METHOD OF STUDY

Materials required

To start the research work in coordination compounds it is required to prepare the compounds which acts as ligands like biguanide sulphate, naphthylbiguanide hydrochloride and piperazinedibiguanide sulphate in pure state. And then these ligands were made to react with the metal salts to form the respective metal complexes. The methods for the preparation of ligands and their metal complexes are described below:

- **Biguanide sulphate**\(^\text{1}\) (m.p. 231–232°C) \( \text{C}_2\text{H}_6\text{N}_5\cdot\text{H}_2\text{SO}_4\cdot2\text{H}_2\text{O} \)

Biguanide sulphate was prepared according to the method described by Smolka\(^\text{1}\) and Friedrich with slight modification which resulted in a better yield. In this method, a mixture of ammonium chloride (NH\(_4\)Cl) and dicyandiamide, C\(_2\)H\(_4\)N\(_4\) (mol. Wt. 84.04) [dried at 100°C] in 2:1 proportion was intimately mixed in mortar and pestle and the mixture so obtained was then transferred to a dry pyrex beaker and heated over asbestos board by means of a Bunsen burner. During this process, the mixture was constantly stirred with the help of a glass rod and the temperature was raised gradually to 155°C. At this temperature, the mixture changed to a thick liquid and was maintained at this temperature \([155\pm2]^\circ\text{C}\) for ten minutes. The molten mass was then poured into a large volume of water and then treated with a solution of Cuprammonium sulphate, \([\text{Cu(NH}_3\text{)}_4]\text{SO}_4\). Cuprammonium sulphate was prepared by adding liquor ammonia (NH\(_3\)) to copper (II) sulphate solution. As a result, rose-red coloured precipitate of copper biguanide sulphate \([\text{Cu(C}_2\text{H}_6\text{N}_5)_2]\cdot\text{H}_2\text{SO}_4\) was obtained at once. This was filtered in a Buchner funnel and was washed thoroughly with cold water. The precipitate should be kept over the Buchner funnel till water
gets drained. The moist copper biguanide sulphate $\text{Cu}(\text{C}_2\text{H}_6\text{N}_5)_2\cdot\text{H}_2\text{SO}_4$ was then decomposed with cold solution of about 10% sulphuric acid ($\text{H}_2\text{SO}_4$). A blue solution was obtained which on keeping in cold [12°C] deposited large crystals of biguanide sulphate. The yield was found to be best when a mixture of 8 gms of dicyandiamide with 16 gms of ammonium chloride was fused. Beside this temperature should also be maintained properly for good yield.

$$\text{H} - \text{N} - \text{C} - \text{N} - \text{C} - \text{N} - \text{H} \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \cdot \text{NH} \quad \text{NH}$$

**Biguanide Sulphate**

Actually, it occurs in the following tautomeric forms:

(a) $\text{H}_2\text{N} - \text{C} \equiv \text{N} - \text{C} \equiv \text{NH}_2$  \hspace{2cm} (b) $\text{H}_2\text{N} - \text{C} \equiv \text{N} - \text{C} \equiv \text{NH}_3$

(c) $\text{H}_2\text{N} - \text{C} \equiv \text{N} - \text{C} \equiv \text{NH}_2$  \hspace{2cm} (d) $\text{H}_2\text{N} - \text{C} \equiv \text{N} - \text{C} \equiv \text{NH}_2$
Found

C = 10.11%; N = 29.90%

C₂H₄N₅•H₂SO₄•H₂O requires

C = 10.21%; N = 29.78%

- **Naphthylbiguanide hydrochloride**

Naphthylbiguanide hydrochloride was prepared by refluxing alcoholic solution of both Naphthylamine hydrochloride C₁₀H₇NH₂•HCl and dicyandiamide C₄H₄N₄ in round bottom flask on water bath. This process continues for about two hours. The crystals get deposited on cooling the mixture obtained. The crystals were filtered and recrystallized with hot water.
Naphthylbiguanide chloride

