

Cobalt(II) and Nickel(II) Complexes of Aroyl Hydrazone Ligand: Synthesis and Characterization

A Dissertation

Submitted in partial fulfillment

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

Under Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

Affiliated to

Deemed University

By

Saritarani Behera

Under the Guidance of

Dr. Rupam Dinda

**Department of Chemistry
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA-769008 (ORISSA)**





**NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA**

CERTIFICATE

This is to certify that the dissertation entitled "*Cobalt(II) and Nickel(II) Complexes of Aroyl Hydrazone Ligand: Synthesis and Characterization*" submitted by Saritarani Behera of the Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bona fide project work carried out by her under my guidance and supervision.

I further certify that to the best of my knowledge Saritarani Behera bears a good moral character.

Date 11/05/09


Dr. Rupam Dinda,
Department of Chemistry
National Institute of Technology,
Rourkela- 76900

ACKNOWLEDGEMENT

I would like to convey my deep regards to my project supervisor Dr. Rupam Dinda, Lecturer, Department of Chemistry, National Institute of Technology, Rourkela. I thank him for his patience, guidance, regular monitoring of the work and inputs, without which this work could have never come to fruition. Indeed, the experience of working under him is one of that I will cherish forever.

I take this opportunity to thank to Prof. R. K. Patel, the Head of Department of Chemistry, National Institute of Technology, Rourkela for providing me the various laboratory and instrumental facilities during my project work.

I would like to thank Professor Nigam P. Rath, Research Professor, Department of Chemistry and Biochemistry, University of Missouri-St. Louis, USA, Professor Ekkehard Sinn, Professor and Chair, WMU Department of Chemistry, Kalamazoo, USA and Mr. Partha Mitra, IACS, Kolkata for single X-ray diffraction facilities.

I would also like to give my sincere thanks to Sagarika Pasayat, Paresh Kumar Majhi, Satish Samantaray for their constant efforts and encouragement was the tremendous sources of inspiration.

I also extend my thanks to Sumanta Kumar Patel, Moumita Chakrabarti. Finally, I wish to thank all of my friends for making my stay in this Institute a memorable experience.

Date:

Saritarani Behera

Contents

CERTIFICATE

ACKNOWLEDGEMENTS

1. Introduction
2. Experimental
3. Physical Measurements
4. Chemicals and Solvents
5. Synthesis of the Ligands
6. Synthesis of the complexes
7. Results and discussion
8. Protonated / Deprotonated form of Schiff's Bases
9. Spectral characteristics
10. Electronic spectra of $\text{Co}^{(\text{II})}\text{L}_2$ in CH_3CN
11. Magnetic properties
12. Expected geometry of $\text{Co}^{(\text{II})}$ complexes
13. Conclusion
14. References

1. INTRODUCTION:

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^[1].

Cobalt is a transition metal, one of several elements found in Rows 4 through 7 between Groups 2 and 13 in the periodic table. The periodic table is a chart that shows how chemical elements are related to each other. Cobalt is located between iron and nickel and shares many chemical and physical properties with these two elements^[2].

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_4O_6), which often occurs with cobalt in nature^[3].

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*^[3].

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_2O_3); cobalt potassium nitrite, or cobalt yellow ($\text{CoK}_3(\text{NO}_2)_6$); cobalt aluminates, or cobalt blue ($\text{Co}(\text{AlO}_2)_2$); and cobalt ammonium phosphate, or cobalt violet (CoNH_4PO_4)^[4].

Another important use of cobalt compounds is as catalysts. A catalyst is a substance used to speed up or slow down a chemical reaction. The catalyst does not undergo any change itself during the reaction. 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^[5].

Attaching a cobalt complex to aspirin significantly changes the molecule's anti-cancer properties, European researchers have found. Their study underlines the potential for discovering new anti-tumor therapies by adding organometallic fragments to established drugs^[5-7].

Ott's team have been studying the hexacarbonyldicobalt [$\text{Co}_2(\text{CO})_6$] species bound to various alkyne ligands, and found that the anti-tumour activity of this cobalt cluster is more potent when attached to aspirin than to other compounds^[8-9].

In particular, the team showed that the bulky cobalt cluster caused aspirin to interact differently with cyclooxygenase (COX) enzymes (which produce prostaglandins and other signaling molecules related to inflammation and blood clotting). Where ordinary aspirin inhibits COX enzymes by acetylating a serine residue in their active sites, Ott's team showed that Co-aspirin leaves the serine residue untouched, instead acetylating lysine residues at other locations. This alters biochemical pathways occurring downstream of COX activity, the researchers say.

Investigating further by performing experiments on zebrafish embryos, the researchers found that Co-aspirin could inhibit cell growth and the formation of small blood vessels - two factors crucial for tumour growth. Medications targeting COX-2 enzymes, such as Merck's Vioxx, have

recently been under scrutiny after it emerged that they could cause cardiovascular side-effects. However, these are unlikely to be a problem with Co-aspirin, Ott says, as it isn't a selective COX-2 inhibitor. In any case, he adds, the drug is still at a very early stage of development and animal trials are the next step.

In the form of vitamin(B₁₂) Cobalamine, this metal plays a number of crucial roles in many biological functions^[10].such as:

Cobalt amine

It is necessary for DNA synthesis

Formation of red blood cell.

Maintenance of the nervous system.

Growth and development of children.

There is evidence to support the importance of Cobalt for immune process.

The following main factor stimulates the increase interest to the putative anticancer properties of this metal. It has been found that the disturbed balance in the essential metal metabolism of mammals increase susceptibility to infections and malignancies. Being involved in the regulation of some definite process of the animal organisms. Cobalt behaves like biological response modifier. Like an essential element Cobalt may be less toxic than non essential metal such as platinum. Different Cobalt containing compound have been provided to express antineoplastic activity.

From some investigating it was found that some complexes of Cobalt(II) with different ligands (Mannich bases, mixed ligand) reduced significantly viability and proliferation of cultured tumor cells and induced DNA damage.

Cobalt catalysts are quite promising for oxidation–reduction processes. It is well known^[11] that the catalytic performance of supported cobalt depends upon the support properties and the nature

of the surface species formed on the final catalysts. Several studies have shown that cobalt supported mainly on aluminosilicates can display high activity for the selective catalytic

Metal complexes with Schiff base ligands have played an important role since the early days of Coordination Chemistry^[11-12]. Indeed, a great deal of work has been carried out on the synthesis and characterization of transition metal compounds with these ligands, mainly due to their applications in organic chemistry, as liquid crystals and in catalytic processes. A number of different synthetic methods have been used in an attempt to obtain these compounds. The synthesis of metal complexes of Schiff bases derived from hydrazones bearing a secondary amide group. It is well known that the formation of metal complexes through substitution of the N-H amide proton by a metal is not an easy process. However, the presence of additional donor atoms in the ligand allows the formation of a stable chelate ring and this situation facilitates the complexation process.

The remarkable biological activity of acid hydrazides $R-CO-NH-NH_2$, their corresponding aroylhydrazones $R-CO-NH-N=CHR$, and also their mode of chelation with transition metal ions has aroused interest in the past due to possible biomimetic applications. Hydrazone Schiff bases and their Cobalt and Nickel complexes have a variety of applications in biological, clinical and analytical fields. Recently there has been a considerable interest in the coordination chemistry of transition metals especially, Cobalt and Nickel with O-N donor hydrazone ligands because of their potential biological and pharmacological applications. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications. The coordination chemistry of aroyl hydrazones are quite interesting as it presents a combination of donor sites such as protonated / deprotonated amide

oxygen, an imine nitrogen of hydrazone moiety and additional donor site (usually N or O) provided from the aldehyde or ketone forming the Schiff base.

From last one year I have been studying the chemistry of transition metal complexes with O-N containing donor environments. In this dissertation I report the synthesis and full characterization of several O-N donor Schiff's base hydrazone ligands and their corresponding cobalt complexes. The single crystal x-ray studies of synthesized Co complexes (**1-3**) are under process with our collaborator. One of the three synthesized Co compound (complex **2**) is successfully characterized by X-ray crystallography. But due to incomplete refinement of x-ray data I am unable to show the x-ray structure in this dissertation. I also report the synthesis of some Nickel complexes of corresponding O-N donor hydrazone ligands but due to shortage of time am unable to present the characterization data in this thesis.

2. EXPERIMENTAL:

2.1. Physical Measurements:

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum RXI. Electronic spectra were recorded on a Shimadzu UV/VIS recording spectrophotometer. Magnetic susceptibility was measured with a Sherwood Scientific MSB MK1 sample magnetometer with Hg [Co (SCN)₄] as calibrant.

2.2. Chemicals and Solvents:

Chemicals were procured from renowned companies like Aldrich E. Merck, and Fluka and used without further purification. HPLC grade acetonitrile, and dichloromethane were used for spectroscopic studies and ethanol, methanol were used for synthesis of ligand and metal complexes. All other solvents were A.R. grade and used as received for synthetic work. CoCl₂ .6H₂O and NiCl₂, 6H₂O were procured from Loba chemie.

2.3. Synthesis of Ligands:

The synthesis of our final ligand consists of two steps.

Step-1: Synthesis of Acid hydrazide

The precursor ligand 2-aminobenzoylhydrazone (**Figure-1.1**) was prepared^[13-15] 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 CaCl₂.

