ATTEMPT TOWARDS THE SYNTHESIS AND CHARACTERIZATION OF SOME MIXED LIGANDS COMPLEXES OF Ni, Cu, AND Cd WITH BIPYRIDINE, PHENANTHROLINE, MALONAMIDE AND UREA

A Thesis
Presented to the
School of Graduate Studies
Addis Ababa University

In Partial Fulfillment of the
Requirement for the Degree of
Master of Science in Chemistry

by

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September, 1985

TO THE MEMORY OF MY PARENTS

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ABBREVIATIONS

Phen	1,10-Phenanthroline
Bipy	2,2-Bipyridine
MA	Malonamide
DMSO	Dimethylsulfoxide
Vis	Visible Spectrum
IR	Infrared Spectrum
NMR	Nuclear Magnetic Resonance
HMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital

ACKNOWLEDGMENTS

I am very much indebted to my advisor Dr. Negussie Retta for his patience, generous advice and devoted assistance. I am also indebted to Dr. Berhanu Abegaz for supplying me with some chemicals and to W/t Yordanos Woldu for taking all NMR spectra.

I would also like to express my thanks to Ato Adinew Geletu, Ato Abdu De Tango and Ato Wedaje Emiru. My thanks also go to my colleagues Ato Aberra Furra, Ato Bizuneh Workie, Ato Zeroum Seyoum, and Ato Alemachew Zewdie. I also like to express my thanks to W/t Ayni Omar and Ato Yilma Tamiru for typing this paper, and to my friend Ato Girmy Yihdago who helped me with all photocopy works. It also gives me pleasure to thank all my teachers in the Chemistry Department.

Last but not least, I am very much indebted to my brother Architect Abdella Kekia who helped me in more than a way to attain this goal.

ABSTRACT

Visible spectra for solutions of Ni:bipy, Ni:bipy:urea, Ni:bipy:MA, Ni:phen:, Ni;phen:urea, Ni:phen:MA, Cu:bipy, Cu:bipy:urea and Cu:bipy:MA were recorded. For the Ni complexes the λ_{max} did not shift with increase in pH but the intensity decreased. For the copper complexes increase in pH shifted the λ_{max} to shorter wave length in the basic medium.

The synthesis was carried out in acidic medium. The complex formed between Ni and bipy in the molar ratio 1:1 could not be isolated, but when the concentration of bipy increased two times pink colored crystals of the formula $Ni(bipy)_3Cl_2.6H_2O$ were isolated. An attempt to synthesise a nickel mixed ligand complex with bipy:urea and bipy:malonamide was done, but in both cases $Ni(bipy)_3Cl_2.6H_2O$ was isolated.

The binary complex $Ni(phen)Cl_2.6H_2O$ was synthesised by the reaction of phen and $NiCl_2.6H_2O$. The synthesis of the mixed ligand complex with phen:urea and phen:malonamide was then tried but in both cases $Ni(phen)Cl_2.6H_2O$ was the product.

When $CuCl_2.2H_2O$ and bipy reacted in the molar ratio 1:1 at pH 4.5 $Cu(bipy)Cl_2$ was isolated but when the pH was adjusted to 7.0 a complex with a probale

formula $Cu(bipy)(OH)Cl.3H_2O$ was isolated.

An attempt was made to synthesise the mixed ligand complex of copper with bipy:urea and bipy:malonamide. In both cases $Cu(bipy)Cl_2$ was formed.

The binary complexes of urea and malonamide with copper were synthesised to give $Cu(urea)Cl_2.H_2O$ and $Cu(MA)_2Cl_2.2H_2O$.

Phenanthroline reacted with $CuCl_2.2H_2O$ in aqueous medium at pH 3.8 to form $Cu(phen)Cl_2$.

Cadmium chloride gave white crystals with both bipyridine and phenthroline. The complexes were obtained as precipitates when the cadmium was added to the ligand solution without heating. These complexes were insoluble in water and other common solvents. Similar results were obtained also in the presence of urea and malonamide.

In methanol:ethanol solvent system the binary complexes $Ni(MA)_2Cl_2$ and $Cu(MA)Cl_2.H_2O$ were synthesised by refluxing the stiochiometric quantities for eight hours. $Cd(MA)Cl_2.H_2O$ was also synthesised in the same manner. The reaction of copper chloride with urea gave a complex of the formula $Cu(urea)_4Cl_2$. From cadmium chloride and urea the complex $Cd(urea)Cl_2.H_2O$ was isolated.

In an attempt to synthesise complexes of Ni:bipy:MA and Ni:phen:MA, Ni(MA)Cl_2 was reacted with both bases separatly and it was found that both bases substitute the malonamide. When Cu(MA)$Cl_2 \cdot H_2O$ reacted with bipyridine a complex of the formula Cu(bipy)$_2Cl_2 \cdot H_2O$ was isolated.

1. INTRODUCTION

Coordination chemistry is the chemistry of adducts formed by metals in their higher oxidation state bonded to inorganic or organic ions, or molecules. The ligands bonded to the metal ion are predominantly sigma donors with moderate to weak acceptor or donor tendencies.

A coordinate bond can be formed between any atom or ion which can accept a share in a pair of electrons, and any atom, ion or molecule which can furnish a pair of electrons. The donor may be a netural molecule like H_2O, NH_3, bipy, or an ion like CO_3^{--}, or $H_2NCH_2COO^-$. Ordinarily an acceptor requires several donors which may be alike or different. The resulting complex may be positive ion, a negative ion or a neutral molecule. Therefore, complex formation is not restricted to association between two ions of opposite charges. A complex can therefore be defined as a species formed by the association of two or more simpler species each capable of independent existence.