Found
C = 53.71; N = 25.35

requires
C = 54.65%; N = 26.56%

Piperazinedibiguanide Sulphate

Piperazine (4.3g) and dicyandiamide (8.4g) were heated with about 75 ml of water in a conical flask on the water bath for about 3 hours with occasional addition of 5 ml of CuSO₄ solution (10g in 30 ml water) at interval of 20 minutes. To the resulting mixture, a solution of NaOH (2.8g) was added and the heating was continued till the mixture turned red. This was cooled and filtered and the red residue was then decomposed with H₂SO₄ (1:3). The white piperazine biguanide sulphate separates out, gradually on cooling. This was filtered and washed with cold water until free from copper. The product was then dissolved in ammonia and a little NaOH the mixture filtered and acidified with dil. H₂SO₄ (1:1). On cooling, shining white crystals of piperazinedibiguanide sulphate separates out from the solution. These were filtered washed with cold water and dried in air.
Found:

N = 29.42%
S = 13.35%

\( \text{C}_{8}\text{H}_{18}\text{N}_{10}\cdot2\text{H}_2\text{SO}_4\cdot1.5\text{H}_2\text{O} \) requires:

N = 29.35%
S = 13.41%

---

\[
\begin{align*}
\text{Piperazine dibiguanide sulphate}
\end{align*}
\]

**Preparation of the metal complexes of ligands**

- **Acetylacetonatobisbiguanidinium cobalt (III) hydroxide**

The Bisbiguanidinium cobalt (III) hydroxide was prepared by adding with stirring calculated amount of biguanide sulphate, dissolved in slight excess of sodium hydroxide to a solution of cobalt sulphate. The yellow silky precipitate obtained was filtered quickly to avoid oxidation, on a Buchner funnel and was washed with ice cold water. This was then transferred to an
aeration flask in which a suspension was made with a little water. Diamminebisbiguanidinium cobalt (III) hydroxide was prepared by passing a brisk current of air through a mixture of bisbiguanidinium cobalt (III) hydroxide and liquor ammonia for several hours, fresh ammonia being added from time to time the silky yellow bisbiguanidinium cobalt (III) hydroxide gradually dissolved to a red solution. The solution containing diamminebisbiguanidinium cobalt (III) hydroxide was filtered. The filtrate on acidification gave the diamminebisbiguanidinium cobalt (III) salt. Acetylacetonatobisbiguanidinium cobalt (III) hydroxide was prepared by heating a solution of diamminebisbiguanidinium cobalt (III) hydroxide, as prepared above, with acetyl acetone on steam bath. Acetyl acetone was added in small portions from time to time to compensate the loss by evaporation. When no further ammonia evolved, the solution on cooling deposited light red crystals in small amounts. The crystals were filtered, washed with water and alcohol. The compound was dried in a CO₂ free atmosphere. It was slightly soluble in water and aqueous solution is alkaline to litmus. On heating it decomposed to cobalt oxide with the evolution of acetyl acetone and ammonia. On analysis it was found to contain:

\[
\begin{align*}
\text{Co} & = 12.66\% \\
\text{N} & = 30.30\%
\end{align*}
\]

Required for \[
\left[ \text{Co}\left(\text{BigH}^+\right)\left(\text{acac}\right)\right]\left(\text{OH}\right)\text{,}4\text{H}_2\text{O}
\]
where “\text{BigH}^+” stands for one molecule of biguanide and ‘acac’ for one molecule of acetyl acetone:

\[
\begin{align*}
\text{Co} & = 12.63\% \\
\text{N} & = 30.04\%
\end{align*}
\]
- **Acetylacetonatobisbiguanidinium cobalt (III) sulphate**

The complex was prepared by heating a solution of diamminebisbiguanidinium cobalt (III) sulphate with acetyl acetone on a steam bath till the evolution of ammonia ceased. On cooling the solution, dark red crystals separated. The crystals were filtered, washed with water and alcohol and then dried in air. The complex is soluble in water. The air dried sample on analysis was found to contain:

- **Co** = 12.23%
- **N** = 29.25%
- **SO$_4$** = 20.18%
- **H$_2$O** = 3.82% (by loss at 110°C)

Required for $[\text{Co(Big}^+\text{)}_2(acac)]\text{SO}_4\cdot\text{H}_2\text{O}$:

- **Co** = 12.43%
- **N** = 29.54%
- **SO$_4$** = 20.24%
- **H$_2$O** = 3.79%

- **Acetylacetonatobisbiguanidinium cobalt (III) chloride**

It was prepared by heating a solution of diamminebisbiguanidinium cobalt (III) chloride with acetylacetone on steam bath. The solution was concentrated to a small volume which on cooling deposited some orange crystals of trisbiguanidinium cobalt (III) chloride. These were filtered off. The filtrate on further cooling deposited dark violet red crystals. The
crystals were filtered, washed with a small quantity of ice cold water and
with alcohol. The air dried sample on analysis was found to contain:

