

SYNTHESIS AND CHARACTERIZATION OF COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF CYCLOHEXYLAMINE-N-METHYL MANNICH BASE LIGANDS

Nduaguba, C.B.¹, Durosinmi, L.M.² and Egharevba G.O.^{1,2*}

¹Department of Chemistry, University of Benin, Benin City, Nigeria.

²Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria.

*Corresponding author: gegharev@yahoo.com

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ABSTRACT

Three Mannich base ligands, Cyclohexylamine-N-methylurea (CHMU), Cyclohexylamine-N-methylacetamide (CHMAA) and Cyclohexylamine-N-methylacetone (CHMA) and their cobalt(II), nickel(II) and copper(II) complexes were synthesized and chelating properties investigated with the view to determine the coordination modes and the stoichiometric ratio of the metal complexes. The Mannich ligands, CHMU, CHMAA and CHMA were prepared by the reaction of cyclohexylamine, formaldehyde and urea; cyclohexylamine, formaldehyde and acetone; cyclohexylamine, formaldehyde and acetamide respectively at 25 °C. They were characterized using infra-red (IR) spectroscopy. Their cobalt(II), nickel(II) and copper(II) complexes were equally prepared and characterized by infrared and UV-Visible spectroscopy. The solubilities of the ligands and their complexes in common solvents were also investigated. All the metal(II) complexes are stable in air and decomposed without melting at temperature > 300 °C. The infra-red spectra of the ligands show absorption bands in the region 3450-3300 cm⁻¹ due to (N-H) stretching vibration and 1644-1636 cm⁻¹ due to (amide C=O) stretching frequency in addition to other characteristic bands. These bands experienced significant shift downwards to 3434 cm⁻¹ and 1634 cm⁻¹ respectively on coordination with the metal ions. The coordination was further confirmed by the appearance of new bands at about (455-534) cm⁻¹ and (600-645) cm⁻¹ which are characteristics of M-N and M-O stretching bands. The coordinating atoms however vary with the metal ion as well as the ligand. With CHMAA, copper(II) ion coordinates through the two nitrogen atoms to form four –membered rings while nickel(II) ion coordinates through the oxygen atom and one of the nitrogen atoms to form six – membered rings. Cobalt(II) ion coordinates through both oxygen and the nitrogen atoms to form four –membered rings. With CHMA, copper(II) ion coordinates through the two nitrogen atoms, nickel(II) ion and cobalt(II) ion coordinate through the oxygen atom and one of the nitrogen atoms to form six – membered rings. The results from the percentage composition of the metals in the complexes of metal-CHMU confirm the preparatory procedure of metal to ligand ratio of 1: 2 (M: L). Thus, the prepared complexes have the general formulae [ML₂].

Keywords: Mannich base ligands, synthesis, characterization, metal complexes.

INTRODUCTION

There had been increasing studies of Mannich base complexes over the years due to the selectivity and sensitivity of the ligands to various metal ions. The quest of a coordination chemist is directed at designing ligands and acquiring more understanding of the ways in which they complex with metal ions. Metal ion complexes act as catalysts and it is necessary to design more effective catalysts for a variety of metal catalyzed

ligand reactions.

Mannich bases are β-amino carbonyl compounds produced from the condensation of ammonia or primary/secondary amine, with formaldehyde and a compound containing at least one hydrogen atom of pronounced reactivity to give an amide functional group. Mannich reaction find applications in the synthesis of many natural products and biologically important compounds,

(Selva, 2013, Visnuvardhanaraj *et al.*, 2013) and it is one of the most fundamental and important C-C bond forming reactions in organic synthesis, (Selva, 2013). Organic chelating ligands containing amide moiety as a functional group have a strong ability to form metal complexes and exhibit a wide range of biological activities, (Raman and Ravichandra, 2003).

Mannich bases have played a vital role in the development of coordination chemistry, (Paul *et al.*, 1976, Sathya *et al.*, 2011, Raman and Ravichandra, 2012). Mannich bases exhibit complexation characteristics with many transition metal ions. These complexes remain an important and growing area of research due to their simple synthesis, adaptability and diverse range of applications. Many potent antibacterial and antifungal compounds synthesized by the condensation of aldehyde, amine and amide have been reported, (Sathya *et al.*, 2012).

Mannich bases have also gained importance because of their technological applications in polymer chemistry, (Maurilioetal, 1988). They are widely employed as polymers or monomeric precursors of polymers in the production of compounds with a large number of different applications in industry. Mannich bases such as aminocyclohexane -N-methylurea, (CHMU), has been used as corrosion inhibitor for mild steel in 1N H₂SO₄, by Thiraviyam *et al.*, 2013. aminocyclohexane N-methylurea, has one amine group and two amide group which is very essential for an organic compound to behave as an effective corrosion inhibitor.

In this work, we report the synthesis, characterisation and the complexing properties of three cyclohexylamine-N-methyl ligands, CHMU, CHMAA and CHMA with copper (II), cobalt(II) and nickel(II) ions. Only the synthesis of cyclohexylamine-N-methylurea, CHMU has been reported in the literature.

MATERIALS AND METHODS

Materials

All the solvents used were of analytical grade and were used without further purification. Cyclohexamine, formaldehyde, urea, acetone,

acetamide, copper(II) chloride, nickel(II) chloride, cobalt(II) chloride, dimethylformamide (DMF), chloroform, methanol, ethanol, hydrochloric acid were BDH products. Materials for complexometric titrations were Murexide dye, Erichrome black T, perchloric acid, nitric acid, ammonia solution, ammonium chloride, disodium ethylene-diamine tetra acetic acid, (EDTA), Zinc(II)sulphateheptahydrate, hydroxylamine hydrochloride, 95 percent ethyl alcohol. Distilled water was used for the preparation of all aqueous solutions.

Instrumentation

Melting points were determined in open capillary tube on a Gallenkamp melting point apparatus (England). Infra-red (IR) spectra using KBr pellets were recorded on a Perkin Elmer FTIR Spectrophotometer. The UV-Visible Spectra were recorded in the visible region from 190-900nm using Perkin Elmer 1650-UV-Visible Spectrophotometer.

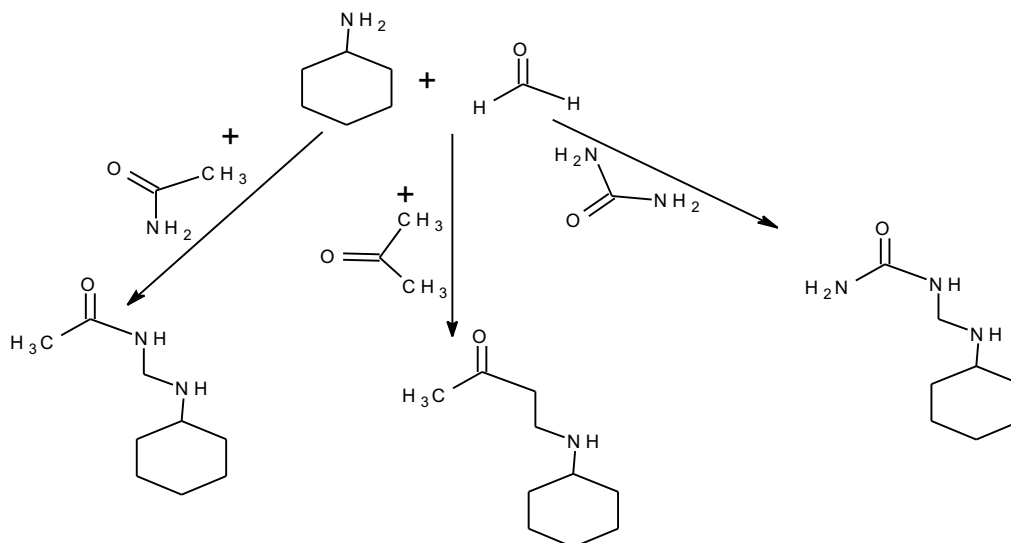
Methods

The synthesis of cyclohexylamine-N-methyl base Mannich ligands and their Cu(II), Ni(II) and Co(II) complexes were carried out in two stages. The first stage is the synthesis of the Mannich bases while the second stage involves the synthesis of Cu(II), Ni(II) and Co(II) complexes.