In general, the small highly charged cations form the most stable coordinate bonds, and it is often mistakenly supposed that the ability to form complexes is limited to the transition metals. Transition metal ions are, however, associated with such interesting properties as small cation size, comparatively large nuclear charge and the availability of a sufficient number of low energy orbitals for bonding purpose.[1]

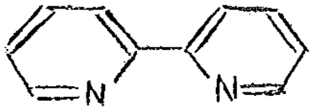
Nearly all of the complexes of the light metals such as metals of IA, IIA, IIIB and IVB contain oxygen as the donor atom (H_2O, OH^-, R-OH, R-O-R^1, $RCOR^1$)[2]. These light metals seldom coordinate with molecules containing N, S, C or halogens. Elements across the right (Cr, Mn, Fe, Co, Ni, Cu and Zn) easily coordinate to nitrogen.[2] For example chromium forms a large number of amines, most of which are slowly destroyed in water. Cobalt, nickel, copper and zinc form stable amines. These metals retain the ability to coordinate with oxygen in even greater degree than do the ions of the lighter metals, but the tendency to form links with nitrogen is still pronounced.[2]

All metalic ions apparently form hydrates in aqueous solutions frequently surrounding themselves with water molecules. This is accounted for by (i) the excess water is not chemically combined but is held in place by the demand of the lattice structure, (ii) the coordination number of the metal is abnormal, (iii) second and third coordination spheres are formed and (iv) part of the water molecules are combined with anions.

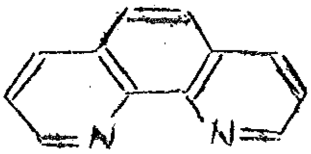
Hetero cyclic amines coordinate readily with transtion metal ions.[3] One such example is pyridine whose complexes are widely reported in the literature.

Chelation greatly enhances coordination and metals which do not ordinarily coordinate with nitrogen form stable compounds with 2,2'-bipyridine and 1,10-phenanthroline.

2,2'-bipyridine (1) and 1,10-phenanthnoline (II) function as typical bidentate chelate molecules through the nitrogen atoms with formation of five membered rings:



(I)



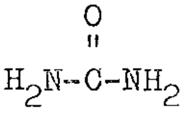
(II)

When crystalized from water, phenanthroline forms well defined monohydrates. The molecule of water is hydrogen bonded to the nitrogen atoms.[4] A hydrate of bipyridine has not been described, becuase the rings are coplanar but in the trans position. However, it is certain that in the metal complex the pyridine rings are in the cis position.[5]

Bipyridine and phenanthroline are both relatively weak bases. Yet they chelate with such a variety of metal ions and the resulting complexes are generally of such a high order of stability. The complexes of phenanthroline are more stable than those of bipyridine.[5]

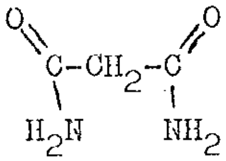
Even Be and Mg, which seldom coordinate with nitrogen compounds form complex ions containing three molecules of phenanthroline. The complexes of 1,10-phenanthroline are chiefly of interest because of their stereochemistry, their usefulness in analytical chemistry, and the ability of phenanthroline to stabilize unusual valency states of some of the metals.[6]

Urea (III) forms rather weak complexes in aqueous solution.[7] A urea molecule usually coordinates through the oxygen atom of the carbonyl group; however, in some instances the urea molecule do coordinate through the nitrogen atom.[8]



$H_2N-\overset{\overset{O}{\parallel}}{C}-NH_2$

(III)



(IV)

Malonamide (IV) has two amide groups each having two pairs of unshared electrons and coordinate readily with certain metals.[9]

Mixed ligand complexes are those in which more than one kind of ligand, other than the solvent molecules, are present in the inner-most coordination sphere of the complex and can be represented by the general formula $[MX_iY_jZ_k..]$[10].

The study of mixed ligand complexes has received considerable attention in recent years. The solution stabilities of mixed ligand systems have been determined by potentiometric, polarographic and spectrophotometric techniques.

Mixed ligand complexes have vital role in physiological systems. Formation of a mixed ligand complexe between an enzyme, metal ion and a substrate is considered to be the reason for the activation of certain enzymes with metal ions. To illustrate this, one can consider the function of carboxy peptidase A, which is an enzyme that helps to cleave the carboxyl terminal of amino acid from a peptide chain by hydrolysing the amide linkage[11].

$$\text{... Pro-Leu-Glu-Phen} \xrightarrow[\text{carboxypeptidase}]{H_2O} \text{...Pro-Leu-Glu} + \text{Phenylalanine}$$

The active site in the enzyme contains a zinc(II) ion. The metal is coordinated tetrahedrally to two nitrogen atoms and an oxygen atom from three amino acids in the protein chain. The fourth coordination site is free and so it can accept a pair of electrons from a donor atom in the substrate to be cleaved.

An enzyme system of particular importance is that which promotes the fixation of atmospheric nitrogen, a very important step in the nitrogen cycle, providing available nitrogen for plant nutrition. Nitrogenase is a molybdoenzyme which catalyses the reduction of molecular nitrogen to ammonia using photosynthesis products as reducing agents. Molybdenum is thought to provide the active site or sites which bind dinitrogen and where it is reduced to ammonia.[12]

Interest in mixed chelates also arise from the study of mechanism of organic reactions where the ligand bond is activated for selective reaction. Mixed complexes are also important as intermediates in ligand displacement reactions. Formation of stable complexes have also been widely exploited by analytical chemists in the development of many selective and highly sensitive analytical methods.