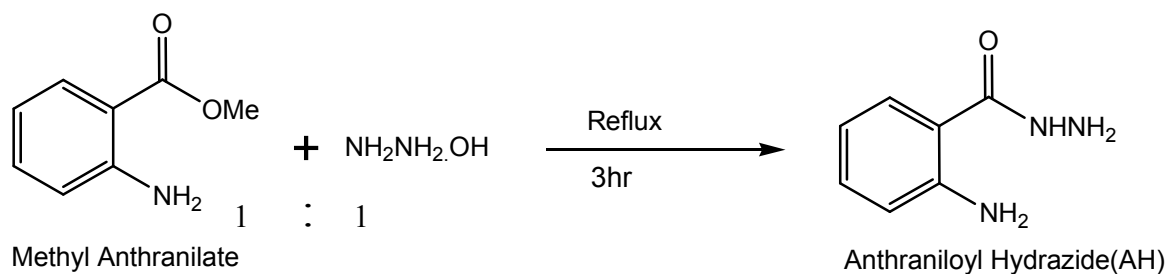


Figure-1.1

M.P. 142°C. Yield: (75%). Anal. Calc for C₇H₉N₃O: C, 55.62; H, 6.00; N, 27.81; Found: C, 60.21; H, 7.24; N, 29.76

The precursor ligand benzoylhydrazone (**Figure-1.2**) was prepared by reacting methyl benzoate (6.26 gm / 50 mmol) and hydrazine hydrate (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 CaCl₂.

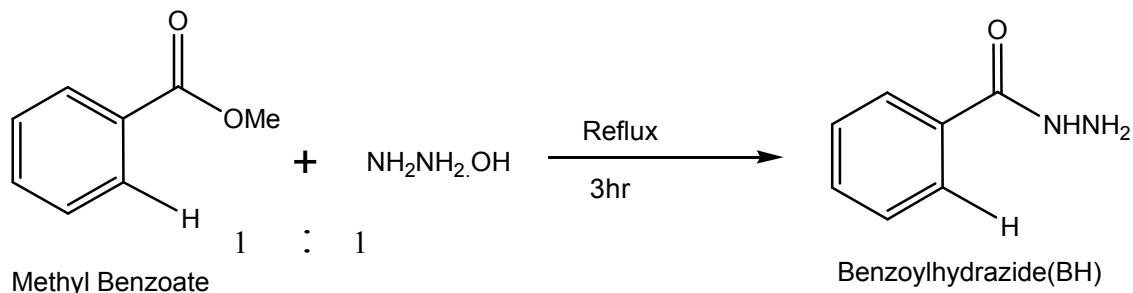


Figure-1.2

M.P. 138°C. Yield: (76%). Anal. Calc for C₇H₈N₂O: C, 61.71; H, 5.92; N, 20.58; Found: C, 63.21; H, 6.54; N, 22.76;

The precursor ligand 2-hydroxybenzoylhydrazone (**Figure-1.3**) was prepared by same method as above. Due to shortage of time I could not able to characterize this compound.

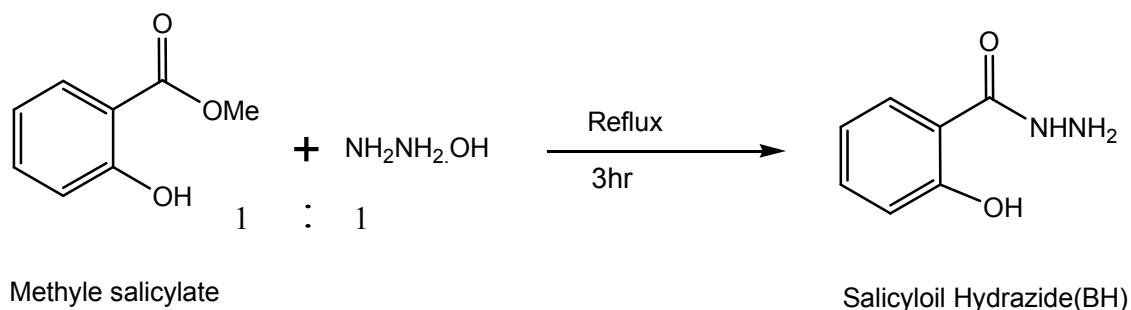


Figure-1.3

Step-2: Synthesis of the Schiff Base Ligands:

We have successfully synthesized and characterized all the Schiff Base ligands (A-C) but due to shortage of time I could not able to characterize other four ligands (D-G) by IR.

A. Acetophenonehydrazone of 2-Aminobenzoylhydrazine Ligand ($L_2^A H_1$)

The ligand 2-aminobenzoylhydrazone of acetophenone ($L_2^A H_1$) (**Figure-2.1**) was prepared by reacting 2-aminobenzoylhydrazide (1.51 gm / 10 mmol) and acetophenone (1.19 gm / 10 mmol) in stirring with ethanol (25 ml) for 3 hr. The resulting white compound was filtered, washed thrice with ethanol and dried over fused $CaCl_2$.

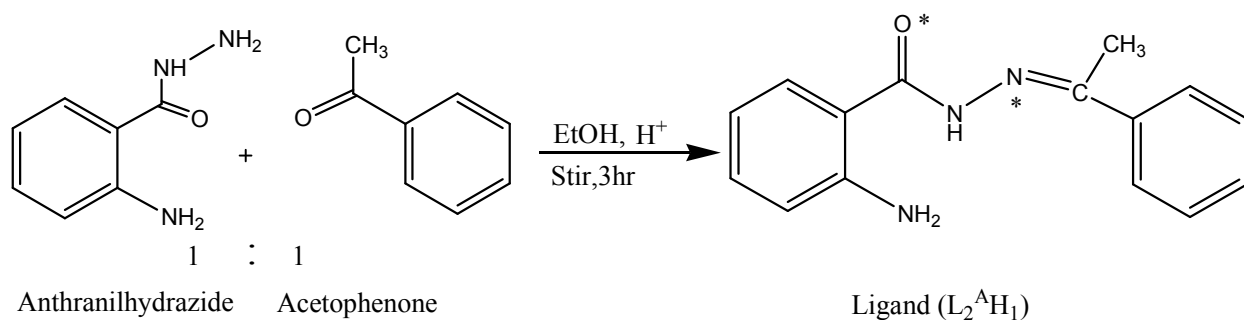


Figure-2.1

M.P: 160°C. Yield: (61%). Anal. Calc for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.92; N, 16.60 Found: C, 69.26; H, 5.19; N, 12.76. Selected IR bands: (ν_{OH}) cm^{-1} , 3469; (ν_{NH}) cm^{-1} , 3190; ($\nu_{C=O}$) cm^{-1} , 1630 .

B. Acetophenonehydrazone of Benzoylhydrazine Ligand ($L_2^B H_1$)

The ligand benzoylhydrazone of acetophenone ($L_2^B H_1$) (**Figure-2.2**) was prepared by reacting benzoylhydrazide (1.36 gm / 10 mmol) and acetophenone (1.19 gm / 10 mmol) in stirring ethanol (25 ml) for 3 hr. The resulting white compound was filtered, washed thrice with ethanol and dried over fused $CaCl_2$.

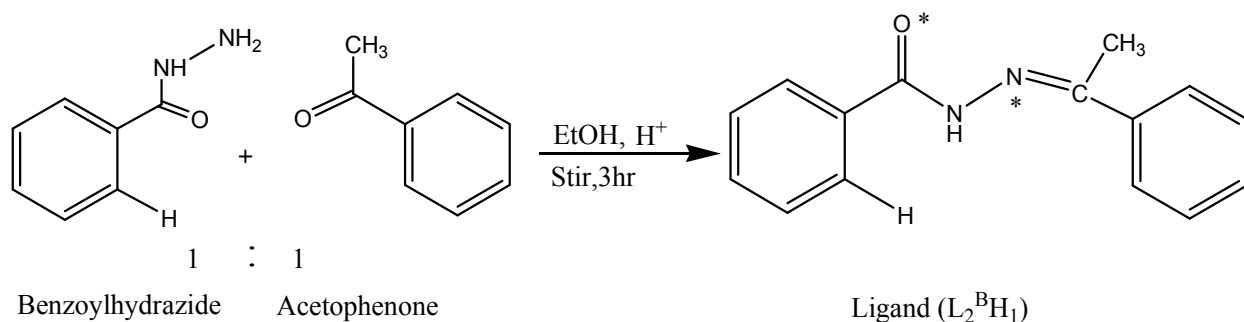


Figure-2.2

M.P. $165^\circ C$. Yield (70%). Anal. Calc for $C_{15}H_{14}N_3O$: C, 75.63; H, 5.88; N, 11.76. Found: C, 70.26; H, 5.54; N, 11.26. Selected IR bands: (ν_{OH}) cm^{-1} , 3176.59; (ν_{NH}) cm^{-1} , 3006.13; ($\nu_{C=O}$) cm^{-1} , 1639.

C. Benzildihydrazone of Benzoylhydrazine Ligand (Benz-BH)

The ligand benzoylhydrazone of bezil (Benz-BH) (**Figure-2.3**) was prepared by reacting benzoylhydrazide (2.72 gm / 20 mmol) and bezil (2.10gm / 10 mmol) in stirring ethanol (30 ml) for 3 hr. The resulting yellowish- white compound was filtered, washed thrice with ethanol and dried over fused $CaCl_2$.