Synthesis of Mannich Base Ligands - CHMU, CHMA, CHMAA (Scheme 1):

Three Mannich bases were prepared by the reaction of cyclohexylamine, formaldehyde and urea; cyclohexylamine, formaldehyde and acetone; cyclohexylamine, formaldehyde and acetamide at 25°C as described by Thiraviyam *et al.*, 2013.

Equimolar quantities of cyclohexylamine (23.16 cm³, 0.20 moles), formaldehyde (24.56 cm³, 0.20moles) and urea (12.01 g, 0.20moles); acetamide (11.82 g, 0.20 moles); acetone (14.88 g, 0.20 moles) were mixed in water and stirred vigorously for about three hours. The product precipitated out as a white solid, which was filtered and washed with ethanol. The compound was then recrystallized in ethanol and dried at 50°C in the oven. (Yields were 25.33 g, 74%, 23.7 g, 70%), 19.43 g, 57%) for CHMU, CHMAA and CHMA respectively).



Scheme 1

Preparation of the Metal(II) Complexes

The metal(II) ligand complexes were all prepared in the ratio 1:2, Metal : ligand. Thus the general complexation reaction is:



Where M is the metal and L is a Mannich base ligand.

Cu(II)cyclohexylamine-N-methylurea Cu(CHMU)₂.

A methanolic solution of the Mannich base ligand CHMU (17.12 g, 0.10 moles), was added to a hot ethanolic solution of Cu(II) chloride dihydrate (8.52 g, 0.05 moles) in the ratio of 2:1, taken in a 200 ml beaker with constant stirring. The content was heated on a water bath for 1hr. The green solid product formed was filtered, washed with ethanol and dried in the oven at 50°C. (Yield 6.10 g, 30%). All other metal (II) complexes were prepared following the same procedure as above.

Characterization of the metal(II) Complexes

The synthesized ligands and complexes were characterized by solubility test, melting/decomposition temperature, Infra-red and UV-visible spectroscopy. The solubility tests of the compounds were carried out in ethanol, methanol, chloroform, N,N-dimethylformamide.

Percentage Metal Analysis of the Complexes

The percentage metal composition of the metal(II)-Cyclohexylamine-N-methylurea (CHMU) complexes were determined by

complexometric titrations using EDTA after digestion of the metal complexes with 1:1 nitric acid/perchloric acid. The result showed a 1:2 (metal:ligand) ratio. The results are shown in Table 5.

Preparation and Standardization of Reagents

i. 0.005 M EDTA Solution

1.8612 g of disodium ethylenediaminetetraacetic acid was weighed, dissolved with distilled water, transferred a 1L standard flask and made up to mark with distilled water.

ii. 0.005 M Zinc(II)sulphate Heptahydrate Solution

0.1437 g of ZnSO₄.7H₂O was weighed, dissolved with distilled water and transferred into a 1L standard flask and made up to mark with distilled water.

iii. Ammonia/Ammonium Chloride Buffer (pH 10)

17.8 g of ammonium chloride salt was weighed and transferred into a 250 mL standard flask, 142 mL of ammonia solution was added and shaken. The solution was made up to mark with distilled water.

iv. Murexide Indicator

25g of analar sodium chloride and 0.1 g murexide dye were mixed together thoroughly and kept in a bottle container.

v. 0.5% Eriochrome Black T

0.5% Eriochrome Black T in Ethanol which was prepared from Eriochrome Black T, (EBT) and hydroxylamine hydrochloride.

vi. Standardization of the EDTA Solution

The EDTA solution was standardized with the $ZnSO_4 \cdot 7H_2O$ solution.

RESULTS AND DISCUSSION

Yield and Physical Properties

Table 1 shows the yields and physical properties of the Mannich base ligands and their complexes respectively. The synthesized Mannich bases: CHMU, CHMAA and CHMA are all white solids. The metal complexes of the ligands gave different shades of green. The Co(II)-complexes of CHMU, CHMAA and CHMA prepared were blue, olive green and dark green respectively. The Cu(II)-complexes were green coloured while Ni(II) complexes were all dark green. Blue or green colours are usually characteristic of Copper(II) and nickel(II) complexes.

The percentage yields obtained for the ligands, CHMU, CHMAA and CHMA were between 57-74%. The percentage yield for Co(II) complexes of CHMU, CHMAA and CHMA were between 27-39%, those of Cu(II) complexes were between

30-36% while Ni(II) complexes gave yields ranging from 12-51%. The low yields may not be unconnected with the solvent used for the preparations.

The values for the melting points range from 73-74 $^{\circ}C$, 71-72 $^{\circ}C$ and 78-79 $^{\circ}C$ for CHMU, CHMAA and CHMA respectively, (Table 1). All the metal complexes decomposed without melting at temperatures above 300 $^{\circ}C$. This is similar to other metalorganic complexes as reported by Andoseh *et al*, 1982. This implies that the metal complexes are very stable. Both the ligands and their metal complexes were also observed to be air stable.

Solubility

All the ligands dissolved in methanol and N,N-dimethylformamide but were sparingly soluble in ethanol. The nickel(II) complexes and the Co(II)CHMA were insoluble in all of the solvents used. All the copper(II) complexes were sparingly soluble in ethanol but insoluble in methanol and DMF. The details of the solubility tests are presented in Table 2.

Table 1: Yields and Physical Properties of CHMU, CHMA, CHMAA and their Metal Complexes.

| LIGAND/ METAL COMPLEX | YIELD (%) | COLOUR | MELTING/DECOMPOSITION POINT ($^{\circ}C$). |
|--------------------------|-----------|-------------|--|
| CHMU | 74 | White | 73-74 |
| CHMAA | 70 | White | 71-72 |
| CHMA | 57 | White | 78-79 |
| Cu(CHMU) ₂ | 30 | Green | >300 |
| Cu(CHMAA) ₂ | 36 | Green | >300 |
| Cu(CHMA) ₂ | 32 | Green | >300 |
| Co(CHMU) ₂ | 27 | Blue | >300 |
| Co(CHMAA) ₂ | 39 | Olive green | >300 |
| Co(CHMA) ₂ | 29 | Dark green | >300 |
| Ni(CHMU) ₂ | 51 | Dark green | >300 |
| Ni(CHMAA) ₂ | 45 | Dark green | >300 |
| Ni(CHMA) ₂ | 12 | Dark green | >300 |

Table 2: Solubilities of CHMU, CHMA, CHMAA and their Metal Complexes.

| SOLVENT | | | |
|--------------------------------|-------------------|-----------------|------------|
| LIGANDS/METAL COMPLEXES | ETHANOL | METHANOL | DMF |
| CHMU | Sparingly soluble | Soluble | Soluble |
| CHMAA | Sparingly soluble | Soluble | Soluble |
| CHMA | Sparingly soluble | Soluble | Soluble |
| Cu(CHMU) ₂ | Sparingly soluble | Insoluble | Insoluble |
| Cu(CHMAA) ₂ | Sparingly soluble | Insoluble | Insoluble |
| Cu(CHMA) ₂ | Sparingly soluble | Insoluble | Insoluble |
| Co(CHMU) ₂ | Sparingly soluble | Insoluble | Insoluble |
| Co(CHMAA) ₂ | Sparingly soluble | Insoluble | Insoluble |
| Co(CHMA) ₂ | Insoluble | Insoluble | Insoluble |
| Ni(CHMU) ₂ | Insoluble | Insoluble | Insoluble |
| Ni(CHMAA) ₂ | Insoluble | Insoluble | Insoluble |
| Ni(CHMA) ₂ | Insoluble | Insoluble | Insoluble |