Co = 13.26%
N = 31.41%
Cl = 15.64%
H₂O = 3.97% (by loss at 110°C)

Required for  \([\text{Co} (\text{BigH}^+) (\text{acac}) \text{Cl}_2 \cdot \text{H}_2\text{O}]\):

Co = 13.12%
N = 31.19%
SO₄ = 15.79%
H₂O = 4.01%

• Acetylacetonatobisbiguanidinium cobalt (III) nitrate

Diamminebisbiguanidinium cobalt (III) hydroxide prepared as described
above was neutralized with dilute nitric acid in cold. The solution on
cooling deposited red crystals of diamminebisbiguanidinium cobalt (III)
nitrate. This was then heated on steam bath with acetylacetone. The colour
of the solution changed to dark red. On cooling, red needle shaped crystals
separated. The crystals were filtered, washed with water and alcohol. The
air dried substance on analysis was found to contain:

Co = 11.84%
N = 33.35%
NO₃ = 24.96%
\[ H_2O = 3.25\% \text{ (by loss at 105°C)} \]

Required for \[ Co(B_{ig}H^+)_{2}(acac)(NO_3)_{2} \cdot H_2O \]

Co = 11.73\%

N = 33.47\%

NO_3 = 24.68\%

\[ H_2O = 3.58\% \]

- **Acetylacetonatobisbiguanidinium cobalt (III) oxalate**

It was prepared by adding a solution of sodium oxalate to a solution of the complex chloride. The first crop of orange crystals was filtered out. The filtrate on cooling gave fine reddish violet crystals of the complex oxalate. The crystals were filtered, washed with water and alcohol and dried in air. The air dried compound on analysis was found to contain:

Co = 11.15\%

N = 26.66\%

C_2O_4 = 16.72\%

Required for \[ Co(B_{ig}H^+)_{2}(acac)C_2O_4 \cdot 4H_2O \]

Co = 11.33\%

N = 26.92\%

C_2O_4 = 16.91\%
When a solution of the complex oxalate was heated with an excess of oxalic acid on the steam bath dark violet crystals of oxalatoxalate were obtained, which on analysis was found to contain:

\[ \text{Co} = 14.01\% \]

Required for \[ \text{Co}(\text{B}i\text{gH}^+)\_2(\text{C}_2\text{O}_4)\] \_2 \text{C}_2\text{O}_4\cdot 4\text{H}_2\text{O} \]

\[ \text{Co} = 13.95\% \]

**Nickel \( \alpha \)-Naphthylbiguanide and its hydrate**

- **\( \alpha \)-Variety:** An ammoniacal solution of NiSO\(_4\) in slight excess was added to that of naphthylbiguanide in hot dil. Ammonia. After sometime the precipitate was filtered and washed several times with water till free from sulphate. The product was dried on a porous plate and then over alkali to a constant weight.

Found: \( \text{N} = 26.61\%; \text{Ni} = 11.12\% \)

\[ [\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_5)]\_2\cdot\text{H}_2\text{O} \text{ requires:} \]

\[ \text{N} = 26.48\%; \text{Ni} = 11.10\% \]

The substance forms flesh coloured crystals, insoluble in water. It can displace NH\(_3\) from boiling NH\(_4\)Cl solution. It is sparingly soluble in alcohol, but dissolves in pyridine giving red solution. When heated at 110°C for about 12 hours it lost whole of its water (3.407; cal. 3.417) and formed the anhydro base without any change of colour.

Found:

\[ \text{Ni} = 11.50\% \]

\[ [\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_5)]\_2 \text{ requires:} \]

\[ \text{Ni} = 11.49\% \]
• **β-Variety:** It was obtained as insoluble yellow crystals by adding a large excess of naphthylbiguanide solution drop by drop to that of nickel chloride at the boiling temperature. The crystals were washed several times with hot water and dried as before. The substance dissolves in pyridine and warm alcohol to a yellow solution.

