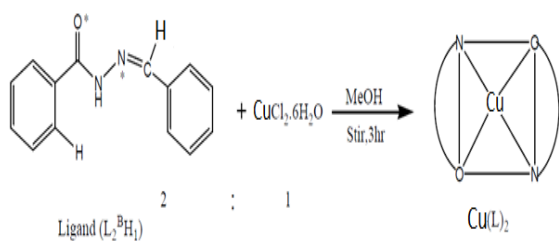


Fig.14 formation of Cu complex with ($L_1^B H_1$) 2 Yield~65%. Anal. Calc for $C_{28}H_{22}N_2O_2Cu$: C, 66.4; H, 4.35; N, 11.07. Found: C, 66.0; H, 4.02; N, 11.34.

3.0 RESULT AND DISCUSSION

The ligands and the complexes have been characterized on the basis of IR spectral data, UV-VIS spectral data, magnetic susceptibility, elemental analysis molar conductivity. I have successfully characterized all the complexes, the different results were discussed below:

3.1 Protonated / Deprotonated form of Schiff's Bases:

Bidentate ligands used in this work have one possible site of deprotonation. The bidentate Schiff's ligands can undergo deprotonation from only enolised amide oxygen. When the Schiff's base ligands are reacted with a Co (II) salt and Cu

(II) salt, the ligands get deprotonated from the enolised amide oxygen as well as from the phenolic oxygen.

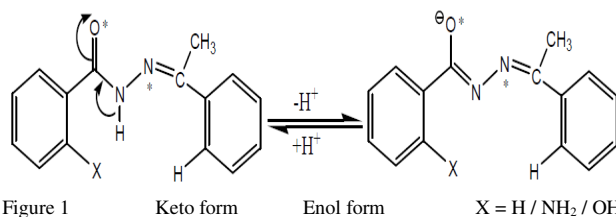


Figure 1

3.2. Spectral characteristics

3.2.1 Infrared spectra

Infrared spectra of the aroylhydrazones were recorded on a JASCOFT-IR-5300 spectrometer in the 4000-400 cm^{-1} range using KBr pellets. The significant bands observed in the IR spectra of the aroylhydrazones along with their relative assignments are presented in the Table 2.1. FT-IR spectral data of the compounds are in accordance with their molecular structure. In the IR spectra of aroylhydrazones, $\nu(C=N)$ bands are observed in the 1597-1609 cm^{-1} range indicating the condensation of hydrazide and the aldehyde/ketone moiety and it is in agreement with the literature reports of aroylhydrazones [40]. In the IR spectra of aroylhydrazones the $\nu(C=O)$.

stretching vibrations are observed at 1669, 1632 and 1683 cm^{-1} for $L_2^A H_1$, $L_1^B H_1$ and $L_1^S H_1$ respectively suggesting that the hydrazones exist in the amido form in the solid state. This is further supported by medium bands in the 3067-3186 cm^{-1} range due to $\nu(N-H)$ vibration. The N-N stretching vibrations are found in the 1102-1127 cm^{-1} region. Figs. 22-25 depict the infrared spectra of the aroylhydrazones.

Coordination of iminolate oxygen is consistent with the presence of new bands in the 1335-1348 cm^{-1} region, assignable to $\nu(C-O)$ stretching vibration for these complexes. This is further confirmed by the appearance of new bands in the 488-559 cm^{-1} region assigned to $\nu(Co-O)$. The bands corresponding to the stretching vibration of the azomethine group of the free hydrazones which appeared in the 1603-1609 cm^{-1} region have been shifted to 1592-1603 cm^{-1} region in the spectra of the complexes indicating the coordination of the azomethine nitrogen to the central metal ion. This is further corroborated with the appearance of new bands in the 1519-1523 cm^{-1} region due to the newly formed C=N moiety. Bonding through the N of the azomethine group has been further confirmed by the observation of $\nu(Co-N)$ bands in the 422-456 cm^{-1} region.