Infra-Red Spectra

The major characteristic bands in the infra-red spectra of the Mannich base ligands and their metal complexes are listed in Table 3. The IR spectra of the ligands, Cyclohexylamine-N-methylurea (CHMU), Cyclohexylamine-N-methylacetamide (CHMAA) and Cyclohexylamine-N-methylacetone (CHMA), Appendices 1-3 respectively, show strong peaks in the region of 3450-3300 cm⁻¹ assigned to the stretching vibration of the secondary amine. The two sharp peaks at 2926cm⁻¹, 2358cm⁻¹ for CHMU, 2926cm⁻¹, 2358cm⁻¹ for CHMAA and 2926 cm⁻¹, 2357cm⁻¹ for CHMAA corresponding to C-H asymmetric and C-H symmetric stretching vibrations respectively while the peaks at 1680 cm⁻¹ to 1630 cm⁻¹ are assigned to amide C=O stretching vibration (Pavis *et al.*, 2001). The band in the region of 1105-1103 cm⁻¹ can be attributed to cyclohexane ring vibrations. These are consistent with values obtained in the literature, (Thiraviyam *et.al*, 2013).

The IR spectra of the complexes, (Appendices 3-6), when compared with those of the free ligands, Appendices 1-2 showed that there are shifts in the positions of the ν N-H band to lower bands in all the complexes, except for that of Cobalt - (CHMAA) complex, (Appendix 5) which shifted to higher frequency. These shifts in the ν N-H band

positions in the Ni(II) and Cu(II) complexes indicate that the nitrogen atom of the secondary amide is coordinated to the metal ion.

The position of amide ν C=O of Co(II) complexes and Ni(II) complexes of the ligands shifted appreciably from 1644-1636cm⁻¹ in the ligands to 1628-1619cm⁻¹ in the metal(II) complexes. The shifts indicate the bonding of the oxygen atom of the amide functional group in bonding to the central metal ion. The coordination of either the nitrogen atom or the oxygen atom or both is further supported by the appearance of new bands between 454 - 534cm⁻¹ and 600-645cm⁻¹ due to M-N and M-O bond stretching vibration respectively. The ν (M-O) band usually occurs at a higher frequency region and is usually sharper and stronger than ν (M-N) (Agawai *et al.*, 2006; Buyukkidan and Ozer, 2013).

The Co(II) complexes of CHMU and CHMAA, (Appendices 4-5) show bands at 529cm⁻¹ and 629cm⁻¹, 534cm⁻¹ and 645cm⁻¹, respectively, which are attributed to ν (M-N) and ν (M-O) stretching vibrations of the coordinated O and N atoms of the ligands, (Buyukkidan and Ozer, 2013). Cu(II) complexes of CHMU, (Appendix 3) shows bands at 445cm⁻¹, attributable to ν (M-N). Ni(II) complexes show bands at 637cm⁻¹, 641cm⁻¹ and 641cm⁻¹ attributable to ν (M-O), Appendix 6.

Table 3: Relevant bands (cm⁻¹) in the Infrared Spectra of the ligands and the metal complexes

| LIGANDS/ COMPLEXES | ASSIGNMENTS | | | | | | |
|------------------------|-------------|----------------------|---------------------|-------------|-------------|-------------|-------------|
| | ν_{N-H} | $\nu_{C-H_{(asym)}}$ | $\nu_{C-H_{(sym)}}$ | ν_{C-O} | ν_{C-C} | ν_{M-O} | ν_{M-H} |
| CHMU | 3440 | 2926 | 2358 | 1639 | 1103 | - | - |
| CHMAA | 3433 | 2926 | 2358 | 1636 | 1104 | - | - |
| CHMA | 3452 | 2926 | 2357 | 1644 | 1105 | - | - |
| Cu(CHMU) ₂ | 3434 | 2933 | 2359 | 1639 | 918 | - | 455 |
| Cu(CHMAA) ₂ | 3434 | 2936 | 2359 | 1634 | 918 | - | 457 |
| Cu(CHMA) ₂ | 3434 | 2936 | 2359 | 1640 | 920 | - | 459 |
| Co(CHMU) ₂ | 3433 | 2923 | 2359 | 1626 | 1003 | 629 | 529 |
| Co(CHMAA) ₂ | 3460 | 2929 | 2353 | 1628 | 1004 | 645 | 534 |
| Co(CHMA) ₂ | 3435 | 2927 | 2358 | 1619 | 1037 | 632 | 534 |
| Ni(CHMU) ₂ | 3430 | 2931 | 2358 | 1624 | 1180 | 637 | - |
| Ni(CHMAA) ₂ | 3431 | 2932 | 2359 | 1624 | 1183 | 641 | - |
| Ni(CHMA) ₂ | 3437 | 2931 | 2353 | 1631 | 1083 | 641 | - |

UV-Visible Spectroscopy

Table 4 shows data from the UV-Visible spectra of some of the metal complexes recorded in ethanol solution. The electronic spectra of the complexes are presented as Appendices 7-11. The electronic spectral bands observed from 216 nm to 259 nm result from $\pi \rightarrow \pi^*$ transitions and 300 nm to 331 nm assigned to $n \rightarrow \pi^*$.

The Co(II)-CHMU complex, (Figure 10) gave peaks at 515 nm and 657 nm. These are most likely due to the transitions, ${}^4T_1(P) \leftarrow {}^4A_2(F)$ and ${}^4T_2(G) \leftarrow {}^4T_1(G)$. The blue colour of the Co(CHMU)₂ and the transition, ${}^4T_1(P) \leftarrow {}^4A_2(F)$ at 515 nm in the complex is typical of cobalt(II) complex absorption in a tetrahedral environment, (Anderson, *et al*).

The Ni(II) complex, (Figure 9) gave bands at

659 nm and 735 nm. These are attributable to ${}^3T_1(F) \leftarrow {}^3A_2(F)$ and ${}^3T_1(P) \leftarrow {}^3A_2(F)$ transitions and they indicate octahedral geometry, (Anderson, *et al*).

Percentage Composition of metals in the complexes

The percentage metal composition of the metal(II)-Cyclohexylamine-N-methylurea (CHMU) complexes were determined by complexometric titration using EDTA after digestion of the metal complexes and titration with standardized disodium salt of ethylenediaminetetraacetic acid. The amount of metal in metal complexes of the ligands showed a good correlation between the experimental and theoretical values. The result showed a 1:2 (metal:ligand) ratio. The result is shown in Table 5.