  Found:
  
  N = 25.%; Ni = 10.58%

\[
[Ni(C_{12}H_{12}N_3)_2] \cdot 2.5H_2O \text{ requires:}
\]

N = 25.20%; Ni = 10.56%

On heating the substance at 140°C for about 12 hours it lost all of its H₂O and forms anhydro base without any change in colour.

  Found:
  
  H₂O = 8.00%; Cal. H₂O = 8.00%

• **γ-Variety:** It was obtained by dissolving the hydrated α-form in the minimum quantity of cold HCl and then adding an excess of caustic soda solution. The light buff coloured crystalline precipitate was filtered, washed with cold water free from chloride and then dried as before.

  N = 25.70%; Ni = 10.70%

\[
[Ni(C_{12}H_{12}N_3)_2] \cdot 2H_2O \text{ requires:}
\]

N = 25.61%; Ni = 10.74%

The substance melts when boiled with H₂O. It is sparingly soluble in alcohol but dissolves in pyridine giving a yellow solution.

• **Nickel α-Naphthylbiguanidinium sulphate:** It was obtained as a buff colored crystalline precipitate by adding a solution of NiSO₄ in slight excess to that of α-Naphthylbiguanide. The substance is sparingly soluble in pyridine, acetone and alcohol.
Found:
SO$_4$ = 15.29%; Ni = 9.38%

\[ \text{[Ni(NaphBigH$^+$)$_2$]} \text{SO}_4 \cdot \text{H}_2\text{O requires:} \]
SO$_4$ = 15.32%; Ni = 9.36%

**Nickel $\alpha$-Naphthylbiguanidinium chloride:** A solution of naphthylbiguanide was added to a hot solution of Nickel chloride in calculated amount. The mixture was filtered from any precipitated $\beta$-base. The filtrate on cooling, gave light yellow crystals of the complex chloride. The substance dissolves completely in hot water as well as in pyridine, acetone and warm alcohol.

N = 22.58%; Ni = 9.51%; Cl = 11.99%

\[ \text{[Ni(NaphBigH$^+$)$_2$]} \text{Cl}_2 \cdot 2\text{H}_2\text{O requires:} \]
N = 22.59%; Ni = 9.47%; Cl = 11.96%

**Copper and Nickel piperazine dibiguanide and their salts**

**Copper piperazine dibiguanide hydroxide:** Piperazine dibiguanide sulphate (4.7g) dissolved in ammonia and a little caustic soda solution (about 20ml of 2N NaOH); was treated with an ammoniacal solution of CuSO$_4$ (1.g) with constant stirring. The precipitate of red violet copper piperazine dibiguanide hydroxide which separated immediately was filtered and washed with cold water till free from sulphate. The product was dried in a dessicator to a constant weight.

Found:
Cu = 15.47%; N = 34.80%; H$_2$O = 21.97% (by loss at 105°C)

\[ \text{[CuPip(BigH$_2$)$\_2$]}\text{(OH)$\_2$}\cdot 3\text{H}_2\text{O requires:} \]
Cu = 15.60%; N = 34.50%; H₂O = 22.10%

The substance forms red violet powder, insoluble in water and alcohol. When heated with solution of ammonium salts it liberates NH₃. It is readily decomposed by dilute acids.

- **Copper piperazine dibiguanide chloride:** It was obtained as a red violet residue when the complex Cu base was heated with a solution of NH₄Cl on the water bath till the evolution of NH₃ ceased. The product was filtered, washed with cold water and dried in air. The substance is sparingly soluble in hot water and practically insoluble in alcohol.

  Found:
  
  Cu = 13.68%; Cl = 15.43%; H₂O = 15.54% (by loss at 105°C)

  \[
  [\text{CuPip(BigH)}_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}
  \]

  requires:

  Cu = 13.70%; Cl = 15.40%; H₂O = 15.60%

  Found (anhydrous product):
  
  Cu = 16.38%; Cl = 18.29%

  Calc. Cu = 16.34%; Cl = 18.27%

- **Copper piperazine dibiguanide sulphate:** It was obtained as violet compound from the complex base and (NH₄)₂SO₄ solution in the same way as the complex chloride. The substance is insoluble in water and alcohol.