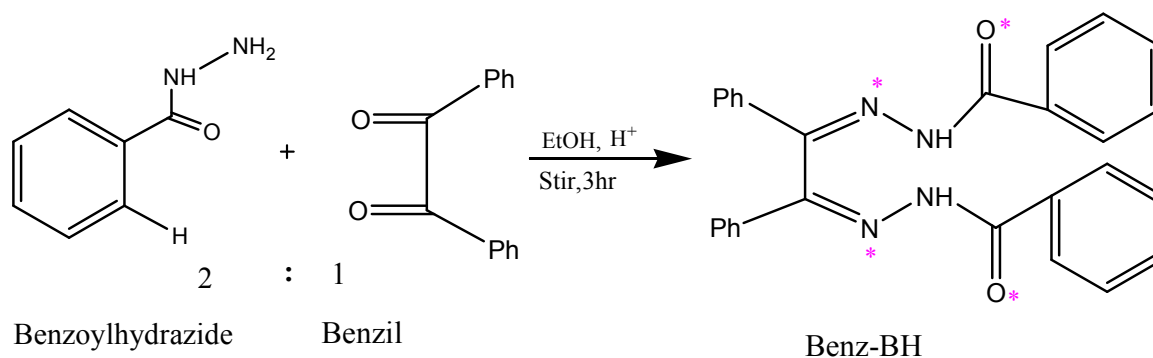


Figure-2.3

M.P. 163°C. Yield (62%). Anal. Calc for $C_{28}H_{22}N_4O_2$: C, 75.34; H, 4.93; N, 12.56. Found: C, 74.96; H, 4.26; N, 12.16. Selected IR bands: $(\nu_{OH})\text{cm}^{-1}$, 3176.34 ; $(\nu_{NH})\text{cm}^{-1}$, 3059.68 ; $(\nu_{C=O})\text{cm}^{-1}$, 1648.

D. Benzaldehydehydrazone of Benzoylhydrazine Ligand ($L_1^B H_1$)

The ligand benzoylhydrazone of benzaldehyde ($L_1^B H_1$) (**Figure-2.4**) was prepared by reacting benzoylhydrazide (1.36 gm / 10 mmol) and benzaldehyde (1.19 gm / 10 mmol) in stirring ethanol (25 ml) for 3 hr. The resulting white compound was filtered, washed thrice with ethanol and dried over fused $CaCl_2$.

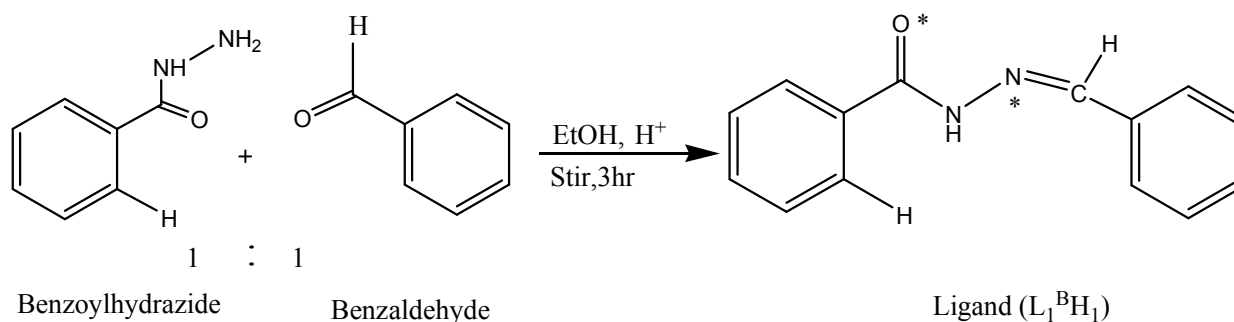


Figure-2.4

M.P. 140°C. Yield (74%). Anal. Calc for $C_{14}H_{12}N_2O$: C, 75.00; H, 5.3; N, 12.50. Found: C, 76.96; H, 6.26; N, 13.16.

E. Benzaldehydehydrazone of Salicyloil hydrazine Ligand ($L_1^S H_1$)

The ligand 2-hydroxybenzoylhydrazone of benzaldehyde ($L_1^S H_1$) (**Figure-2.5**) was prepared by reacting 2-hydroxybenzoylhydrazide (1.52 gm / 10 mmol) and benzaldehyde (1.06 gm / 10 mmol) in stirring ethanol (30 ml) for 3 hr. The resulting white compound was filtered, washed thrice with ethanol and dried over fused $CaCl_2$.

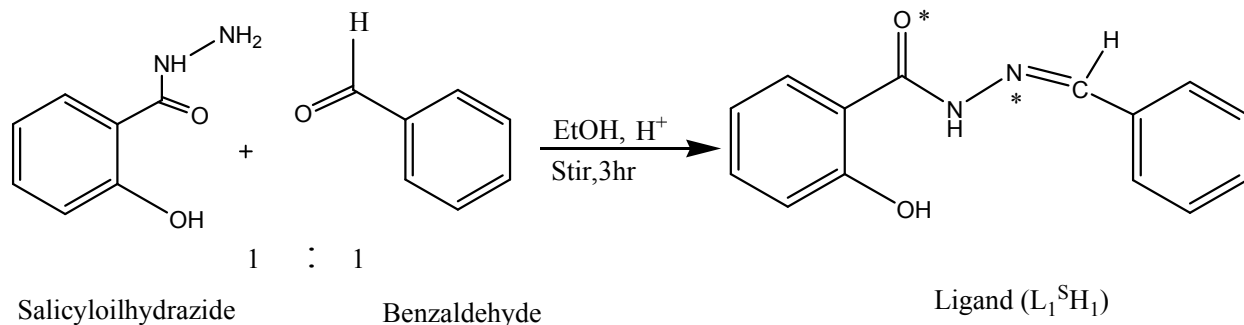


Figure-2.5

M.P. 155°C . Yield (75%). Anal. Calc for $C_{14}H_{12}N_2O_2$: C, 70.00; H, 5.00; N, 11.67. Found: C, 73.96; H, 6.11; N, 12.16.

F. Benzilhydrazone of Anthraniloil hydrazine Ligand (Benz-AH)

The ligand 2-aminobenzoylhydrazone of bezil (Benz-AH) (**Figure-2.6**) was prepared by reacting 2-aminobenzoylhydrazide (3.02 gm / 20 mmol) and benzil (2.10gm / 10 mmol) in stirring ethanol (30 ml) for 3 hr. The resulting yellowish white compound was filtered, washed thrice with ethanol and dried over fused $CaCl_2$.

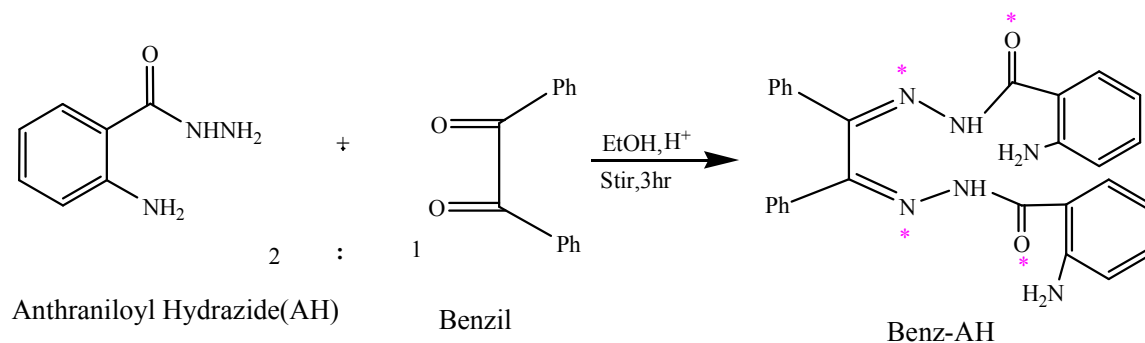


Figure-2.6

M.P. 170°C. Yield (55%). Anal. Calc for C₂₈H₂₄N₆O₂: C, 70.59; H, 5.04; N, 17.65. Found: C, 73.16; H, 6.16; N, 18.16.

G .Benzilhydrazone of Salicyloil hydrazine Ligand (Benz-SH)

The ligand 2-hydroxybenzoylhydrazone of bezil (Benz-SH) (**Figure-2.7**) was prepared by reacting 2-hydroxybenzoylhydrazide (3.04gm / 20 mmol) and benzil (2.10gm / 10 mmol) in stirring ethanol (25 ml) for 3 hr. The resulting yellowish- white compound was filtered, washed thrice with ethanol and dried over fused CaCl₂.

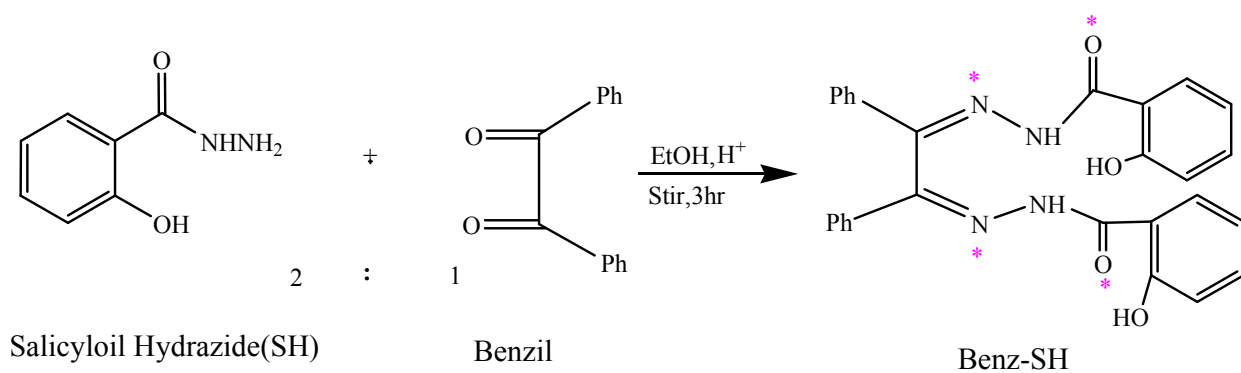


Figure-2.7

M.P. 168°C. Yield (65%). Anal. Calc for C₂₈H₂₂N₄O₄: C, 70.29; H, 4.60; N, 11.72. Found: C, 72.16; H, 5.16; N, 12.14.