2. LITERATURE SURVEY

In recent years it have become increasingly apparent that several transition metal ions favour coordination with mixed ligand systems to a greater extent than would be expected on statistical basis. The equilibrium distribution of Cu(II) ions among a mixture of seventeen amino acids have been computed from stability constants and blood plasma composition data. At pH 7.4, 98% of the copper in the simulated plasma is coordinated to histidine and cystine predominantly as the mixed ligand [Cu.His.Cyst] and [Cu.H.His.Cyst][13]

2.1 Complexes of 2,2'Bipyridine and 1,10-Phenanthroline

Bipyridine and phenanthroline form binary and ternary mixed ligand complexes with a variety of transition metal ions. With the exception of the rare metals, numerous examples are known for each periodic group, including the alkali and alkaline earth elements. These complexes were known for a long time.[14] The reaction between iron(II) and bipyridine with formation of an intensly red colored substance was first observed by Blau[15-17] in 1888. The analogous phenanthroline complex was first synthesised by Balu[17], and was shown to form similarly colored salts of the same type.

Nickel coordinates with either of the base i.e.

bipyridine and phenanthroline. The tris complexes of nickel are bright pink. Salts of the $[Ni(bipy)^{++}]$ with a wide variety of anions are known.[14]

Copper(II) complex salts containing one, two or three molecules of either chelate have also been described.[12] Most are hydrated and of a blue or violet color. The complexes of cadmium and zinc are colorless. They are four or six covalent containing one, two or three molecules of the base.

The binary complexes of nickel, copper and cadmium with bipyridine and phenanthroline with a variety of anions were synthesised in the thirties and thereafter. Most of these complexes are hydrated, as complexes of bipyridine and phenanthroline with bivalent metals differ from similar amines in combining with a large quantity of water.

The synthesis of $[Ni(bipy)_3]Cl_2 \cdot 7H_2O$, $[Ni(bipy)(H_2O)]Cl_2$ and $[Cu(bipy)_3]Cl_2 \cdot 7H_2O$ was reported by Jaeger and Dijk[19] in 1935. The synthesis was done when 1,2 or 3 equivalent of the ligand was added to the solution of the salt and evaporated at room temperature.

$Ni(bipy)_2Cl_2$ and $Ni(phen)_2Cl_2$ were also reported in 1933.[18] $Ni(bipy)_2Cl_2$ was obtained by heating rose red $[Ni(bipy)_3]Cl \cdot 6H_2O$. $Ni(bipy)_2Cl_2$ is grass green and it is stable in air but cannot be recrystalized from water.

Controlled thermal decompositon of $Ni(bipy)_3Cl_2.7H_2O$ was studied by Lee, Griswold and Klienbergy.[20] The product of this were $Ni(bipy)_2Cl_2$; $Ni_3(bipy)_4Cl_6$, and $Ni(bipy)Cl_2$.

The diamagnetic white crystals of the tetrahedral complex $CdLCl_2$ (L = bipyridine, phenanthroline), were synthesised by refluxing the stoichiometric quantities of $CdCl_2$ and the ligand in methanol for half an hours.[21]

The synthesis of $Cd(bipy)_2.H_2O$ was also reported by Taeger and Dijk[22] in 1935. The complex $Cd(bipy)Cl_2$ and the analogous complexes with the anions acetates, sulfates and nitrates were also reported in 1936.[23]

The mono complex of 2,2'-bipyridine and 1,10-phenanthroline with the halide of Ni(II) were prepared in good yield by reaction of the base with an excess of the anhydrous metal halide in boiling dimethylformamide.[24] The mixed ligand complexes of bipyridine and phenanthroline with many transition metal atoms are reported in the literature. Most of the secondary ligands are nitrogen or oxygen donor ligands.[14]

Some of the secondary ligands that can be mentioned are the aminoacids. Mixed ligand complexes of the type $Cu(bipy)\ (glycinate)^+$, $Cu(bipy)glycine)^{++}$, $Cu(bipy)\ (alanine)^{++}$, NiAL (A = bipyridine, L = glycine, analine

The elemental analysis results were, found% (calculated%), Cu: 17.90 (1947), Cl: 10.6 (10.8), water loss:12.85 (16.55), Visible spectrum: λ_{max} = 625 nm. IR spectrum is given as Fig. 13 (a). 3400-3300 cm^{-1} (O-H str.), 1600 cm^{-1}, 1580 cm^{-1} (C=C str. and C=N str., 1450 cm^{-1} (C-H bend). It is insoluble in CH_2Cl_2, $CHCl_2$, CCl_4 and CH_3COCH_3, slightly soluble in CH_3OH but soluble in H_2O and DMSO.

4.2.4 Preparation of Dichloro monourea copper(II) monohydrate $Cu(urea)Cl_2.H_2O$.

1.70 g $CuCl_2.2H_2O$ (0.01 moles) and 6.006 g (0.01 moles) urea were dissolved in 100 ml distilled water and the pH of the solution was adjusted to 3.5. On heating the color of the solution changed from blue to green. The solution was slowly concentrated by evaporation and cooled. On cooling green crystals were isolated. The isolated compound was dried at 80°C for one hour. The yield was 0.87 g (41.42%). It does not melt but at about 175-180°C its color changes to black. The elemental analysis was: found% (calculated%) : Cu: 29.79 (29.88), N: 11,7 (13.17). It is slightly soluble in water but insoluble in organic solvents. Its IR spectrum is given as Fig. 13 (b).

4.2.5 Attempt to prepare copper: bipy: malonamide complex: 0.4261 g $CuCl_2.2H_2O$ (0.0025 moles) was dissolved in 30 ml distilled water. To this 0.39 g of bipyridine (0.0025 moles) dissolved in 5 ml ethanol and 25 ml water was added. The pH of the solution was adjusted to 2.0, and 0.25 g malonamide (0.0025 moles) dissolved in 30 ml water was added drop wise while heating and stirring. The solution was intense blue in color. The solution was concentrated giving green crystals. Yield was 0.24 g (33.15%), Melting point: at about 290°C the compound changes colour to dark green. Elemental analysis: found% (calculated%): Cu: 19.87 (21.85), Cl: 18.92 (24.42). Visible spectrum: λ_{max} = 670 nm. Its IR spectrum is given as Fig. 12 (c).