The IR spectra of the Copper complexes show the disappearance of C=O bands at 1669, 1632, and 1683 and

appearance of new C=O bands at 1284, 1244, and 1272. In addition the disappearance of N-H bands at 3067, 3075 and 3069 is a clear indication of the coordination of ligands in the deprotonated form. Upon complexation, stretching vibrations of azomethine bond are found to be weakened due to coordination with Copper center. This results in a negative shift in azomethine stretching frequencies in comparison with free hydrazones. Here in all compounds the azomethine bands are shifted to lower wavenumbers and the newly formed $-C=N-N=C-$ moiety gave bands in between 1520-1550 cm^{-1} . The bands around 415 cm^{-1} indicate the coordination of azomethine nitrogen to copper centre.

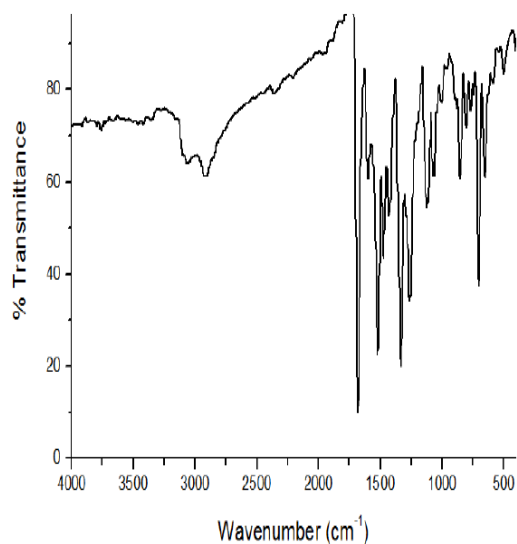


Figure 2 IR spectra of ligand $[L_2^A H1]$