2.4. Synthesis of the Metal complexes:

I have successfully synthesized and characterized all the cobalt Schiff Base complexes (**1-3**) but due to shortage of time I could not able to characterize the corresponding Nickel complexes (**4-8**).

2.4.1: Complex 1, $[\text{Co}^{\text{II}}(\text{L}_2^{\text{A}})_2]$:

(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 stirring solution. Color of the solution (**Figure-3.1**) slowly changed to wine red. After 3 hr of stirring, then solution was filtered. Slow evaporation of the filtrate solution over 4 days produced green colored crystals

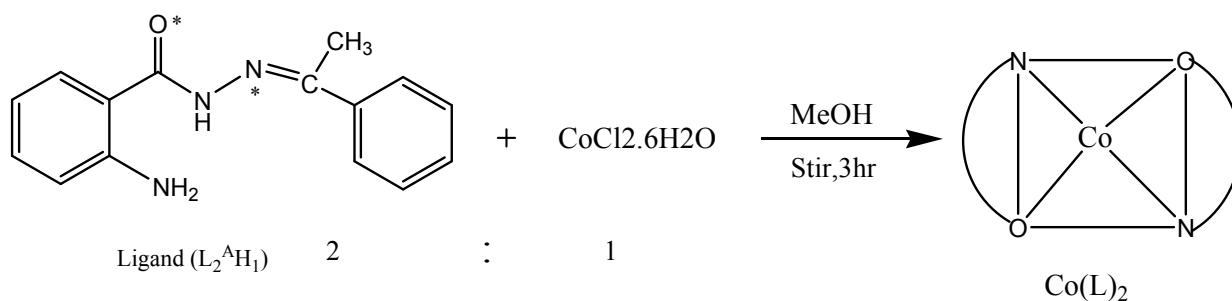


Figure-3.1

Yield~75%. Anal. Calc for $\text{C}_{30}\text{H}_{28}\text{N}_6\text{O}_2\text{Co}$: C, 63.94; H, 4.65; N, 14.96. Found: C, 65.54; H, 5.72; N, 16.34. Selected IR bands (cm^{-1}): at 3278 cm^{-1} (ν_{NH_2}), 1626 cm^{-1} ($\nu_{\text{C}=\text{N}}$) and 1561 cm^{-1} ($\nu_{\text{C}=\text{N}}$). Electronic spectrum in acetonitrile solution, $\lambda \text{ nm}$ ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$): 658 (3013), 343 (3900).

2.4.2: Complex 2, $[\text{Co}^{\text{II}}(\text{L}_2^{\text{B}})_2]$:

A (0.476gm/2.00-mmol) sample of ligand $L_2^B H_1$ was dissolved in 30 ml of methanol and (0.238gm/1.00-mmol) of $CoCl_2 \cdot 6H_2O$ was added to the stirring solution. Color of the solution (**Figure-3.2**) slowly changed to dark pink. After 3 hr of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 7 days produced green colored crystals.

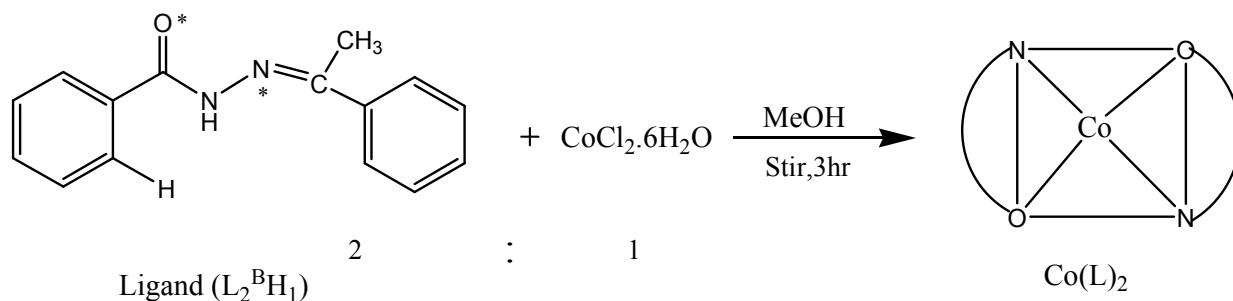


Figure-3.2

Yield~65%. Anal. Calc for $C_{30}H_{28}N_6O_2Co$: C, 56.87; H, 4.45; N, 13.27. Found: C, 57.77; H, 5.12; N, 14.34. Selected IR bands: $1532\text{ cm}^{-1}(\nu_{C=N})$, $1572\text{ cm}^{-1}(\nu_{C=N})$. Electronic spectrum in acetonitrile solution, $\lambda\text{ nm} (\epsilon\text{ M}^{-1}\text{ cm}^{-1})$: 683 (6788), 342 (5628).

2.4.3: Complex 3, $[Co^{II}(\text{Benz-BH})]$:

A (0.446 gm/1.00-mmol) sample of ligand $L_2^B H_1$ was dissolved in 30 ml of ethanol and (0.238gm/1.00-mmol) of $CoCl_2 \cdot 6H_2O$ was added to the stirring solution. Color of the solution (**Figure-3.3**) slowly changed to darty green. After 3 hr of stirring, the solution was filtered. Slow

2.4.5: Complex-5 $[\text{Ni}^{\text{II}}(\text{L}_1^{\text{S}}\text{H}_1)_2]$:

A (0.480gm /2.00mmol) sample of ligand $\text{L}_1^{\text{S}}\text{H}_1$ was dissolved in 30 ml of methanol and (0.238gm /1.00-mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the stirring solution. Color of the solution (**Figure-3.5**) slowly changed to light green. After 3 hr of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 3 days produced green colored compound.

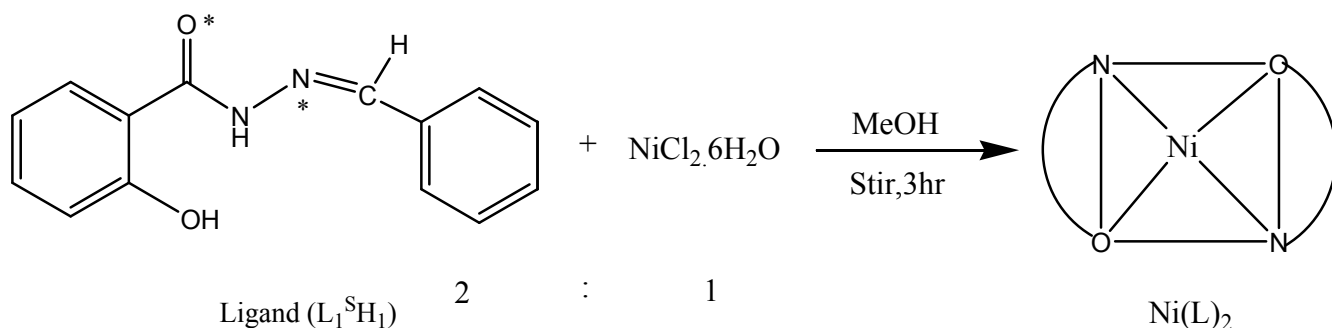


Figure-3.5

2.4.6: Complex-6, $[\text{Ni}^{\text{II}}(\text{L}_1^{\text{B}}\text{H}_1)_2]$:

A (0.448gm /2.00-mmol) sample of ligand $\text{L}_1^{\text{B}}\text{H}_1$ was dissolved in 30 ml of methanol and (0.238gm /1.00-mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the stirring solution, to this solution drop of Et_3N was added. Color of the solution (**Figure-3.6**) slowly changed to light green. After 3 hr of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 4 days produced light green colored compound.

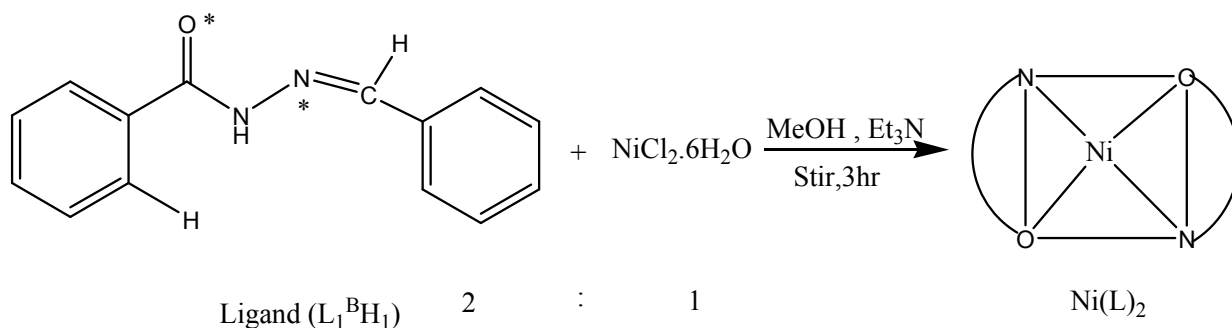


Figure-3.6

2.4.7: Complex 7, [Ni^{II}(Benz-BH)]:

A (0.446gm /1.00-mmol) sample of ligand Benz-BH was dissolved in 30 ml of ethanol and (0.238gm /1.00-mmol) of NiCl₂.6H₂O was added to the stirring solution. Color of the solution (**Figure-3.7**) slowly changed to deep yellow. After 3 hr of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 4 days produced light yellow colored compound.