It is similar to spectrum of 4.2.1. Solubility: it is soluble in H_2O and DMSO. But insoluble in CH_2Cl_2, $CHCl_3$, CCl_4, and CH_3OH. The compound isolated was established to be $Cu(bipy)Cl_2$.

4.2.6 Preparation of Dichloro dimalonamide copper(II) 2-water: $Cu(MA)_2Cl_2.2H_2O$. A solution of 3.41 g $CuCl_22H_2O$ (0.02 moles) was added dropwise while heating to a solution of 2.041 g malonamide dissolved in 30 ml water. The color of solutions was green. After concentration and cooling, brown crystals were isolated.

yield was 0.80 g. (21.35%). The melting point is at 240°C the complex changes color to black. Elemental analysis were, found% (calculated%), Cu: 16.79 (16.90); Cl: 17.10 (18.9); N: 12.57 (14.9). Solubility: insoluble in CH_2Cl_3, CCl_4 and CH_3OH. Slightly soluble in water and DMSO. IR spectrum is given as Fig. 13 (c). 3400-3200 cm^{-1} (OH, N-H str.); 1620 cm^{-1} (C-O str.), 1450 cm^{-1} (C-N str.).

4.2.7 Preparation of Dichloro mono (1,10-phenthroline) copper(II) $[Cu(phen)Cl_2]$

0.39 g phen dissolved in 5 ml ethanol and 10 ml distilled water was added to 0.34 g $CuCl_2.2H_2O$ dissolved in 30 ml water. The pH was adjusted to 3.8. The solution was bright blue. After concentration and cooling it gave green crystals. Yield: 0.54 g (87.2%); Melting point: at about 300°C changes to dark green. Elemental analysis: found % (calculated): Cu: 20.13 (20.06); Cl: 12.92 (22.57); N: 7.93 (8.90). Visible spectrum λ_{max}: 710 nm. IR spectrum is given as Fig. 14 (a). 1600 cm^{-1} (C=N str.), 1510 cm^{-1} (C=C str.), 1425 cm^{-1} (C-H bend). Solubility: insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4, but soluble in H_2O and DMSO.

4.2.8 Attempt to prepare copper: phen: urea complex

0.34 g. $CuCl_2.2H_2O$ (0.002 moles) dissolved in 30 ml water was mixed with 0.24 g urea (0.004 moles) in 20 ml water. To this 0.39 g phen (0.002 moles) in 10 ml ethanol and 20 ml water was added drop wise while heating and stirring. Green crystals, were obtained. The yield obtained was 0.39 g. Melting point: at 300°C changes to black. Visible spectrum λ_{max} = 710 nm. IR spectrum is given as Fig. 14 (b). As this complex was found to be slightly soluble in water the elemental analysis was not carried.

In another experiment the reacting substances $CuCl_2.2H_2O$, phen and urea were taken in the molar ratio 1:1:40. While heating fine blue crystals were isolated. The yield was 0.19 g. Melting point: at 190 - 200°C changes to dark blue. Visible spectrum λ_{max} = 710 nm. IR spectrum: appears on appendix: Fig. 15. 2250 cm^{-1} 2200 cm^{-1} (doublet). 1450 cm^{-1}, 1150 cm^{-1} 850 cm^{-1}. Elemental analysis: because it is insoluble in water it was not possible to analyse content of Cu and Cl. Digestion with concentrated HCl was tried but the complex precipitates on dilution.

4.2.9 <u>Attempt to prepare copper: phen malonamide complex</u> Equal quantities of $CuCl_2.2H_2O$ and phen as in the above case (4.2.8) was reacted with 0.408 g malonamide (0.004 moles) as described. Green crystals were obtained. The Yield was 0.18 g (28.1%), Melting point: at about 290°C changes to black. Elemental analysis: found% (calculated%), Cu: 19.80 (20.06), Cl: 11.25 (22.57). Visible spectrum: λ_{max} = 710 nm. IR spectrum is given as Fig. 14 (c). It is similar to the spectrum of 4.2.7. Solubility: insoluble in CH_2Cl_2, CH_3Cl_3, CCl_4, CH_3OH slightly soluble in H_2O and DMSO. The isolated complex was found to be Cu(phen)Cl_2.

4.3 Complexes of Cadmium

4.3.1 Cadmium: bipyridine complexes. 0.45 g $CdCl_2 \cdot 2H_2O$ (0.002 moles) dissolved in 30 ml distilled water was added to 0.31 g bipyridine (0.002 moles) dissolved in 10 ml ethanol and 20 ml distilled water. When adding the cadmium salt solution to the bipyridine solution, a white precipitate was formed. The solution was well stirred and then left to stand. The precipitate was filtered off, washed with cold water and air dried. Yield: 0.67 g. Melting point: > 300°C. IR spectrum: given as appendix. Fig. 16 (a). 3100 cm^{-1} (C-H str.) 1600°cm^{-1} (C=C str. and C=N str.). 1450 cm^{-1} (C-H bend.) 780 cm^{-1} (C-H out of plane bend). Elemental analysis: because the complex was insoluble in water and concentrated HCl it was not possible to do the analysis for Cd and Cl. The content of nitrogen was 10.2%. The complex is insoluble in all common organic solvents, water and DMSO.

In a similar experiment cadmium chloride, urea and bipyridine were reacted. A white precipitate was obtained, which has the same IR spectrum (Fig. 16 (b) as the spectrum of the Cd: bipyridine binary complex, Fig. 16 (a). The complex also does not melt up to 300°C.

Malonamide, cadmium chloride and bipyridine also gave a white precipitate, which has the same IR spectrum, Fig. 17 (a) to that of the binary complex of Cd and bipyridine, Fig. 16 (a). It does not melt or decompose up to 300°C.