  Found:
  
  Cu = 12.56%; S = 6.15%; H₂O = 19.28% (by loss at 105°C)

  \[
  [\text{CuPip(BigH)}_2]\text{SO}_4 \cdot 5.5\text{H}_2\text{O}
  \]

  requires:

  Cu = 12.40%; S = 6.20%; H₂O = 19.31%

  Found (anhydrous product):
  
  Cu = 15.41%; S = 7.72%
Calc. Cu = 15.30%; S = 7.73%

- **Copper piperazine dibiguanide nitrate**: It was prepared from the complex base and a solution of ammonium nitrate as described in the previous case. The substance forms red powder insoluble in water and alcohol.

  Found:
  
  Cu = 13.69%; H₂O = 3.87% (by loss at 105°C)

  \[
  [\text{CuPip(BigH)}_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}\text{ requires:}
  \]

  Cu = 13.80%; H₂O = 3.90%

  Found (anhydrous product):
  
  Cu = 14.38%

  Calc. Cu = 14.39%

- **Nickel piperazine dibiguanide nickel hydroxide**: It was obtained as a buff coloured precipitate by adding an ammoniacal solution of NiSO₄ to that of piperazine dibiguanide sulphate in presence of an excess of caustic soda. The product was filtered, washed well with cold water and dried in a dessicator to a constant weight. When the colour of the substance changes to yellow. The substance is insoluble in water and alcohol and liberates NH₃ from NH₄⁺ salt solution.

  Found:
  
  Ni = 21.94%; N = 29.40%; H₂O = 16.80% (by loss at 105°C)

  \[
  [\text{NiPip(BigH)}_2](\text{OH})_2\cdot\text{Ni(OH)}_2\cdot5\text{H}_2\text{O}\text{ requires:}
  \]

  Ni = 22.17%; N = 26.40%; H₂O = 17%

  Found (anhydrous compound):
  
  Ni = 26.51%; N = 31.85%

  Calc. Ni = 26.70%; N = 31.80%
Nickel piperazine dibiguanide chloride: It was obtained as insoluble orange yellow product by heating the complex nickel base, described above, with a solution of NH₄Cl on the water bath until the evolution of NH₃ ceased. The product was washed with cold water and dried in air to a constant weight.

Found:
Ni = 11.35%; N = 27.22%; Cl = 13.48%; H₂O = 25.89% (by loss at 110°C)

\[
\left[ \text{NiPip(BigH)₂} \right] \text{Cl}_2 \cdot 7\text{H}_2\text{O} \text{ requires:}
\]
Ni = 11.31%; N = 27.00%; Cl = 13.60%; H₂O = 26%

Found (anhydrous compound):
Ni = 15.18%; Cl = 18.48%
Calc. Ni = 15.20%; Cl = 18.50%

Nickel piperazine dibiguanide hydroxide: It was obtained as an insoluble orange coloured product by keeping the complex nickel chloride (1 mol) in contact with a solution of caustic soda (2 mol) for two days and then heating the mixture on the water bath for some time. The product was washed with cold water and dried in a desiccator to a constant weight.

Found:
Ni = 15.69%; N = 37.33%; H₂O = 16.72% (by loss at 105°C)

\[
\left[ \text{NiPip(BigH)₂} \right] (\text{OH})_2 \cdot 1.5\text{H}_2\text{O} \text{ requires:}
\]
Ni = 15.70%; N = 37.46%; H₂O = 16.80%

Found (anhydrous compound):
Ni = 15.18%; Cl = 18.47%
Calc. Ni = 15.20%; Cl = 18.50%
Chemicals required for the preparation of the above described ligands and their complexes are given below:

1. Dicyandiamide
2. Ammonium Chloride
3. Copper Sulphate
4. Liquor Ammonia
5. Cobalt Sulphate
6. Acetyl Acetone
7. Hydrochloric Acid
8. Sulphuric acid
9. Nitric Acid
10. Sodium Oxalate
11. Naphthyl Amine
12. Ethyl alcohol
13. Nickel Chloride
14. Nickel Sulphate
15. Piperazine
16. Distilled Water
17. Sodium Hydroxide
18. Ammonium Sulphate
19. Ammonium Nitrate

To carry out the reactions for the preparation of ligands and their complexes the following materials were required:
1. Oven
2. Beaker
3. Bunsen flame
4. Dessicator
5. Electronic and physical balance
6. Buchner funnel
7. Mortar and pestle
8. Aeration flask
9. Reflux condenser
10. Water bath
11. Basin
12. Porous plate

Kjeldahl’s flask was used for determining the melting point of the ligands,

- **Methods of analysis**

**Nitrogen** was determined by Semi-Micro Dumas method in the Department of Chemistry, Patna University, Patna.

**Carbon, Hydrogen and Nitrogen** were analysed by Elemental analyser, Euro vector EA 3000, from Central Drug Research institute, Lucknow. The anions and metal ions were estimated by standard methods$^4$-$^7$.