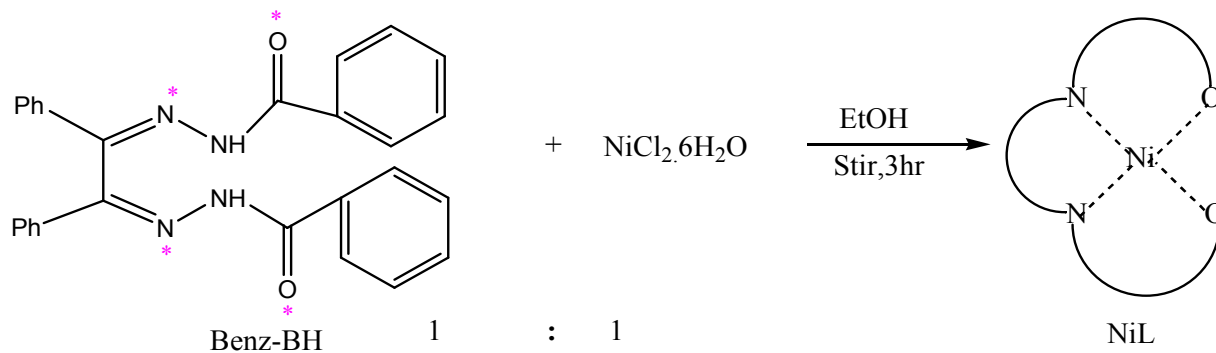


Figure-3.7

2.4.8: Complex-8, [Ni^{II}(Benz-SH)]:

A (0.478gm /1.00-mmol) sample of ligand Benz-BH was dissolved in 30 ml of ethanol and (0.238gm /1.00-mmol) of NiCl₂.6H₂O was added to the stirring solution. Color of the solution (**Figure-3.8**) slowly changed to greenish yellow. After 3 hr of stirring, the solution was filtered.

low evaporation of the filtrate solution over 4 days produced light green colored compound.

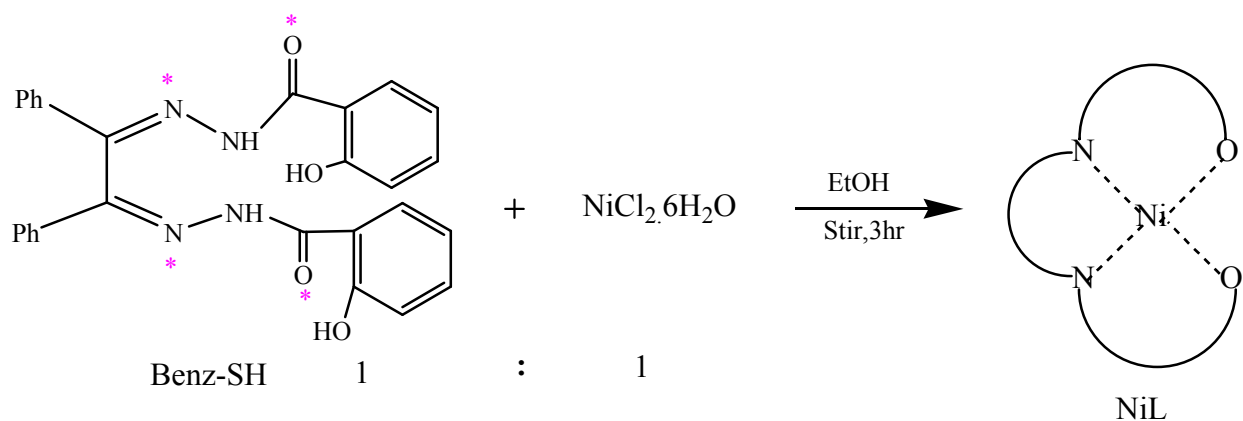


Figure-3.8

2.5. Magnetic susceptibility measurements:

2.5.1: Magnetic Study of the complex [Co^{II}(L₂^A)₂]:

Magnetic susceptibility can be calculated by the given equation:

$$\chi_g = C \times L(R - R^0) / 10^9 \times M$$

C = Constant = 1

l = length of the tube

M = Mass of the sample

R⁰ = Reading for empty tube

R = Reading for sample with tube

$$\chi_g = [C \times L(R - R^0) / 10^9] \times 10^6$$

As the reaction is carried out in 2:1 ratio, the molecular weight of the metal complex [Co^{II}(L₂^A)₂] is given below.

Molecular weight of (L₂^A)₂ = 253 × 2 = 504

Molecular weight of Co^{II} = 59

Hence the Molecular weight of metal complex =504+59=563

Wt. of the sample (M) = 0.072 gm

$$R^0 = -0.30$$

$$l = 1.75 \text{ cm}$$

$$R = 630$$

$$\chi_g = 1 \times 1.75(630 + 30) \div (10^9 \times 0.0720)$$

$$= 16041.66 \times 10^{-9}$$

$$\chi_g \times 10^6 = 16041.66 \times 10^{-9} \times 10^6$$

$$= 16.041$$

$$\chi_m = \chi_g \times 10^{-6} \times \text{molecular wt. of complex}$$

$$= 16.041 \times 10^{-6} \times 563$$

$$= 9031.64 \times 10^{-6}$$

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_m} \text{ T}$$

$$= 2.84 \sqrt{9031.64 \times 302 \times 10^{-6}} = 4.6 \text{ (Observed Value)}$$

CoL₂ = Tetrahedral Ligand which have 3 unpaired electron

$$\text{So it's } \mu_{\text{eff}} = \sqrt{3(3+2)}$$

$$= \sqrt{15} = 3.84 \text{ (theoretical value)}$$

2.5.2: Magnetic Study of the complex [Co^{II}(L₂^BH₁)]

As the reaction is carried out in 2:1 ratio, the molecular weight of the metal complex

[Co^{II}(L₂^B)₂] is given below.

$$\text{Molecular weight of (L}_2^{\text{B}}\text{)}_2 = 238 \times 2 = 476$$

$$\text{Molecular weight of Co}^{\text{II}} = 59$$

Hence the Molecular weight of metal complex =476+59=535

Magnetic susceptibility of the metal complex

Wt. of the sample (M) = 0.071 gm

$$R^0 = -0.32$$

$$l = 1.75 \text{ cm}$$

$$R = 630$$

$$\chi_g = 1 \times 1.75(630 + 32) \div (10^9 \times 0.0710)$$

$$= 16316.90 \times 10^{-9}$$

$$\chi_g \times 10^6 = 16316.90 \times 10^{-9} \times 10^6$$

$$= 16.316$$

$$\chi_m = \chi_g \times 10^{-6} \times \text{molecular wt. of complex}$$

$$= 16.316 \times 10^{-6} \times 535$$

$$= 8729.06 \times 10^{-6}$$

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_m} \text{ T}$$

$$= 2.84 \sqrt{8729.06 \times 302 \times 10^{-6}} = 4.6 \text{ (Observed Value)}$$

CoL_2 = Tetrahedral Ligand which have 3 unpaired electron

$$\text{So it's } \mu_{\text{eff}} = \sqrt{3(3+2)}$$

$$= \sqrt{15} = 3.84 \text{ (theoretical value)}$$

3. RESULT AND DISCUSSION:

I have successfully synthesized and characterized all the Cobalt Schiff Base complexes (**1-3**) but due to shortage of time could not able to characterize the corresponding Nickel complexes (**4-8**).

3.1. Protonated / Deprotonated form of Schiff's Bases:

Bidentate ligands used in this work have one possible sites 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 Ni^{II} salt, the ligands get deprotonated from the enolised amide oxygen as well as from the phenolic oxygen.

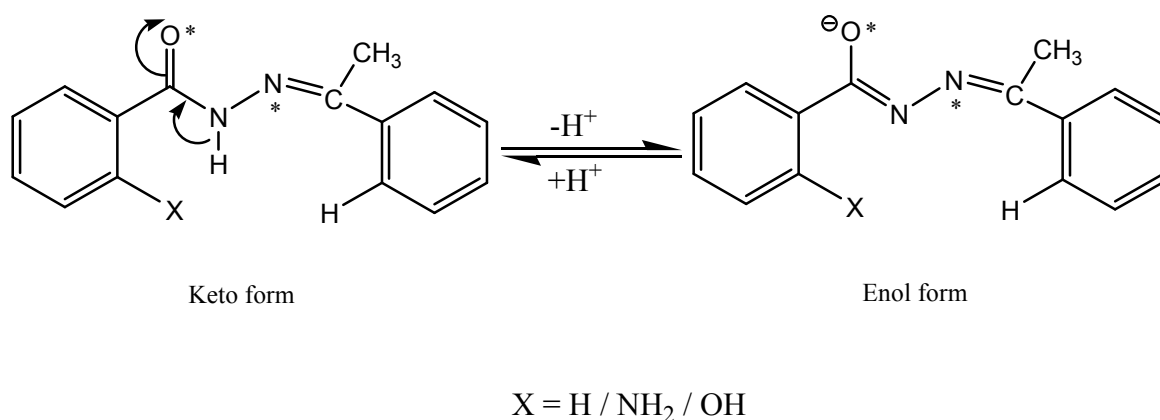


Figure-3.9

3.2. Spectral characteristics

IR spectra of the ligand $\text{L}_2^{\text{A}}\text{H}_1$ and corresponding Co complex **1, $[\text{Co}^{\text{II}}(\text{L}_2^{\text{A}})_2]$:**

IR spectra of the ligand, $\text{L}_2^{\text{A}}\text{H}_1$ (**Figure-4.1**) has several prominent bands at 3355, 3190 and 1630 cm^{-1} due to $\nu(\text{NH}_2)$, $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ stretching modes respectively. Characteristics strong bands in the spectra of the ligand are located at 1574 cm^{-1} and 1534 cm^{-1} which arise due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C}/\text{aromatic})$ stretching modes of the ligand. In the metal complex, **1** the