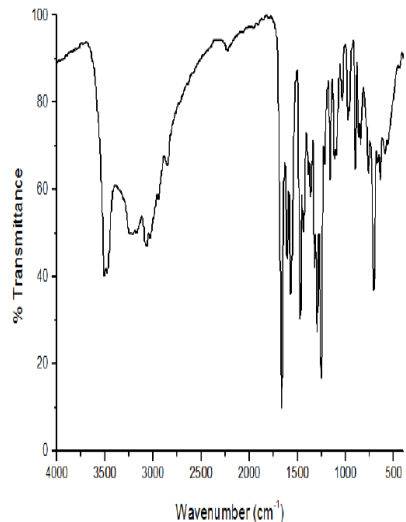


Figure 3 IR spectra of ligand $[L_1^B H1]$

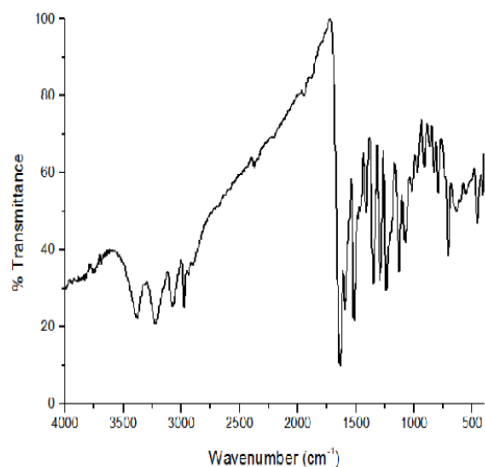


Figure 4 IR spectra of ligand $[L_1^S H1]$

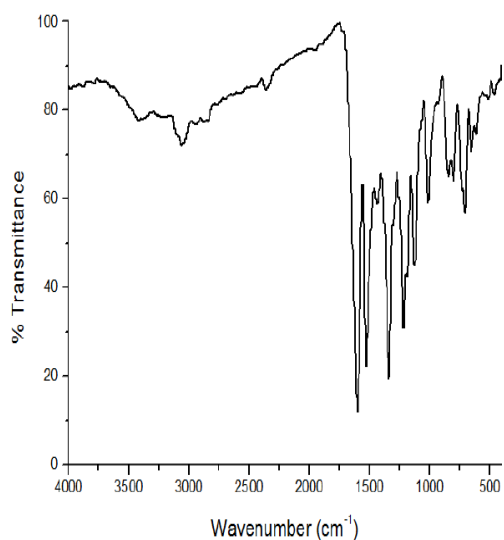


Figure 5 IR spectra of Co-complexes of $[L_2^A H_1]$

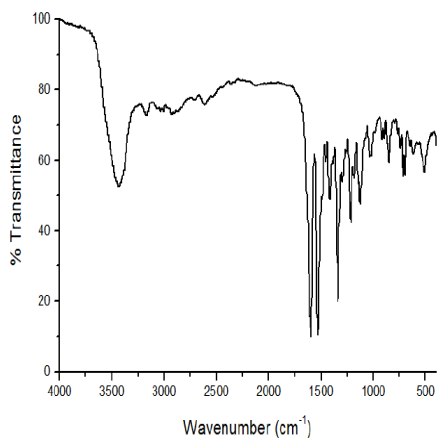


Figure 6 IR spectra of Co-complexes of $[L_1^B H_1]$

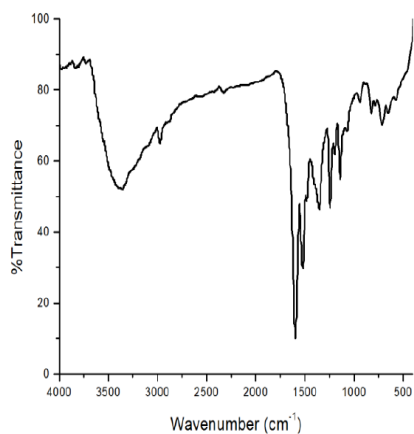


Figure 7 IR spectra of Co-complexes of $[L_1^S H_1]$

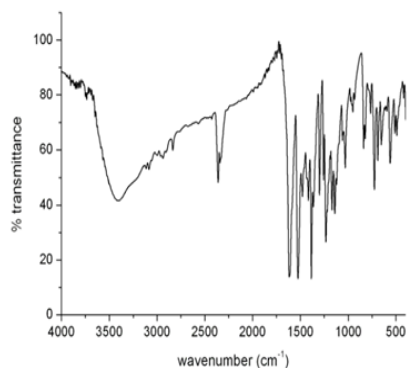


Figure 8 IR spectra of Cu-complexes of $[L_2^A H_1]$

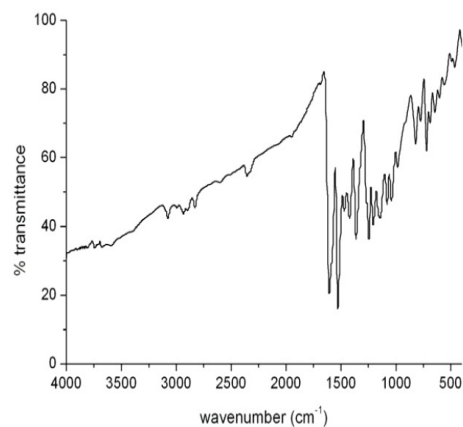


Figure 9 IR spectra of Cu-complexes of $[L_1^B H_1]$

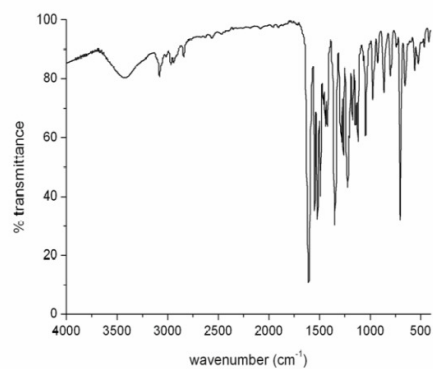


Figure 10 IR spectra of Cu-complexes of $[L_1^S H_1]$

Table 1 IR spectral data of the ligands

Ligands	$\nu(C=N)$	$\nu(C=O)$	$\nu(N-H)$	$\nu(N-N)$
$L_2^A H_1$	1609	1669	3067	1110
$L_1^B H_1$	1603	1632	3075	1124