**Halogens**: Accurately weighed sample (about 150-200mg) of the compound was fused with fusion mixture in a nickel crucible. The fused mass was extracted with hot water and the insoluble residue was filtered off. The clear extract was neutralized with nitric acid and the halogen content was precipitated as silver halide was boiled until it gets coagulated and the supernatant liquid was clear. The precipitate was then allowed to settle for an hour. The halide was filtered with sintered glass crucible and washed
thoroughly with very dilute nitric acid. It was dried at 130-150°C and finally weighed as silver halide. The process was continued till constant weight was obtained.

\[
X^- + AgNO_3 \rightarrow AgX + NO_3^-
\]

Wt. of watch glass = \(w_1\) g

Wt. of watch glass + sample = \(w_2\) g

Wt. of sample = \((w_2 - w_1)\) g

Wt. of sintered glass = \(w_3\) g

Wt. of sintered glass + silver halide = \(w_4\) g

Wt. of silver halide = \((w_4 - w_3)\) g

\[
\% \text{ of halide} = \frac{\text{wt. of } AgX + \text{wt. of } X^- \text{ in } 1 \text{ g of } AgX}{\text{Wt. of sample}} \times 100
\]

**Sulphate:** It was estimated gravimetrically as Barium sulphate \(BaSO_4\).

About 100-150 mg of ligand sulphate or complex sulphate was taken in a pyrex beaker and digested with 100ml water and 1gm (A.R.) \(Na_2CO_3\) for 2 hours and filtered. The filtrate was acidified with conc. \(HCl\) and sulphate was separated as \(BaSO_4\) by adding \(BaCl_2\) solution. \(BaSO_4\) was filtered on Whatman No. 42 filter paper, dried and ignited in a crucible and weighed as \(BaSO_4\). In the process of ignition, \(BaSO_4\) is slightly reduced.

\[
BaSO_4 + 4C \rightarrow BaS + 4CO
\]

So, finally a drop of conc. \(H_2SO_4\) was added over the precipitate in the crucible and heated.

\[
BaS + H_2SO_4 \rightarrow BaSO_4 + H_2S
\]
The crucible was cooled and weighed with lid. This process was continued till constant reading was obtained.

\[
\begin{align*}
\text{Wt. of watch glass} & = w_1 \text{ g} \\
\text{Wt. of watch glass + sample} & = w_2 \text{ g} \\
\text{Wt. of sample} & = (w_2 - w_1) \text{ g} \\
\text{Wt. of crucible + lid} & = w_3 \text{ g} \\
\text{Wt. of crucible + lid + BaSO}_4 + \text{Ash} & = w_4 \text{ g} \\
\text{Wt. of BaSO}_4 & = (w_4 - w_3 - \text{wt. of ash}) \text{ g} = w \text{ g (say)}
\end{align*}
\]

\[
\% \text{ of SO}_4^{2-} = \frac{\text{wt. of BaSO}_4 + \text{wt. of SO}_4^{2-} \text{ in } 1 \text{ g of BaSO}_4}{\text{Wt. of sample}} \times 100
\]

\[
= \frac{w \times 0.4112 \times 100}{w_1}
\]

**Copper:** It was estimated iodometrically. About 150-200mg of Copper (II) complex was taken in a pyrex beaker and decomposed with conc. \(\text{HClO}_4 + \text{HNO}_3\) mixture till a clear solution. The resulting clear solution was evaporated to dryness and treated with 10-5 ml conc. \(\text{HCl}\) and evaporated to expel any oxide of nitrogen and diluted with 50-60 ml distilled water. The volume of solution was made 100 ml and 25 ml from the stock solution was taken in a conical flask and Copper (II) content was estimated iodometrically using sodium thiosulphate solution.