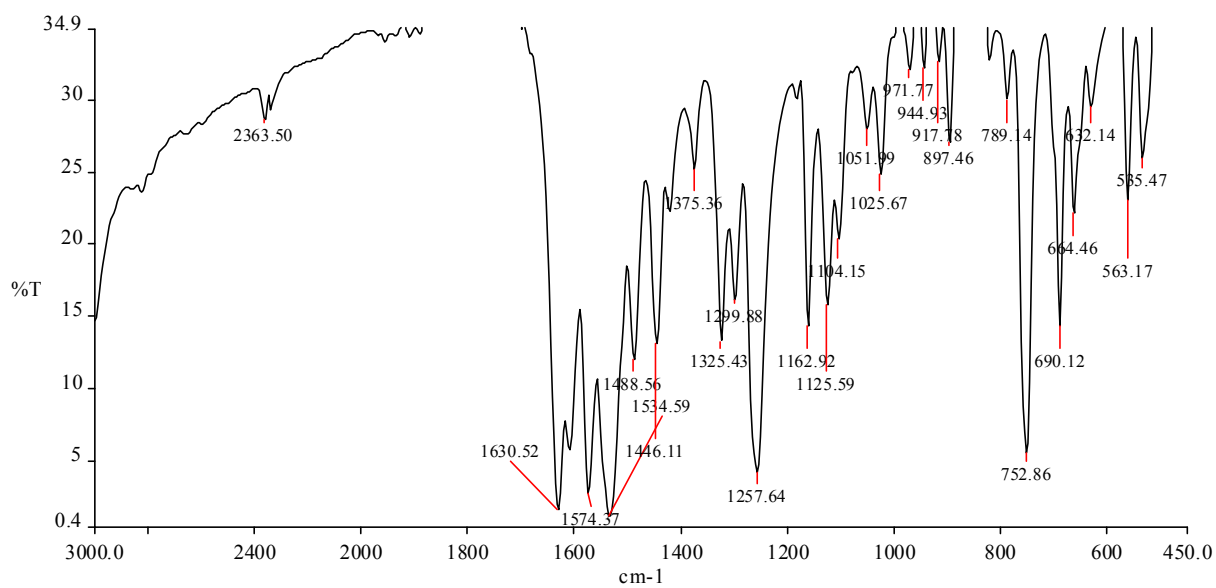
bands (**Figure-4.2**) are located at 3278 cm^{-1} , 1626 cm^{-1} and 1561 cm^{-1} which arise due to $\nu(\text{NH}_2)$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{N})$ stretching modes of the ligand.

IR spectra of the ligand $\text{L}_2^{\text{B}}\text{H}_1$ and corresponding Co complex 2, $[\text{Co}^{\text{II}}(\text{L}_2^{\text{B}})_2]$:

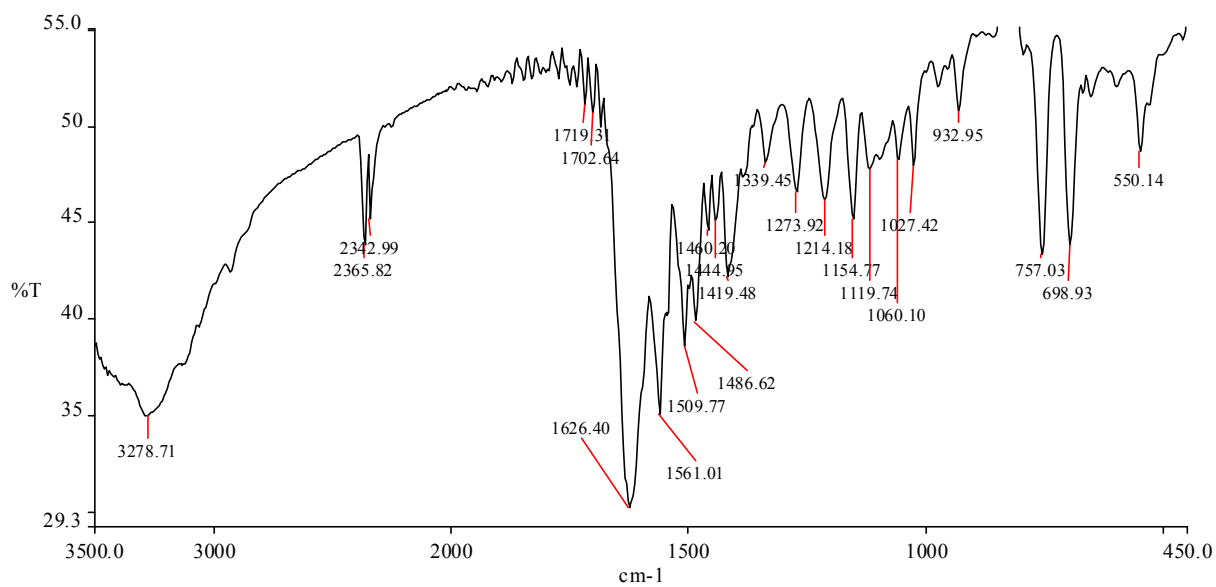
IR spectra of the ligand $\text{L}_2^{\text{B}}\text{H}_1$ (**Figure-4.3**) has several prominent bands at 3006 and 1639 cm^{-1} due to $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ stretching modes respectively. Characteristics strong bands in the spectra of the ligand are located at 1577 cm^{-1} and 1540 cm^{-1} which arise due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C}/\text{aromatic})$ stretching modes of the ligand. In the metal complex, **2** the bands (**Figure-4.4**) are located at 1540 cm^{-1} and 3253 cm^{-1} which arise due to $\nu(\text{C}=\text{N})$ and $\nu(\text{NH}_2)$ stretching modes of the ligand.

IR spectra of the ligand Benz-BH and corresponding Co complex 3, $[\text{Co}^{\text{II}}(\text{Benz-BH})]$:

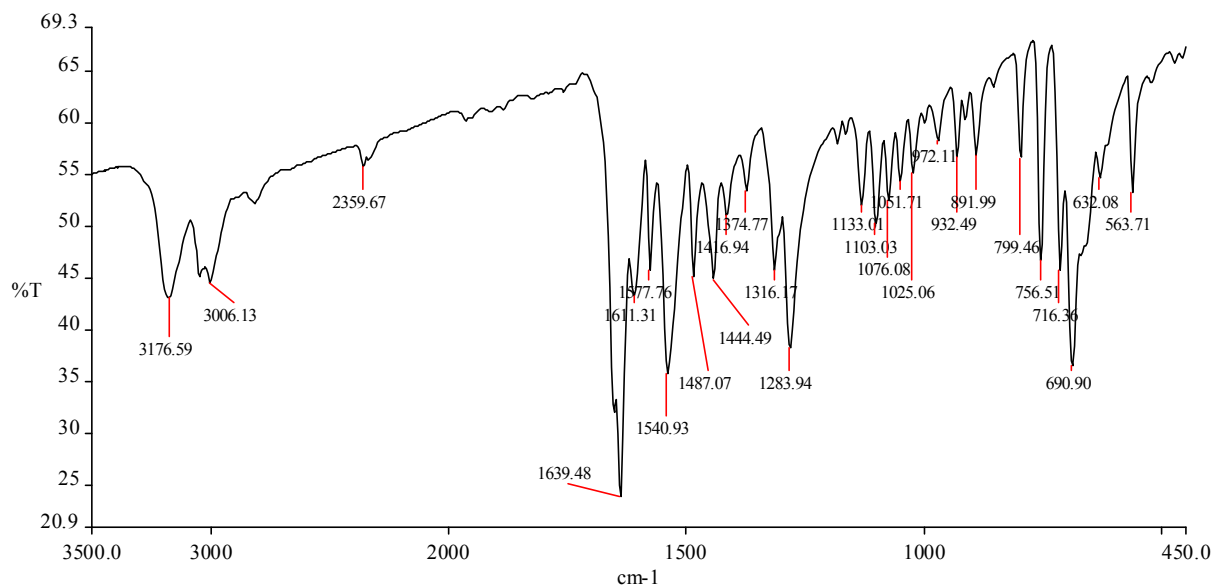
IR spectra of the ligand **Benz-BH** (**Figure-4.5**) has several prominent bands at 3176 and 1676 cm^{-1} due to $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ stretching modes respectively. Characteristics strong bands in the spectra of the ligand are located at 1587 cm^{-1} and 1544 cm^{-1} which arise due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C}/\text{aromatic})$ stretching modes of the ligand. In the metal complex, **3** the bands (**Figure-4.6**) are located at 1561 cm^{-1} and 1509 cm^{-1} which arise due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C}/\text{aromatic})$ stretching modes of the ligand.