$L_1^S H_1$	1597	1683	3069	1122
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Table 2 IR spectral data of Cobalt (II) Complexes

Complexes	$\nu(C=N)$	$\nu(C-O)$	$\nu(N-N)$	$\nu(Co-O)$	$\nu(Co-N)$
Co $[L_2^A H_1]_2$	1607	1348	1155	488	429
Co $[L_1^B H_1]_2$	1590	1335	1140	426	456
Co $[L_1^S H_1]_2$	1593	1345	1165	559	445

Table 3 IR spectral data of Cupper (II) complexes

Complexes	$\nu(C=N)$	$\nu(C-O)$	$\nu(N-N)$	$\nu(Cu-O)$	$\nu(Cu-N)$
Cu $[L_2^A H_1]_2$	1594	1233	1140	486	420
Cu $[L_1^B H_1]_2$	1591	1244	1155	480	419
Cu $[L_1^S H_1]_2$	1588	1225	1172	475	419

3.2.2 Electronic spectra:

The electronic spectral study also proves the generation of a tetrahedral Co(II) center when the complexes are present in solution of CH_3CN . Uv-vis spectra (Figure 31-33) of the Co(II) complexes (1-3) exhibit several absorption bands in the 250-750 nm regions. The absorption band exhibits a d-d transition at 565- 590 nm regions, a charge transfer transition (CT) at 330-340 nm region which may be assigned to the ligand-to-metal charge transfer and the bands in the range 220-250 nm may due to intra ligand transition.

In the copper complexes several absorption bands were also found around 200-760nm regions the absorption bands at the 550-765nm regions may be due to a d-d transition, a charge transfer transitions (CT) at 300-395nm regions, which may be due to ligand-metal charge transfer transitions and the band at 200-250 may assigned to intra ligand transition.

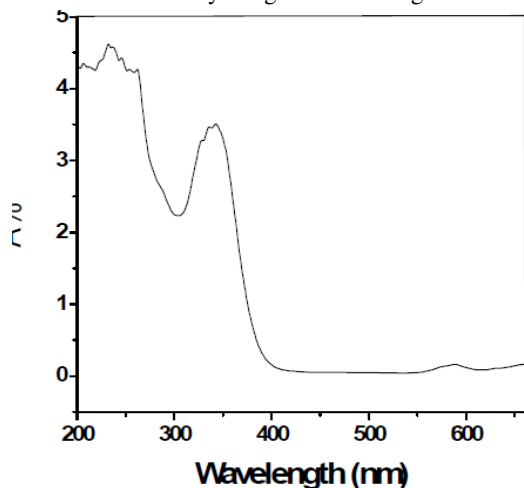


Figure 11 Electronic spectra Co-complex of [L2AH1]

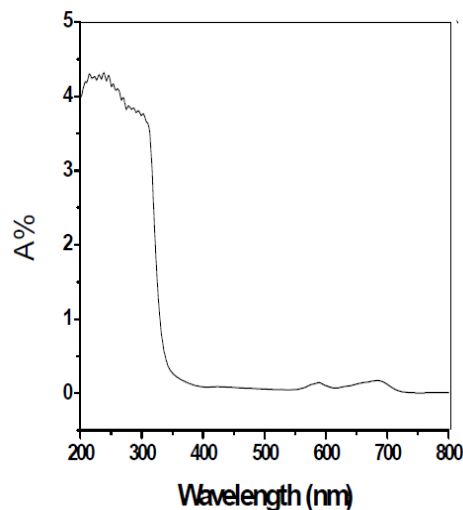


Figure 12 Electronic spectra of Co-complexes of [L1BH1]

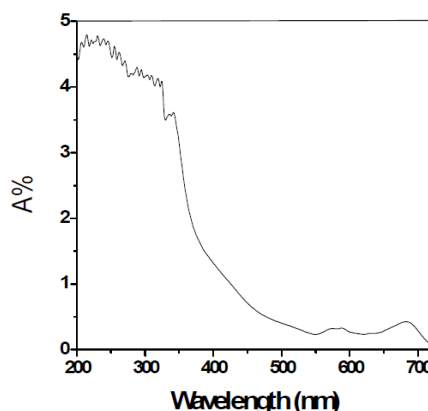


Figure 13 Electronic spectra Co-complexes of [L1SH1]