In similar two other reactions the concentrations of the urea and malonamide were increased four times and reacted with cadmium chloride and bipyridine. In both experiments, a white precipitate was obtained. Their IR spectra were taken (Fig. 18 (a) and (b)) and found to be identical with the Cd: bipyridine complex, Fig 16 a.

4.3.2 <u>Cadmium: phenanthroline complex</u>: 0.45 g of cadmium chloride (0.002 moles) dissolved in 20 ml distilled water was added to 0.39 g phenanthroline (0.002 moles) dissolved in 10 ml ethanol and 20 ml water. On adding the cadmium salt to the phenanthroline solution, a white precipitate was formed immediately. The precipitate was filtered off and washed with cold water. The yield was 0.64 g. Melting point: > 280°C. The complex is insoluble in H_2O, DMSO and common solvents. Elemental analysis was done only for nitrogen: 8.1%. IR spectrum is given as Fig. 19 (a), 3050 cm^{-1}: (C-H str.); 1620 cm^{-1} (COC str.), 1520 cm^{-1}: (C=N str.); 1440 cm^{-1} (C-H bend). 850 cm^{-1}; (C-H out of plane bend).

In another reaction cadmium chloride was first reacted with urea and then phenanthroline solution was added drop wise. A white precipitate was formed, which has the same IR spectrum (Fig. 19 (b)) as the cadmium: phenanthroline binary complex. It also has similar solubility behaviour. Its melting point is higher than 280°C.

The amount of urea was then increased ten times. A white precipitate was formed. Its IR spectrum (Fig. 19 (c)) shows a sharp peak at 2180* cm^{-1}, otherwise it is similar to the above spectrum. When phenanthroline was reacted with a solution mixture of cadmium chloride and malonamide, a white precipitate was formed. It has a similar IR spectrum to the cadmium: phenanthroline complex.

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* Could not be assigned to any known peak of urea.

5. SYNTHESIS OF SOME COMPLEXES IN ALCOHOLIC MEDIUM

5.1 The Reaction Between $Ni(MA)_2Cl_2$ and Bipyridine

The complex $Ni(MA)_2Cl_2$ was synthesised according to the procedure described by Aggrawal[50] by dissolving the stoichiometric quantities of hexa hydrate nickel chloride and malinomide in a methanol: ethanol mixture, 50:50 (v/v), and refluxing the solution for eight hours. The yellowish green complex separated during refluxing. Its IR spectrum is given as Fig. 20 (a).

0.39 g bipyridine (0.0025 molex) in 50 ml methanol: ethanol mixture was reacted with 0.835 g of $Ni(MA)_2Cl_2$, (0.0025 moles). At first the color of the solution was pink but on heating it changed to blue. The solution was refluxed for four hours. It was then concentrated by distilling off most of the solvent and on standing over night white crystals with some blue crystals co-crystalized. The white crystals were separated by washing off the blue crystals with a small quantity of ethanol and charactrized, by melting point determination and NMR, to be malonamide. However, the blue crystals were not characterized because it could not be isolated from the solvent in appreciable quantity.

5.2 The Reaction Between Ni(MA)$_2$Cl$_2$ and 1,10-Phenanthroline 0.49 g 1,10-Phenanthroline was reacted with 0.83 g Ni(MA)$_2$Cl$_2$, (0.0025 moles), following a procedure similar to 5.1. The color of the solution was pale pink at the begining of the reaction. On refluxing, after about one hour, the color of the solution changed to light blue. White and blue crystals were isolated after long standing. The blue crystals were separated by dissolving them in a mimimum quantity of water and then recrystalized from ethanol. The white crystals were characterized to be malonamide on the basis of melting point determination and NMR. The blue crystals were characterized to have the formula Ni(phen)Cl$_2$.6H$_2$O, on the basis of elemental analysis. Yield: 0.4 g (38.5%). Melting Point: at 140°C it changes to green. Elemental analysis: found% (calculated%). Ni: 13.68 (13.8); Cl: 15.4 (16.9), N: 5.9 (6.7). Visible spectrum: λ_{max} = 700 nm. IR spectrum: is given as Fig. 20 (b).

5.3 Attempt to Prepare Nickel: Urea Complex 2.77 g urea (0.02 moles) was dissolved in 100 ml methanol and the resulting green solution was refluxed for six hours. The solvent was then distilled off and the volume reduced to 20 ml and cooled. No crystals were isolated. The solution was then left standing and most of the methanol was evaporated at room temperature, however, crystals were not isolated and the complex remained in solution.

5.4 Preparation of Dichlorobis(bipyridine)copper(II) Monohydrate $Cu(bipy)_2Cl_2 \cdot H_2O$:

$Cu(MA)Cl_2 \cdot H_2O$ was synthesised as described by Aggrawal.[50] Its IR spectrum is given as Fig. 21 (a).

0.78 g of bipyridine (0.005 moles) and 1.27 g $Cu(MA)Cl_2 \cdot H_2O$ (0.005 moles), was added to 100 ml ethanol. On the additon of the bipyridine the solution immediately turned to brown and this solution was refluxed for eight hours. During refluxing green crystals were isolated. The solution was filtered and the crystals washed with small portions of ether. The filtrate was concentrated by evaporation and some more crystals (0.25 g) were obtained. Total yield: 1.25 g (54.11%). Melting point: at 150°C changes to dark green. Elemental analysis: Found% (calculated%), Cu: 13.92 (13.66), Cl: 12.92 (15.27), N: 11.4 (12.04). Visible spectrum: λ_{max} = 650 nm. IR spectrum given as Appendix Fig. 21 (b). 3400 cm^{-1} (O-H str.), 1610 cm^{-1} (C=C str.). 1450 cm^{-1} (C-H bend), 780 cm^{-1} (C-H out of plane deformation). Solubility: slightly soluble in alcohol. Soluble in water and dimethylsulfoxide. Insoluble in chloroform and carbon tetrachloride.