Table 4: UV-Visible Spectra data of some of the Metal Complexes

| Metal Complexes | Intra-Ligand Transitions (nm) | | Ligand Field Transition (nm) | |
|------------------------|-------------------------------|---------------|------------------------------|---|
| Cu(CHMU) ₂ | 232 | $\pi - \pi^*$ | 520 | CT |
| | 316 | $n - \pi^*$ | 662 | ${}^2E_g - {}^2T_{2g}$ |
| | | | 781 | |
| Ni(CHMU) ₂ | 227 | $\pi - \pi^*$ | 401 | CT |
| | 318 | $n - \pi^*$ | 659 | |
| | | | 735 | ${}^3A_{2g}(F) \quad {}^3T_{1g}(F)$ |
| Co(CHMU) ₂ | 300 | $\pi - \pi^*$ | 515 | ${}^4A_2(F) \quad {}^4T_1(P)$ |
| | | | 657 | ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, |
| Cu(CHMAA) ₂ | 216, 259 | $\pi - \pi^*$ | 670 | ${}^2E_g - {}^2T_{2g}$ |
| | 330 | $n - \pi^*$ | | |
| Ni(CHMAA) ₂ | 242 | $\pi - \pi^*$ | 731 | ${}^3A_{2g}(F) \quad {}^3T_{1g}(F)$ |
| | 331 | $n - \pi^*$ | | |

Table 5: Percentage composition of metal in the metal(II)-Cyclohexylamine-N-Methylurea complexes, the stoichiometry and the probable Formulae

| Compounds | % Metal Found (Cal) | Stoichiometry, (M:L) | Probable Formula |
|--|---------------------|----------------------|-----------------------|
| Copper(II)-Cyclohexylamine-N-methylurea | 20.69 (20.79) | 1:2 | Cu(CHMU) ₂ |
| Nickel(II)-Cyclohexylamine-N-methylurea. | 19.37 (19.55) | 1:2 | Ni(CHMU) ₂ |
| Cobalt(II)-Cyclohexylamine-N-methylurea | 19.45 (19.58) | 1:2 | Co(CHMU) ₂ |

PROPOSED STRUCTURES FOR THE METAL(II) COMPLEXES OF CHMAA, CHMU AND CHMA

From the Infra-red, UV-Visible spectroscopic data and Percentage metal composition, the following structures can be proposed for the metal(II) complexes of the cyclohexylamine –N-methyl ligands.

The ligands coordinate with the metal ions in different ways; the coordinating atoms however vary with the metal ion. With CHMAA and CHMU, copper(II) ion coordinates through the

two nitrogen atoms to form four –membered rings while nickel(II) ion coordinates through the oxygen atom and one of the nitrogen atoms to form six – membered rings. Cobalt(II) ion coordinates through both oxygen and the nitrogen atoms to four –membered rings, Figures 1-4. The blue colour of the Co(CHMU)₂ and the transition, ${}^4A_2(F) \rightarrow {}^4T_1(P)$ at 515nm in the complex is typical of cobalt(II) complex absorption in a tetrahedral environment.

The non-interaction of copper (II) ion with the oxygen atom is confirmed by the fact that the infra-red spectral band for $\nu_{C=O}$ for the

copper(II) complexes are unaffected.

With CHMA, copper(II) ion coordinates through the two nitrogen atoms, nickel(II) ion and

cobalt(II) ion coordinate through the oxygen atom and one of the nitrogen atoms, They all form six – membered rings, Figures 5-6.

METAL: CHMAA COMPLEXES

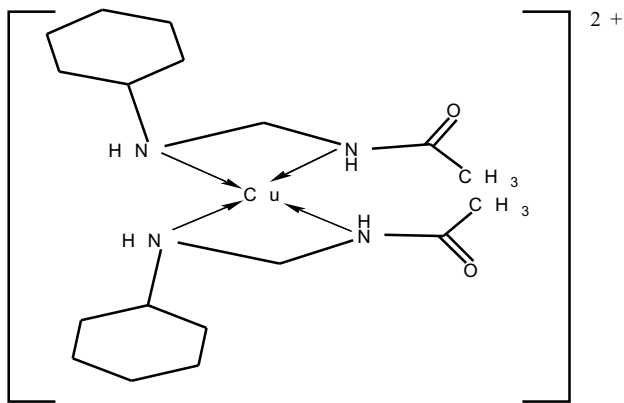


Figure 1: Copper(II) - CHMAA

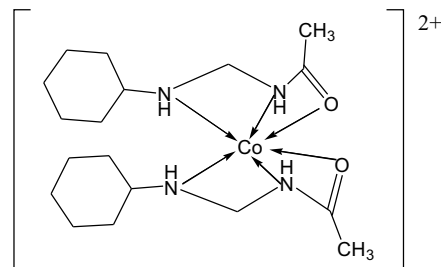


Figure 2: Cobalt(II) - CHMAA

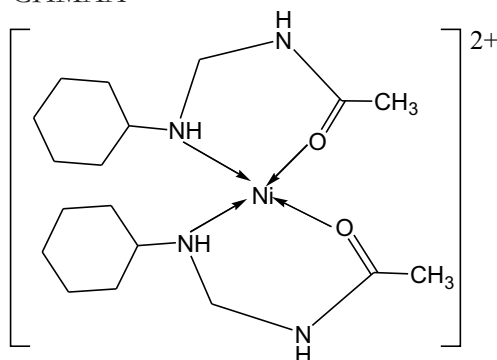


Figure 3: Nickel(II) - CHMAA

METAL: CHMU COMPLEXES

Copper(II) ion forms four-membered ring structures with CHMU, Fig.4.

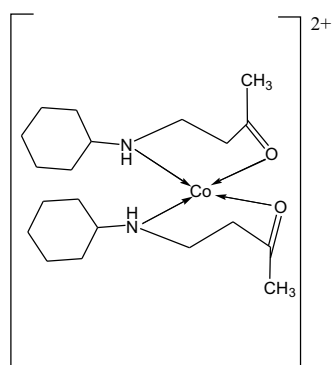


Figure 5: Cobalt(II) - CHMA

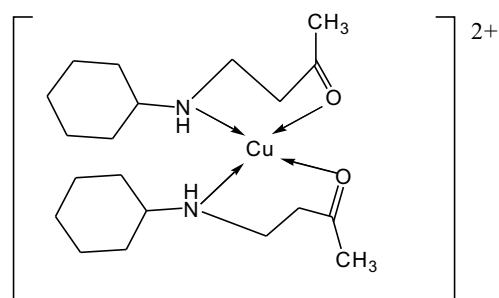


Figure 6: Copper(II) - CHMA

CONCLUSION

The synthesis of the Mannich ligands namely cyclohexamine-N-methylurea (CHMU), cyclohexylamine-N-methylacetamide (CHMAA), cyclohexylamine-N-methylurea (CHMA) and their Co(II), Ni(II) and Cu(II) complexes were successfully achieved. They were characterized by Infra-red and UV-Visible spectroscopic analysis and percentage metal composition.

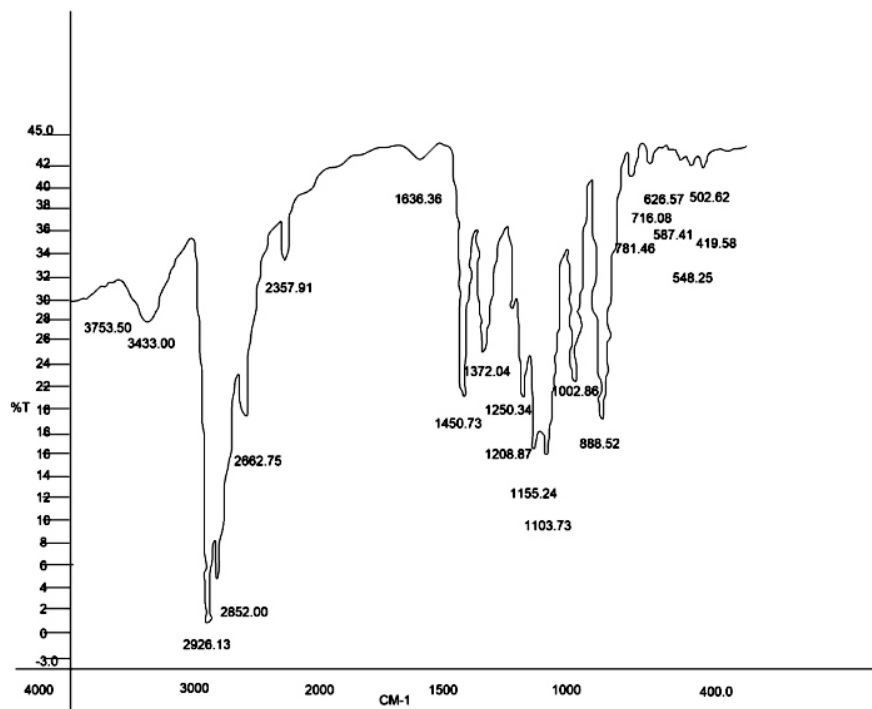
All the compounds synthesized were air stable. The decomposition of the metal complexes at very high temperature without melting is an indication of the ability of the ligands to form very stable complexes.