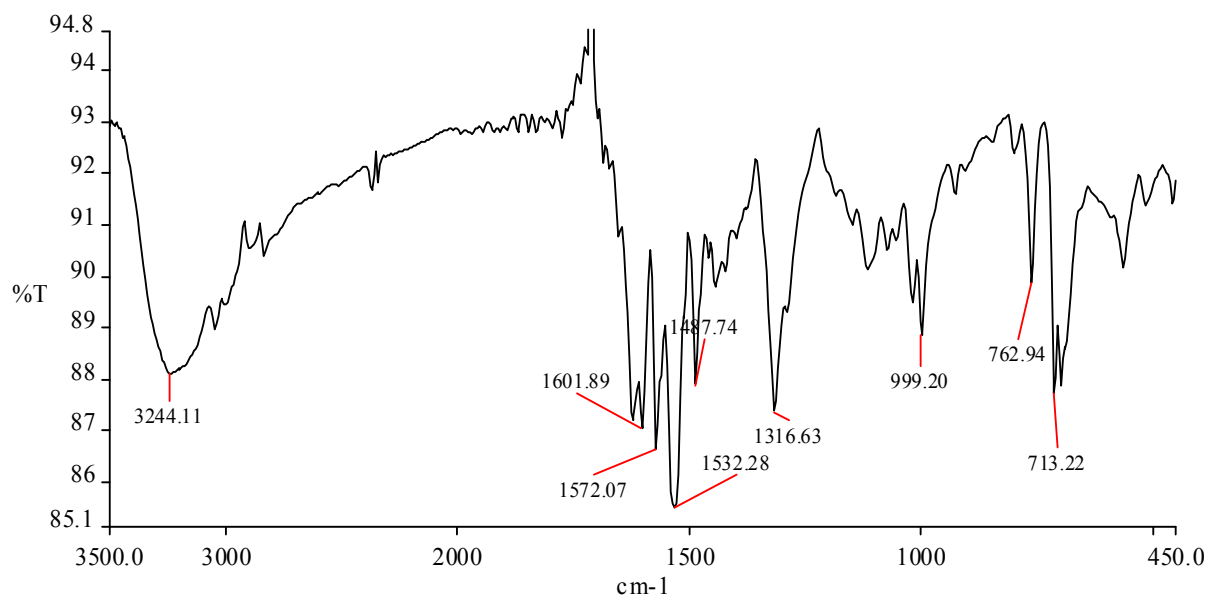
IR spectra of the ligand $L_2^A H_1$, **Figure-4.1**



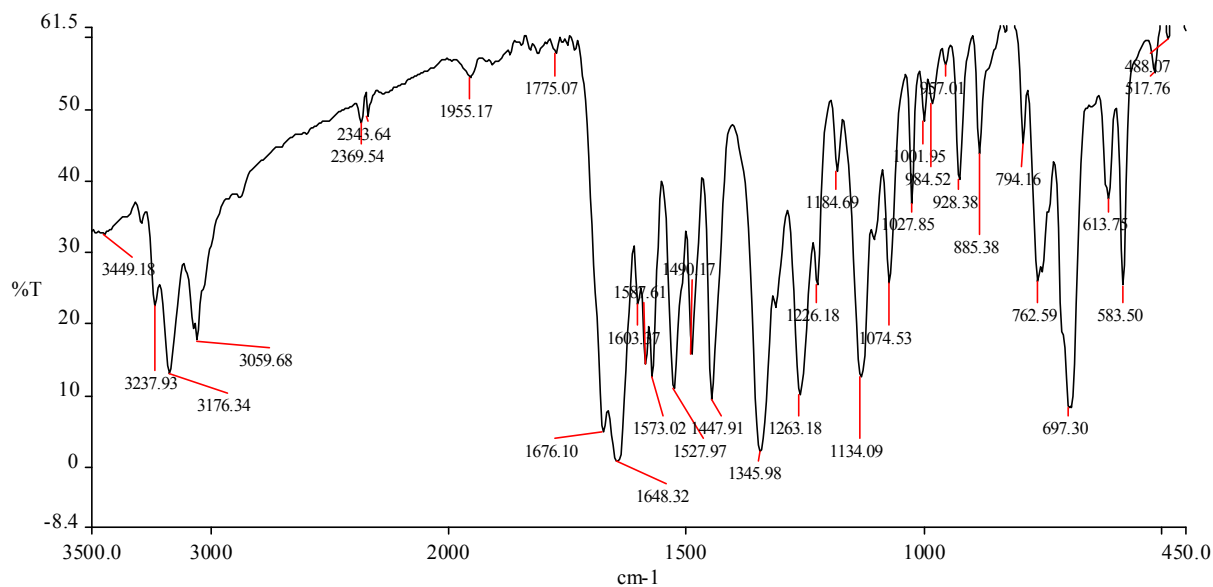
IR spectra of Co complex **1**, $[Co^{II}(L_2^A)_2]$, **Figure-4.2**



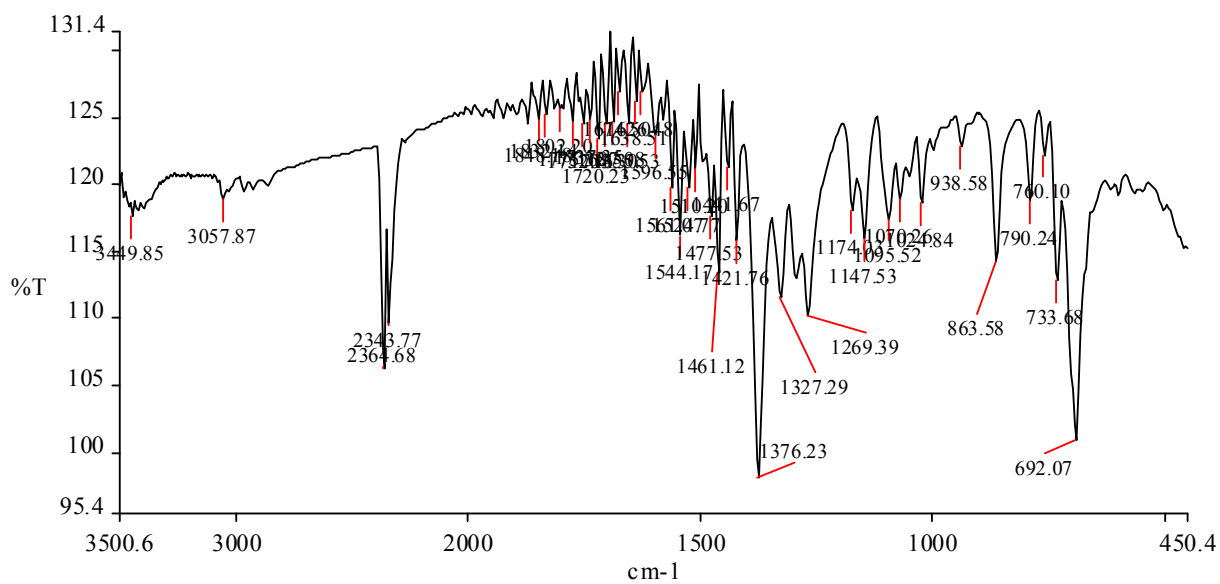
IR spectra of the ligand $L_2^B H_1$, **Figure-4.3**



IR spectra of Co complex **2**, $[Co^{II}(L_2^B)_2]$, **Figure-4.4**



IR spectra of the ligand Benz-BH, **Figure-4.5**



IR spectra of Co complex 3, [Co^{II} BenBH], **Figure-4.6**

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 4.7-4.9**) 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 ^[16-21]

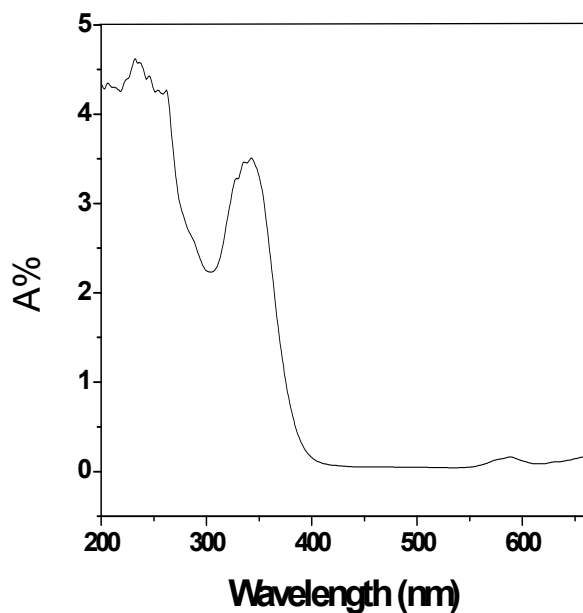


Figure-4.7: Electronic spectra of Co complex.1, $[\text{Co}^{\text{II}}(\text{L}_2^{\text{A}})_2]$

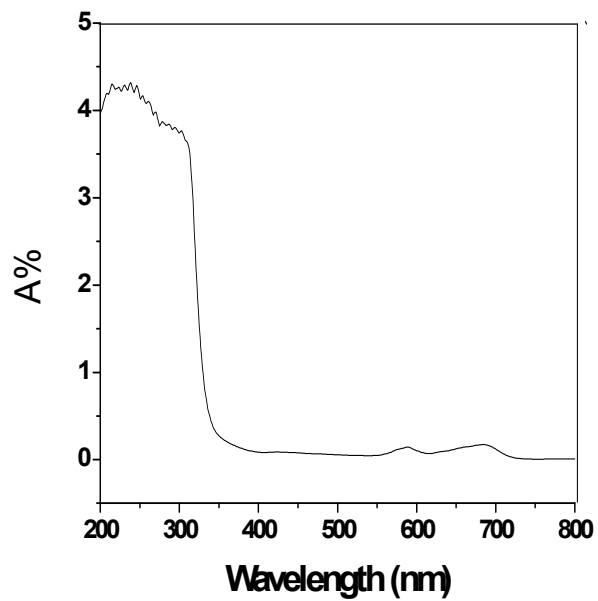


Figure-4.8: Electronic spectra of Co complex,2, [Co^{II}(L₂B)₂]