5.5 Preparation of Dichlorotetraureacopper(II) $Cu(urea)_4Cl_2$.

2.4024 g urea (0.04 moles) and 3.4094 g $CuCl_2.H_2O$ (0.02 moles) were dissolved in 100 ml alcohol mixture (50:50). The color of the solution was intense green. It was refluxed for eight hours. During refluxing the color of the solution turned more dark. The solution was concentrated by distilling off about 80 ml of the solvent. Green crystals were obtained on cooling. The crystals were washed with small portions of ether and then air dried. Yield: 3.55 g (94.9%). Elemental analysis: Found% (calculated%). Cu: 16.08 (16.95), N: 29.2 (29.88), Cl: 18.15 (18.94) Melting point: at 160°C changes to dark green. IR spectrum is given as Fig. 22 (b). 3500-3300 cm(N-H str.), 1580 cm (C-O str.) 1480 cm^{-1} (C-N str.). Solubility: Soluble in water, alcohol and dimethylsulfoxide. Insoluble in acetone, dichloromethane, chloroform and carbontetrachloride.

5.6 Preparation of Dichloromonomalonamidecadmium(II)-Monohydrate $Cd(MA)Cl_2.H_2O$:

1.0209 g malonamide (0.01 moles) and 2.2835 g (0.01 moles) were dissolved in 100 ml methanol: ethanol mixture (50:50). The solution was colorless. It was refluxed for eight hours. The clear solution was then concentrated by distilling off about 70 ml of the solvent. The concentrated solution was then cooled over night in a refrigirator. White crystals were isolated. The crystals were dried at 70°C. Yield 1.8 g (94.7%), Elemental analysis: found% (calculated%). Cd: 36.12 (37.02), Cl: 21.55 (23.38), N: 8.9 (9.22). Melting Point: at 194°C - 205°C melts and changes to yellow. Solubility: highly soluble in water and alchol.

5.7. Preparation of Dichloromonoureacadmium(II)monohydrate Cd(urea)$Cl_2.H_2O$ 2.3 g $CdCl_2.2H_2O$ and 1.2 g urea were added to 100 ml ethanol. The mixture was gently heated with continuous stirring for four hours. During heating white crystals were isolated. The crystals were filtered off, washed with small portions of ether and then dried in the oven at 70°C. Yield: 2.1 g (40.3%). Melting point: it does not melt up to 250°C. Elemental analysis: found% (calculated%). Cd: 45.17 (43.05), N: 9.81 (10.72), Cl: 26.99 (27.19). IR spectrum: appears as Appendix Fig. 22 (a). 3500-3400 (O-H and N-H str.)., 1640 cm^{-1}(C-O str.), 148 cm^{-1} (C-N str.). Solubility: soluble in water and dimethyl sulfoxide. Slightly soluble in alcohol. Insolluble in chloroform and carbon tetrachloride.

6. RESULTS AND DISCUSSION

The synthesis of all complexes in the aqueous medium was carried in the pH range 2-5, because if the pH is greater than 7, the metal ions precipitated as the hydroxide.

To synthesis the binary complexes of nickel and bipyridine, the metal ion and the ligand were taken in the molar ratio of 1:1. The solution was blue in color and absorbs at λ_{max} 560 nm. After concentration and cooling the complex was not isolated. The effect of prolonged heating was investigated in another experiment by refluxing the solution for three hours and then concentrated and cooled, but crystals were not isolated.

In an attempt to synthesis the nickel:bipyridine:urea complex and nickel:bipyridine:malonamide complex, the metal halide and the ligands were taken in the molar ratio of 1:1:1. The complexes could not be isolated having the same blue color and the same visible spectra, λ_{max} 560 nm, as the nickel:bipyridine complex in the molar ratio of 1:1. Hence, it was necessary to investigate the effect of prolonged refluxing and increased concentration.

The concentration of urea and malonamide were then increased four times, and the solutions refluxed for six hours each. However, this varied condition did not have any effect on the product formed. The solutions have the same visible spectra, λ_{max} 560 nm, and was blue in color as shown when the molar ratio of metal ion and ligands was 1:1:1. It is therefore possible to conclude that in aqueous medium at pH 2-5, the formation of a mixed ligand complex was not attainable when the molar ratio of Ni:bipy:malonamide were 1:1:1 or 1:1:4.

Hence, it was necessary to work with an excess of the second ligands namely urea and malonamide. Therefore, the concentration of the second ligand was increased ten folds, and the same procedure was followed but the results obtained were similar to the above case.

When the synthesis of Ni:bipyridine complex was done at a higher concentration of the ligand, by adjusting the concentration in the molar ratio of 1:2 respectively, pink crystals were isolated. From the IR spectrum (Fig. 10 a) of the complex it shows that it is hydrated, as there is a strong O-H stretching peak at 3400 cm^{-1}. The sharp peak at 1600 cm^{-1} is for the aromatic C=N stretching vibration. At 1480 cm^{-1} the C-H bending peak is observed. The elemental analysis data obtained suggest that the complex has the formula $Ni(bipy)_3Cl_2 \cdot 6H_2O$. The nickel content was 9.97% (cal. 8.31), nitrogen content was 10.82% (cal.

11.89) and chlorine content was 10.60% (cal. 10.05%). The water loss was 16.01% (cal. 15.29%). It absorbs in the visible spectrum with a λ_{max} of 510 nm. It is soluble in H_2O, CH_3OH and DMSO, but insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. It decomposes at 175°C to give a green colored complex, probably due to the formation of the anhydrous bis complex.[18] Original literature on the tris complex was not available, and hence it was not possible to make any comparison.