The coordinating atoms of the cyclohexylamine-N-methyl ligands vary with the metal ion to give different geometries. Copper(II) ion coordinates through the two nitrogen atoms in CHMAA and CHMU, to form four-membered rings while nickel(II) ion coordinates through the oxygen atom and one of the nitrogen atoms to form six-membered rings. Cobalt(II) ion coordinates through both oxygen and the nitrogen atoms to form four-membered rings. They all form six-membered rings with CHMA.

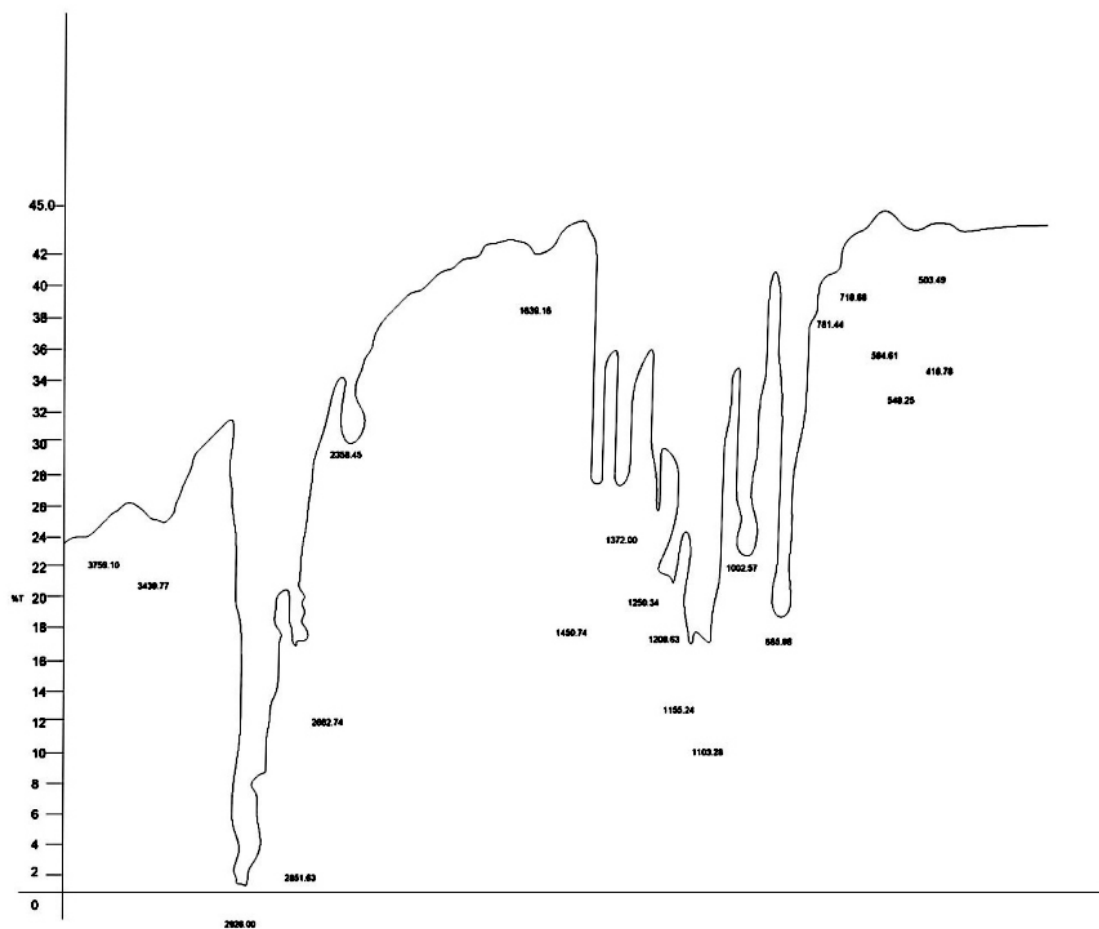
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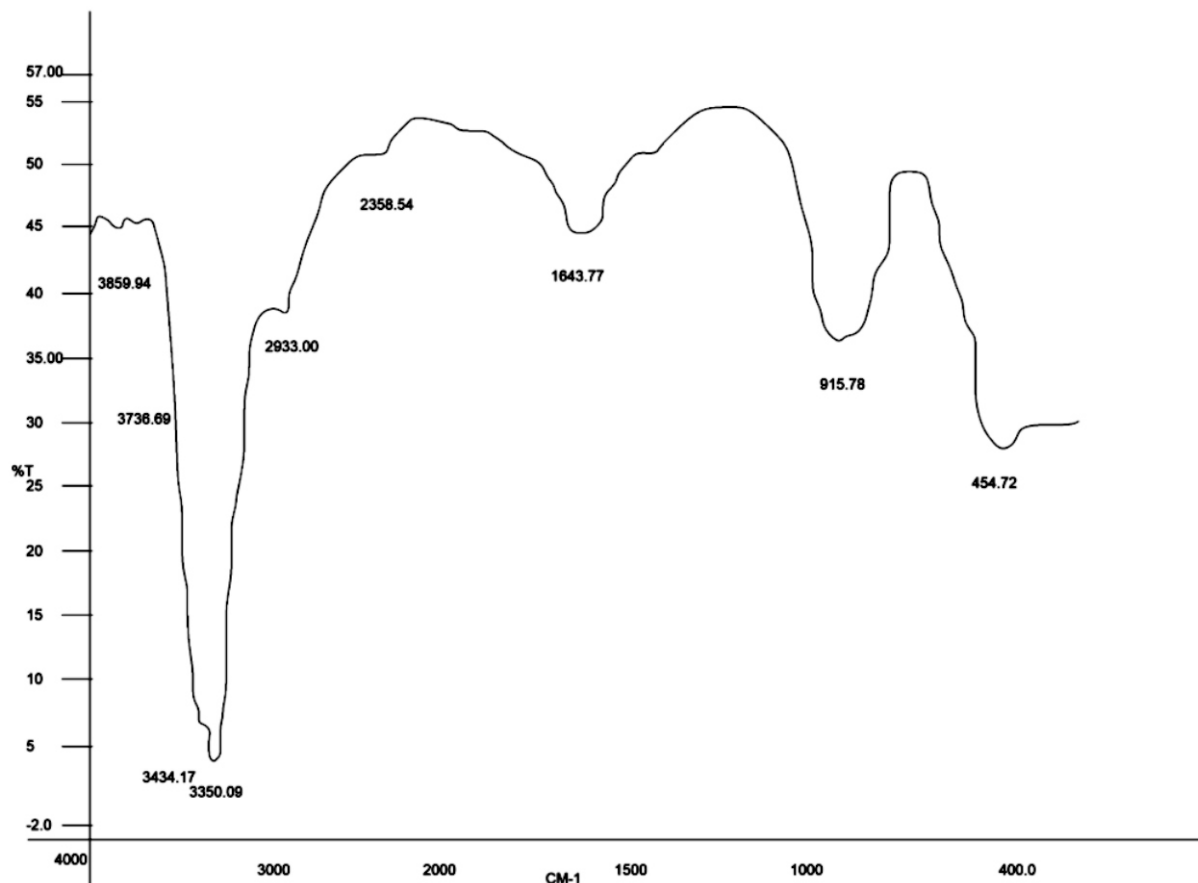
APPENDICES