\[
\begin{align*}
\text{Wt. of watch glass} & = w_1 \text{ g} \\
\text{Wt. of watch glass + sample} & = w_2 \text{ g} \\
\text{Wt. of sample} & = (w_2 - w_1) \text{ g}
\end{align*}
\]
25 ml of Cu sample solution = x ml of \( \frac{1}{10} \) (f) \( \text{Na}_2\text{S}_2\text{O}_3 \)

\[
250 \text{ ml of Cu sample solution} = \frac{250 \times x \text{ ml} \times f}{25 \times 10}
\]
\[
= x \text{ ml} \times f \text{ of } (\text{Na}_2\text{S}_2\text{O}_3)
\]

1 ml of \( (\text{N}) \text{Na}_2\text{S}_2\text{O}_3 \) = 0.06357 g of Cu

Amount of Cu in the sample = \[
\frac{x \text{ ml} \times f \times 0.06357 \times 100}{(w_2 - w_1)}
\]

**Nickel:** Nickel complexes were decomposed first by taking its weight as 100-150 mg and keeping it in a pyrex beaker covered with a watch glass. It was decomposed by repeated evaporation with perchloric acid and concentrated nitric acid mixture on a sand bath. The decomposed complex was finally treated with 20-25 ml of conc. HCl and evaporated to a small volume. It was diluted with water to a clear solution and heated to 70-80°C. A slight excess of 1% solution of dimethylglyoxime \( (\text{C}_4\text{H}_8\text{N}_2\text{O}_2) \) in alcohol was added followed by dilute ammonia solution drop wise with constant stirring until it was faintly alkaline. The precipitate obtained was digested on a steam bath, allowed to stand for an hour and filtered through a sintered crucible. The precipitate was dried at 110° - 120°C and weighed as \( \text{Ni(}\text{C}_4\text{H}_7\text{N}_2\text{O}_2\text{)}_2 \).

\[
\text{Ni}^{2+} + 2 \text{C}_4\text{H}_7\text{N}_2\text{O}_2 + 2 \text{NH}_4\text{OH} \rightarrow 2\text{H}_2\text{O} + 2\text{NH}_4^+ + (\text{C}_4\text{H}_7\text{N}_2\text{O}_2)\text{Ni}\downarrow
\]

Let the weight of the precipitate be \( x \), then

Since, 288.91 g of Ni complex contains 58.71 g Ni

Therefore, \( x \) g of Ni complex will contain \[
\frac{58.71 \times x \text{ g}}{288.91} = 0.2032 \times x \text{ g of Ni}
\]

And since 0.5 g Ni salt contains 0.2032 g of Ni
Therefore, 100 g of Ni salt contains \( \frac{0.2032 \times 100 \text{ g of Ni}}{0.5} \)

i.e., % of Ni in the sample = \( \frac{0.2032 \times x \text{ g}}{0.5} \)

**Cobalt:** It was determined by igniting the complex in a crucible for a few minutes, cooling and treating with a few drops of concentrated nitric acid (A.R.) to oxidize any residual carbon and to convert the oxide into nitrate. It was then heated carefully to expel the excess of nitric acid. Finally a drop of concentrated sulphuric acid was added to convert the nitrate to sulphate. It was then heated between 450°-500°C and weighed as CoSO\(_4\). Complex was decomposed cautiously with concentrated perchloric acid to syrupy mass. It was diluted with water and precipitated as cobalt benzimidazolate\(^6\).

**Physical measurements:**

**Magnetic Property**

The magnetic property was determined by the Vibrating sample magnetometer (VSM) Model 7410 at CIF, IIT Guwahati.

**Infra-Red spectroscopy**

The complexes of biguanide and substituted biguanides prepared as above were in solid state. Therefore, the analysis were recorder on Perkin Elmer Spectrum version 10.03.06 in the range 4000 – 450 cm\(^{-1}\) in KBr disc at SAIF, CDRI, Lucknow.

**Diffuse Reflectance Spectroscopy**

Since, the complexes were sparingly soluble therefore, the diffuse reflectance spectroscopy was performed in the solid state on Carry 5000 in
the range 200 – 800 nm which were converted into absorbance by Kubelka – Munk equation at SAIF, STIC, Cochin.

*NMR Analysis*

Since the complexes were almost insoluble in all type of solvents therefore the $^1$H NMR analyses could not be performed.