The synthesis of $Ni(bipy)_2(urea)Cl_2$ was attempted by reacting bipyridine, urea and nickel chloride in the molar ratio of 2:1:1 following the procedure for the synthesis of the nickel:bipyridine tris complex. In this case also pink colored crystals were isolated. The IR spectrum of this complex (Fig. 10 b) was similar to that of $Ni(bipy)_3Cl_2.6H_2O$, (Fig. 10 a). The elemental analysis were carried out and was found to have nickel 9.35% (cal. 8.31%), chlorine 12.72% (cal. 10.05%) and nitrogen 9.64% (cal. 11.89). It decomposes at about 172°C and changes to green. In the visible spectrum it absorbes at 520 nm. It is soluble in H_2O, CH_3OH and DMSO, but insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. These data suggest that the complex isolated was $Ni(bipy)_3Cl_2.6H_2O$ and therefore, it can be concluded that the urea molecule does not coordinate, and instead of a mixed ligand complex, the binary complex of nickel and bipyridine was obtained.

In similar manner the synthesis of $Ni(bipy)_2(MA)Cl_2$ was attempted. In this case also pink crystals were isolated. The IR spectrum (Fig. 10 c) is similar to that of $Ni(bipy)_3Cl_2.6H_2O$. The elemental analysis, nickel content, 4.3% (cal. 8.31%), nitrogen content 10.35% (cal. 11.89%) and chlorine content 10.14% (cal. 10.05%), suggests that it has the formula $Ni(bipy)_3Cl_2.6H_2O$. It is then concluded that following this procedure it was not possible to synthesise the mixed ligand complex.

In the attempt to synthesise and isolate the binary complex of nickel with urea, it was found that the complex could not be isolated and remains in solution in the form of a suspension. In the case of nickel: malonamide binary complex, the malonamide recrystalized on cooling. This was confirmed by melting point determination and NMR.

When nickel chloride and phenthroline were reacted in the molar ratio 1:1 at pH 2-5, the color of the solution was blue. After concentration and cooling, however, crystals of the formed complex were not isolated. The solution absorb at λ_{max} 525 nm.

To synthesise the mixed ligand complex of nickel with phenanthroline and urea, the urea solution was added dropwise to a solution of nickel chloride and phenanthroline in the molar ratio 1:1:1, while heating and stirring. On long standing, light blue crystals in low yield (25.4%) were isolated. This complex was analysed to be $Ni(phen)_2Cl_2.6H_2O$ from the elemental analysis from which it was found the nickel content to be 8.02% (cal. 9.81%) and the chlorine content to be 11.5% (cal. 11.8%). The IR spectrum of the complex (Fig. 11 a), show that it is hydrated, showing an O-H stretching peak at 3350 cm^{-1}. The aromatic C=N stretching peak appears at 1620 cm^{-1}. The peaks in the finger print region of the IR spectrum are all similar to that found in the free phenanthroline IR spectrum (Fig. 23 b). It is soluble in H_2O, CH_3OH and DMSO, but insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. The conclusion arrived at is, therefore, the mixed ligand complex of nickel with phenanthroline and urea was not isolated.

In another experiment in place of urea malonamide was used and the same procedure was followed. In this case also blue crystals were isolated, which have the same IR spectrum (Fig. 11 b) to that of $Ni(phen)_2Cl_2.6H_2O$ (Fig. 11 a). Elemental analysis results show that these two complexes are the same. The nickel content was 8.7% cal. 9.81) and the chlorine content was 11.2% (cal. 11.8%). It decomposes at 140°C. It is soluble in

H_2O, CH_3OH and DMSO, but is insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4.

Dichloro monobipyridine copper(II), Cu(bipy)Cl_2, was synthesised from copper chloride and bipyridine in the molar ratio of 1:1 at pH 4.5. The crystals obtained were green, and decompose at 280°C. The elemental analysis results were, copper content 21.1% (cal. 21.15%), nitrogen content 10.1% (cal. 9.63%) and chlorine content 24.46%). The IR spectrum of this complex (Fig. 12 a) indicates that it is not hydrated, as the O-H stretching peak at about 3600-3200 cm^{-1} was not observed. C-H stretching peak at 3050 cm^{-1}, C=C stretching peak and C=N stretching peak at 1500 cm^{-1} were also observed. The absobtion peaks in the finger print region were similar to that of bipyridine (Fig. 23 a). The complex absorb in the visible region with a λ_{max} of 660 nm.

To synthesise the mixed ligand complex of copper with urea and bipyridine, the reacting substances were taken in the molar ratio 1:1:1 and the pH adjusted to 2.2. The IR spectrum of this complex (Fig. 12 b) did not show any absorbtion at 3500-3200 cm^{-1} indicating that it is not hydrated. Moreover, the N-H stretching peak at 3400 cm^{-1} and the C=O stretching peak at about 1600 cm^{-1} were not also observed, which is a conclusive evidence for the absence of urea as a ligand in the complex isolated. The elemental analysis results suggest that the complex is Cu(bipy)Cl_2. The content of copper was 21.52% (cal. 21.85%), that of nitrogen was 8.09% (cal. 9.63%) and that of chlorine was 16.26% (cal. 24.42%). The results of the chlorine analysis show a deviation from the theoritical value which may be due to experimental error. The decomposition temperature is about 300°C. The absorbtion in the visible region was found with a λ_{max} of 660 nm.

IR and elemental analysis results show that the urea is not coordinated and therefore, the synthesis of the mixed ligand complex was not realized.

In the attempt to synthesise the mixed ligand complex of copper with urea and bipyridine in neutral medium the reacting substances were taken in the molar ratio 1:1:1 and the pH adjusted to 7.0. From the deep blue colored solution, blue crystals were isolated. The IR spectrum (Fig. 13 a) of this complex showed a peak at 3460-3300 cm^{-1}, which is attributed to O-H stretching. The typical carbonyl peak at about 1650 cm^{-1} was not observed, but at 1600 cm^{-1} there was a sharp peak which is assigned to C=O stretching vibration. At 1450 cm^{-1}, the C-H bending peak was sharp. The formula assigned is Cu(bipy)(OH)Cl.$3H_2O$, as the elemental analysis show the copper content to be 17.9% (cal. 19.4%) and the chlorine content to be 10.6%

(cal. 10.8%). The water loss was 12.85% (cal. 16.55%). Its decomposition temperature is 165°C and it is soluble in water and DMSO, slightly soluble in CH_3OH, but insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. A hydroxo complex of this type is not mentioned in the lite[illegible] and hence, this is assumed to be a newly isolated complex.