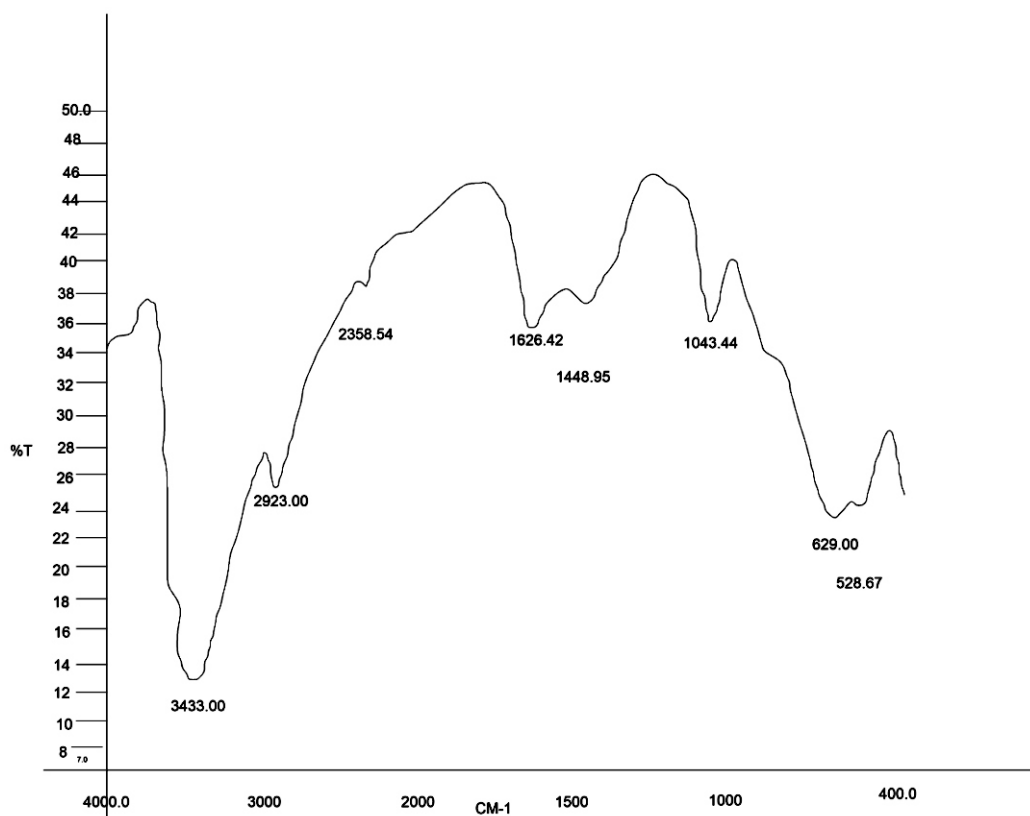
Appendix 1: Infrared spectrum of CHMAA



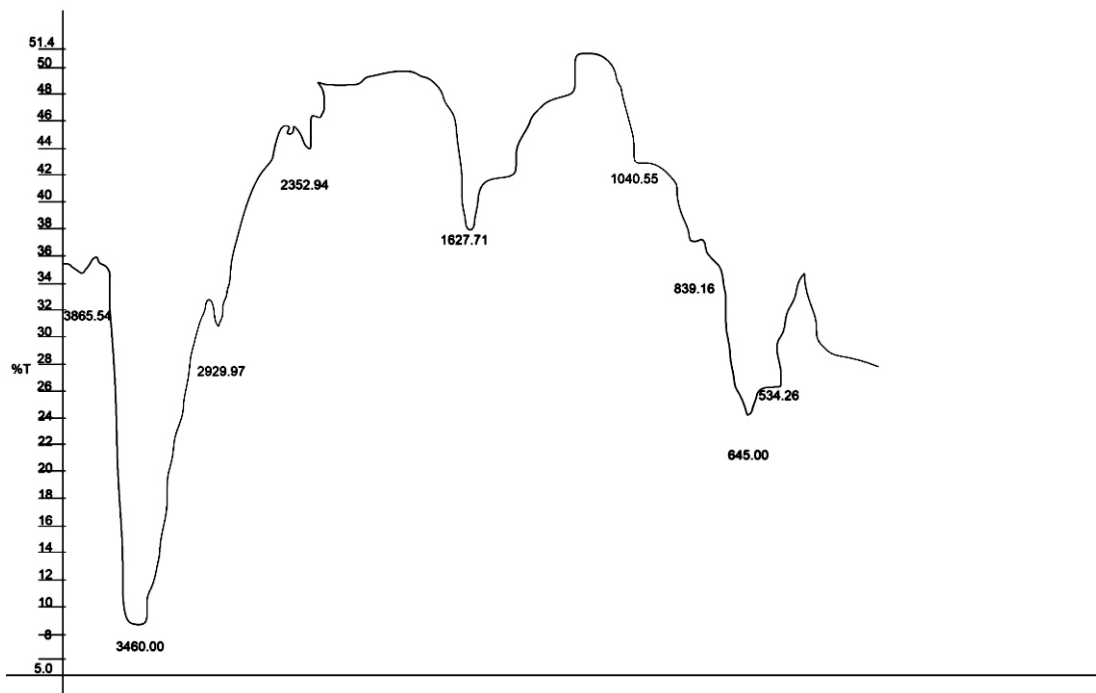
Appendix 2: Infrared spectrum of CHMU



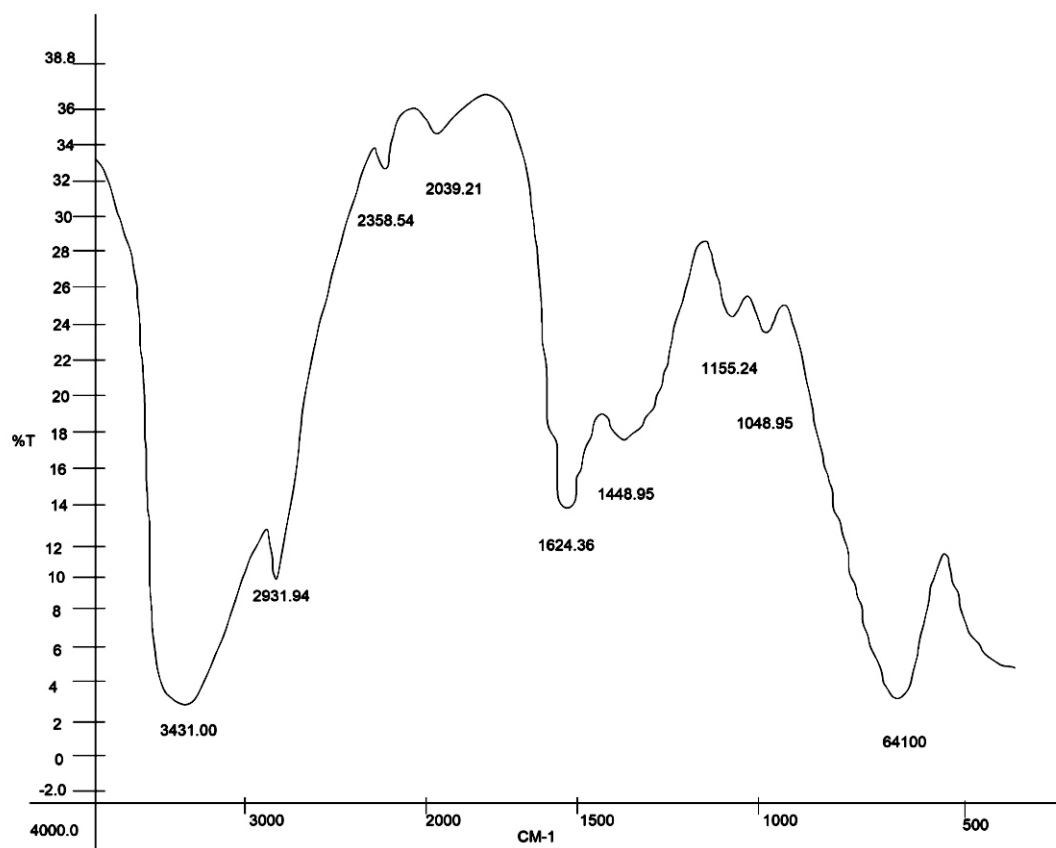
Appendix 3: Infrared spectrum of Copper (II) CHMU