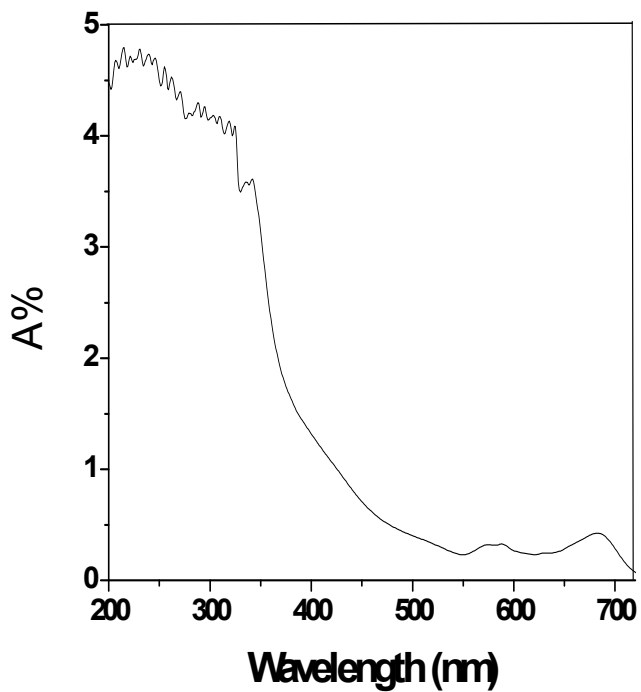


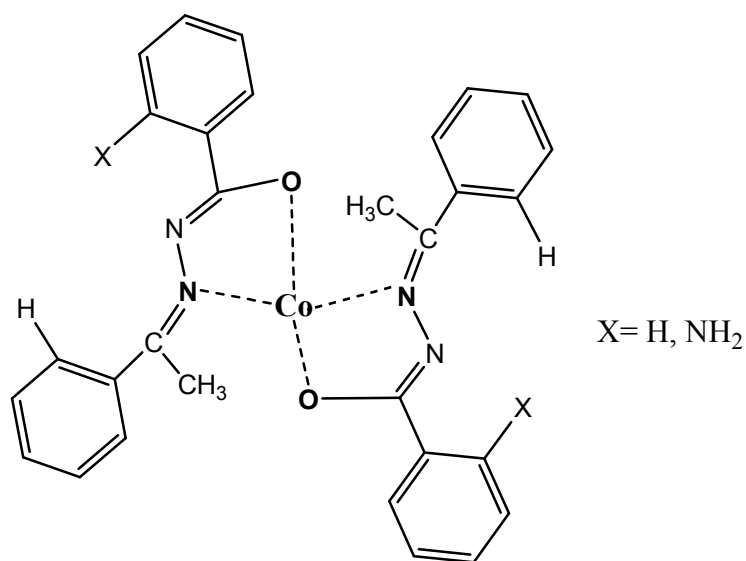
Figure-4.9: Electronic spectra of Co complex 3, [Co^{II} BenBH]

3.3. Magnetic Studies:

The Cobalt(II) complexes (**1-2**) was found to be paramagnetic which excludes of square planar configuration. The measured magnetic moment value for Cobalt(II) complexes are found in the range of 4.60-4.65 BM are evidence for tetrahedral geometry ^[16-18]. This higher experimental value (theoretical value 3.84 BM) is may be due to orbital contribution. Due to shortage of time I could not able to report the magnetic susceptibility value of complex **3**.

3.5. Expected geometry of Co complexes(1-2) containing bidentate hydrazone ligands:

Having all the characterization data of two Co complexes (1-2) in hand we can predict the preliminary geometry of those two as following but final structure can be predicted after having the corresponding X-ray structure only. From the preliminary characterization data we have also predicted the expected structures of the other synthesized complexes in our experimental section.



Expected geometry of Co complexes (1-2) with bidentate ligand

Conclusion:

Several tri- and bidentate O-N donor Schiff's base hydrazone ligands were synthesized and successfully characterized by IR spectrophotometer and C H N analyzer. The basic and electronic properties of these ligands have been nicely explored in the syntheses of various Cobalt and Nickel hydrazone complexes. All Co complexes are characterized by elemental analysis, IR, UV Visible spectrophotometer and Magnetic susceptibility measurement. The single crystal x-ray studies of synthesized Co complexes (**1-3**) are under process with our collaborator. One of the three synthesized Co compound (complex **2**) is successfully characterized by X-ray crystallography. But due to incomplete refinement of x-ray data I am unable to show the x-ray structure in this dissertation.

References:

- 1 .Azojomo (ISSN 1833-122X) volume **3** December **2007**
- 2 Feng Liang et al. *Bioorganic & Medicinal Chemistry Letters* **14** (**2004**) 1901–1904
3. (a) R.H. Holm, in: G.L. Eirchorn (Ed.), *Inorganic Biochemistry*, vol. **2**, Elsevier, Amsterdam, **1974**, p. 1137;
(b) S. Yamada, *Coord. Chem. Rev.* **1** (**1966**) 126;
(c) L. Sacconi, *Coord. Chem. Rev.* **1** (**1966**) 112.
4. S. Naskar , S. Biswas, D. Mishra , B. Adhikary , L.R. Falvello , T. Soler , C.H. Schwalbe , S.K. Chattopadhyay, *Inorg. Chim. Acta* **357** (**2004**) 4257–4264
- 5 Pedrares et al. *Polyhedron* **27** (**2008**) 3391–3397
6. a) M. Ruben, J. –M. Lehn and G. Vaughan, *Chem. Commun.*, **2003**, 1338 b) L. H. Uppadine, J. –P. Gisselbrecht, J. -M. Lehn, *Chem. Commun.*, **2004**, 718 c) L. H. Uppadine, J. -M. Lehn, *Angew Chem. Int. Ed.* **2004**, 43, 240.
7. Yamagata et al. *journal of radiation research* 3-1 4-8(march **1962**)
8. Y. Qi and Z.Y.Wang, *Macromolecules*, **2003**, 36, 3146
9. Kimura, E.; Nakamura, *Journal of Applied sciences* **8**(13):2480-2485,**2008**
10. a) P. J. Melz, R. B. Champ, L. S. Chang, C. Chiou, G. S. Keller, L. C. Liclican, R. R. Neiman, M. D. Shattuck and W. Weiche, *J. Photogra. Sci. Eng.*, **1977**, 21, 73 b) R. B. Champ and Shattuck, US patent **3**, 824, 099, **1974** c) H. W. Anderson and M. T. Moore, US patent **4**, 150, 987, **1979**.
11. (a) E.S. Raper, *Coord. Chem. Rev.* **165** (**1997**) 475;
(b) J.A. García-Vázquez, J. Romero, A. Sousa, *Coord. Chem. Rev.* **193** (**1999**) 475;

12 . a) E. Massarani, D. Nardi, A. Tajana and L. Degen, *J. Med. Chem.*, **1971**, 14, 633 b) M. Carcelli, P. Mazza, C. Pelizzi, G. Pelizzi and F. Zani, *J. Inorg. Biochem.*, **1995**, 57, 43 c) A. Bacchi, A. Bonardi, M. Carcelli, P. Mazza, P. Pclagatti, C. Pelizzi, G. Pelizzi, C. Solinas and F. Zani, *J. Inorg. Biochem.*, **1998**, 69, 101 d) A. R. Todeschini, A. L. P. Miranda, K. C. M. Da Silva, S. C. Parrini and E. J. Barreiro, *Eur. J. Med. Chem.*, **1988**, 33, 189.

13.a) S. Pal, J. Pushparaju, N. R. Sangeetha and S. Pal, *Transition Metal Chemistry*, **2000**, 25, 529 b) S. Pal and S. Pal, *J. Chem Soc., DaltonTrans.*, **2002**, 2102 c) N. R. Sangeetha, C. K. Pal, P. Ghosh and S. Pal, *J. Chem Soc., Dalton Trans.*, 1996, 3293 d) A. Mukhopadhyay and S. Pal, *Polyhedron*, **2004**, 23, 199 e) S.C. Davies, M.C. Durrant, D.L. Hughes, A. Pezeshk, R.L. Richards, *J. Chem. Res. (S)*, **2001**, 100 f) R. Dinda, P. Sengupta, S. Ghosh and T. C. W. Mak, *Inorg. Chem.*, **2002**, 41, 1684 g) N. R. Sangeetha and S. pal, *Bull. Chem. Soc. Jpn.*, **2000**, 73, 357 h) S. Dutta, P. Basu and A. Chakravarty, *Inorg. Chem.*, **1993**, 32, 5343 i) R. Dinda, P. Sengupta, S. Ghosh and W. S. Sheldrick, *Eur. J. Inorg. Chem.*, **2003**, 363 j) M. R. Maurya, S. Khurana, W. Zhang and D. Rehder, *J. Chem Soc., Dalton Trans.*, **2002**, 3015 k) C. M. Armstrong, P. V. Bernhardt, P. Chin and D. R. Richardson, *Eur. J. Inorg. Chem.*, **2003**, 1145.

14. S. Naskar, M. Corbella, A. J. Blake and S. K Chattopadhyay *Dalton Trans.*, **2007**, 14150–1159

15. S. Naskar, D. Mishra, S. K. Chattopadhyay, M. Corbella and A. J. Blake, *Dalton Trans.*, **2005**, 2428-2435

16. Guzar et al. *Journal of Applied Sciences* **8**(13):2480-2485, 2008

17. (a) Sibert, J. W.; Cory, A. H.; Cory, J. G. *J. Chem. Soc., Chem. Commun* **2002**, 154 and references cited therein. (b) Messori, L.; Abbate, F.; Marcon, G.; Orioli, P.; Fontani, M.; Mini, E.; Mazzei, T.; Carotti, S.; O'Connell, T.; Zanello, P. *J. Med. Chem.* **2000**, 43, 3541

18. Christian H. Stapfer, and Richard W. D'Andrea *Inorg. Chem.*, **1971**, **10** (6), 1224-1227

19. Liang, F.; Wu, C Chem. Commun., **2005**, 1474–1475
20. J. K. Sears and J. R. Derby, The technology of plasticizers, Wiley: New York, **1992**
21. B. Robinson, Chem. Rev., **1963**, 63, 373.
22. N. Noshimo, Coord. Chem. Rev. **113** (**1998**) 87
23. L. Canali, D.C. Sherrington, Chem. Soc. Rev. **28** (**1999**) 85.