3.3. Magnetic Studies:

The Cobalt (II) complexes (1-3) and the copper (II) complexes were found to be paramagnetic which excludes of square planar configuration. The measured magnetic moment value for Cobalt (II) complexes were found to be in the range of 4.60-4.65 BM (theoretical value 3.84 BM) and for copper(II) complexes(1-3) in the range of 1.80-1.20BM (theoretical value 1.73BM) are evidence for tetrahedral geometry This higher experimental values may be due to orbital contribution.

Table 4 Molar Conductivity & Magnetic susceptibility of Cobalt II Complexes and Cupper II complexes

Complexes	$\lambda m^\#$	μ_{eff} (BM)
Co $[L_2^A H_1]_2$	15	4.60
Co $[L_1^B H_1]_2$	10	4.42

Co [L ₁ ^S H ₁] ₂	12	4.60
Cu [L ₂ ^A H ₁] ₂	8	1.80
Cu [L ₁ ^B H ₁] ₂	5	1.90
Cu [L ₁ ^S H ₁] ₂	7	1.20

[#]Molar conductivity (in mho cm² mol⁻¹) taken in 10⁻³ M DMF.

3.5. Expected geometry of Co (II) and Cu (II) complexes containing bidentate hydrazone ligands:

Having all the characterization data of all the Six Cobalt (II) and Copper (II) complexes we can predict the preliminary geometry of these Six complexes as the final structure can be predicted after having the corresponding X-ray structure only. From the preliminary characterization data I have predicted the expected structures of these synthesized complexes as depict below:

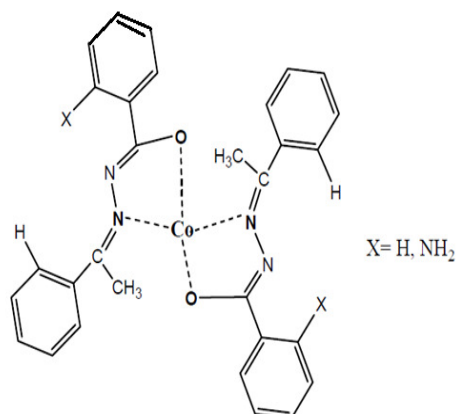


Figure 14 structure of Co[L₂^AH₁]₂

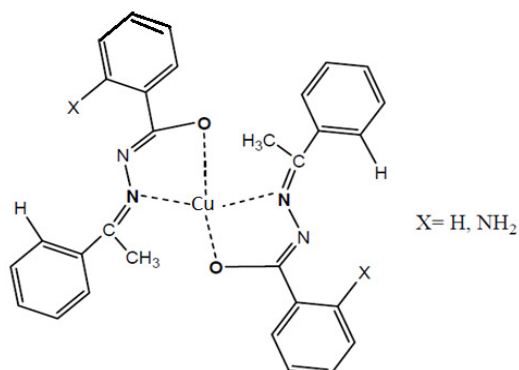


Figure 15 structure of Cu[L₂^AH₁]₂

3.6 CONCLUSION:

Three bidentate O-N donor Schiff's base of Aroylhydrazone ligands were synthesized and successfully characterized by IR and UV spectrophotometer, C H N analyzer and magnetic susceptibility measurement. The basic and electronic

properties of these ligands have been nicely explored in the syntheses of various Cobalt and Copper Aroylhydrazone complexes. All the complexes are characterized by elemental analysis, IR, UV-Visible spectrophotometer, conductivity measurement and magnetic susceptibility measurement. The result shows that all the complexes are non-electrolytes and paramagnetic. From the preliminary findings, the complexes were also suggested to have tetragonal geometry. However the actual structure of the complexes can be found using single crystal x-ray studies, which was not able to carried out here.

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