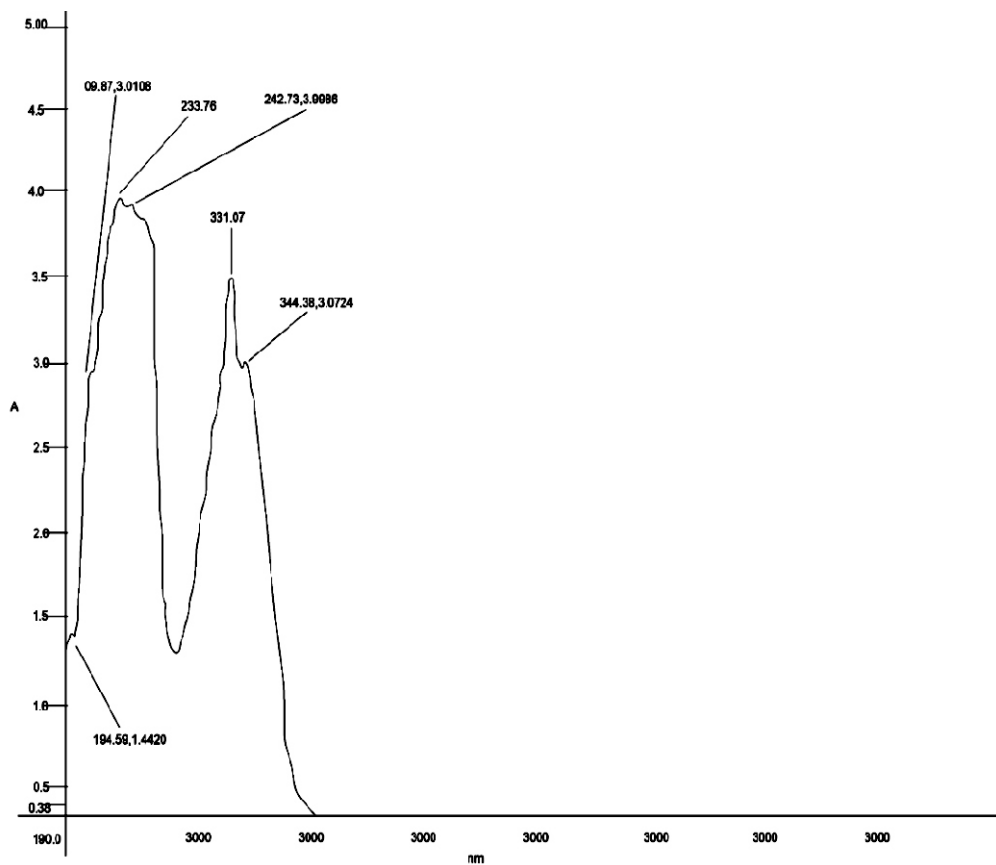
Appendix 4: Infrared spectrum of Cobalt (II) CHMU



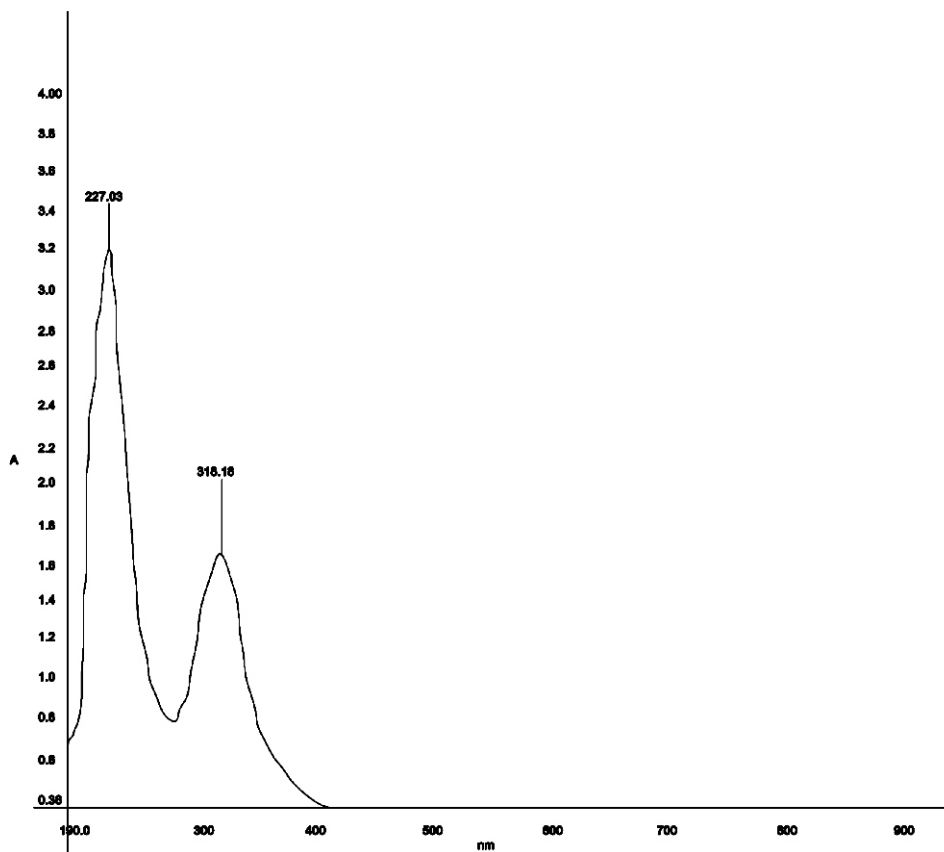
Appendix 5: Infrared spectrum of Cobalt (II) CHMAA



Appendix 6: Infrared spectrum of Nickel (II) CHMAA

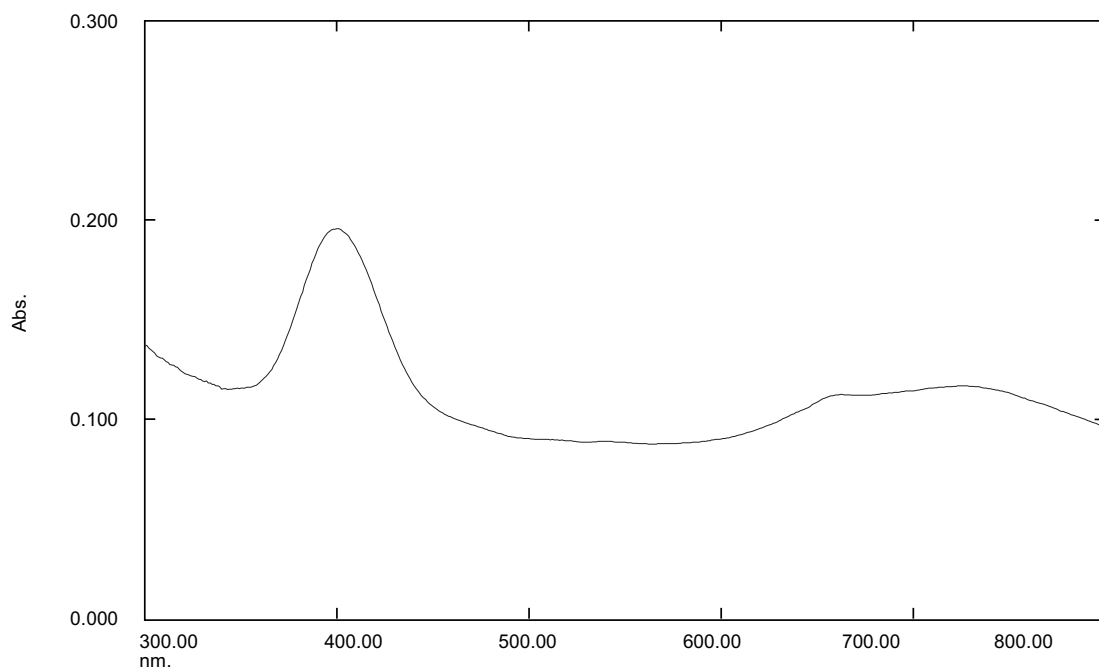


Appendix 7: UV-spectrum of Nickel (II) CHMAA



Appendix 8: UV spectrum of Nickel (II) CHMU

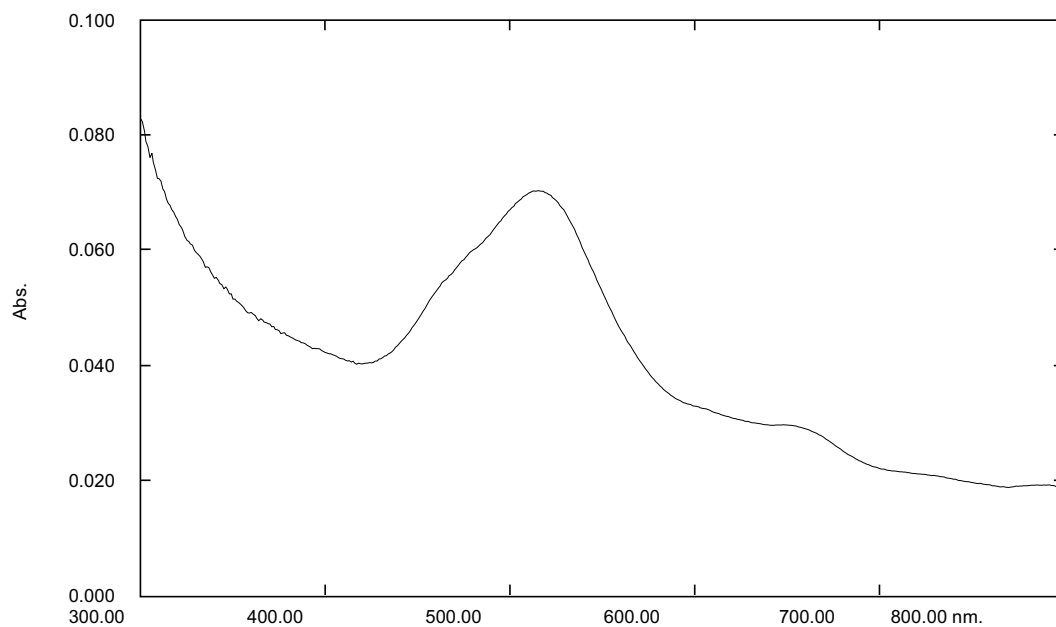
Ni -CHMU



| No. | Wavelength | Absorbance | Description |
|-----|------------|------------|-------------|
| 1 | 735.00 | 0.116 | |
| 2 | 659.00 | 0.112 | |
| 3 | 401.00 | 0.196 | |
| 4 | | | |

Appendix 9: UV-Visiblespectrum of Nickel(II)-CHMU

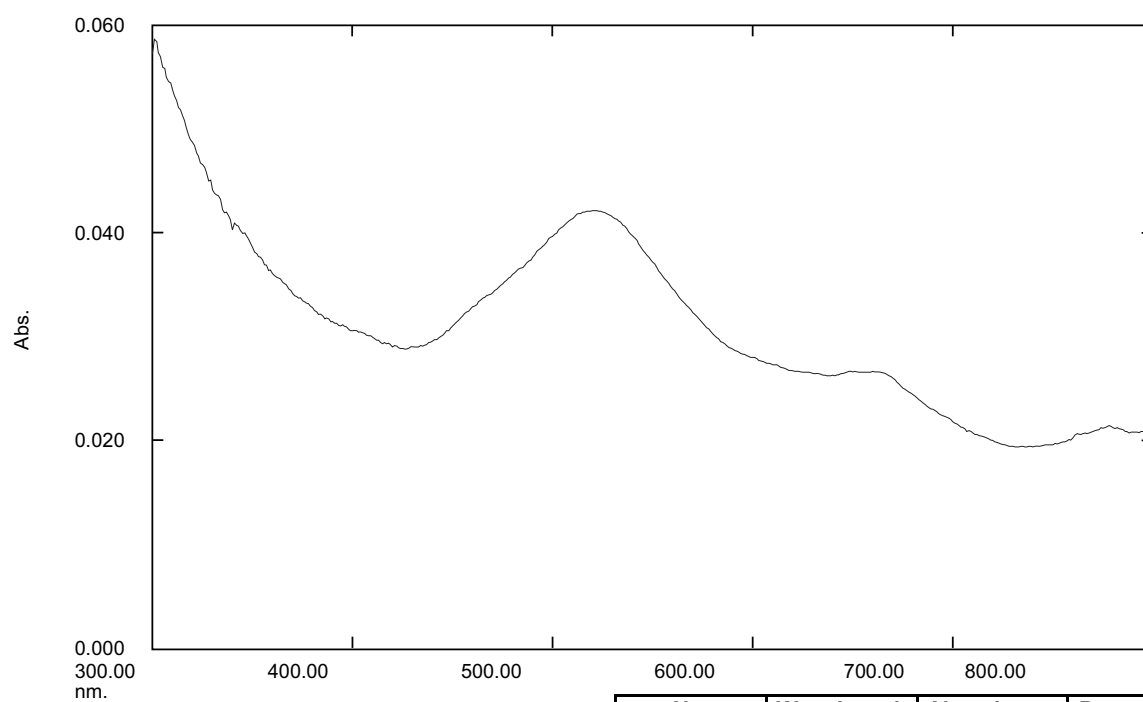
Co-CHMU



| No. | Wavelength | Absorbance | Description |
|-----|------------|------------|-------------|
| 1 | 657.00 | 0.029 | |
| 2 | 515.00 | 0.070 | |
| 3 | | | |

Appendix 10: UV-Visiblespectrum of Cobalt(II)-CHMU

Cu -CHMU



| No. | Wavelength | Absorbance | Description |
|-----|------------|------------|-------------|
| 1 | 781.00 | 0.021 | |
| 2 | 662.00 | 0.027 | |
| 3 | 520.00 | 0.042 | |
| 4 | | | |

Appendix 11: UV-Visible spectrum of Copper(II)-CHMU.