An attempt was made to synthesise the mixed ligand complex of copper with bipyridine and malonamide. The reacting substances were taken in the molar ratio 1:1:1 and the pH adjusted to 2.0. Green crystals were isolated. The IR spectrum of this complex (Fig. 12 C) was similar to that of $Cu(bipy)Cl_2$. The elemental analysis obtained were, copper content was 19.87% (cal. 21.85%) and chlorine content was 18.92% (cal. 24.42%). It is soluble in H_2O and DMSO but insoluble in CH_2Cl_2 $CHCl_3$ and CCl_4. It can therefore be concluded that the mixed ligand complex was **not isolated**.

Dichloro monourea copper(II) monohydrate was synthesised in acidic medium at pH 3.5. The green crystals isolated were analysed and found to contain copper 29.79% (Cal. 29.88%), and nitrogen 11.7% (cal. 13.17%). As this complex was not completely soluble in water the analysis for the chlorine content using the chloride sensetice electrode was not possible with the procedure followed. Its IR spectrum

(Fig. 13 b) showed an absorbtion peak, a doublet for the O-H and N-H stretching vibrąations. The absorbtion peak of the C=0 at 1600 cm^{-1} was not strong and slightly shifted indicating that the urea molecule [illegible]rdinates through the carbonyl oxygen. From the literature survey done the isolation of the a monohydro monourea of copper is not metnioned. Therefore, this complex is a newly isolated complex.

Dichloro dimalonamide copper(II) dihydrate, $Cu(MA)_2Cl_2 \cdot 2H_2O$, was synthesised, by the reaction of copper chloride and monamide, in 21.3% yield. The complex has a brown color. Its IR spectrum (Fig. 13 c) showed two prominant peaks, one at 3400-3200 cm^{-1}, which is an O-H and N-H stretching vibrations, and another at 1620 cm^{-1} for the carbonyl group. In the free malonamide the carbonyl vibration peak is broad and appears at about 1650 cm^{-1}. Hence, the shift of this peak in the coordinated molecule to lower frequency is an indication of the envolvement of the carbonyl oxygen in bonding. Therefore, it is concluded that the malonamide molecule coordinates through the oxygen atom.

The copper content of this complex was 16.79% (cal. 16.9%) and that of chlorine was 17.10% (cal. 18.9/) and the nitrogen content was 12.57% (cal. 14.9%). Its decomposition temperature is 240°c. It is slightly soluble in H_2O and DMSO and insoluble in other organic solvents. The unhydrated $Cu(MA)_2Cl_2$ and the monohydrate $Cu(MA)\ Cl_2.H_2O$ are reported in the literature[50], but the dihydrate is not reported. Therefore, this is a newly isolated complex.

The reaction between copper chloride and phenanthroline at pH 3.8 gave $Cu(phen)Cl_2$ in 82.2% yield. The IR spectrum of this complex, (Fig. 14 a) showed that it is not hydrated because of the absence of the intense O-H peak near 3500-3200 cm^{-1}. The other peaks that appear in the free phenanthroline molecule (Fig. 23 b) were also observed here. Its elemental analysis showed copper content of 20.13% (cal. 20.06%), chlorine content of 12.92% (cal. 22.57%), and the nitrogen content of 7.93% (cal. 8.9%). The chlorine content is close to half the calculated value which suggest that the two chlorine atoms are in different sphere of coordination, with only one of them to be ionizable. Its visible spectrum showed a λ_{max} at 710 nm. Its decomposition temperature is 300°C. It is soluble in H_2O and DMSO but insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. Original literature on this complex was not available and therefore, it was not possible to make any comparison.

The synthesis of a mixed ligand complex of copper with phenanthroline and urea was attempted by taking the reactants in the molar ratio 1:1:2, respectively. Green crystals having a similar IR spectrum, (Fig. 14 b) to that of Cu(phen)Cl_2 (Fig. 14 a) were obtained. Its visible spectrum also shows a λ_{max} at 710 nm. Hence a mixed ligand complex was not isolated.

In a similar experiment the reactants copper, phenanthroline and urea were taking in the molar ratio 1:1:40, respectively, and fine blue crystals in very low yield were isolated. This isolated compound was insoluble in water. To do the elemental analysis it was digested with concentrated HCl, but it precipitates on dilution. Therefore, the elemental analysis were not done. The IR spectrum of this complex (Fig. 15) showed a sharp doublet at 2250 cm^{-1} and 2200 cm^{-1}. This peak was also observed in complexes where a large concentration of urea was used. A similar case was when urea reacted with $CdCl_2$ and phenanthroline in the molar ratio of 10:1:1 (Page 63).

In another experiment urea was replaced with malonamide and the product obtained was green in color. Its IR spectrum (Fig. 14 c) was similar to that of Cu(phen)Cl_2,(Fig. 14 a). The elemental analysis results were also reasonably close to each other. content of copper was 19.8% (cal. 20.06%) and chlorine content was 11.25% (cal. 22.57%), but one of the chlorine atoms is assumed to be unionizable. In the visible region it absorbed at 710 nm. Its decomposition temperature was 290°C. It is therefore possible to conclude that the malonamide molecule did not coordinate and a mixed ligand complex was not isolated.

Cadmium chloride reacts readily in aqueous medium with bipyridine and a white complex is separated immediatly as a precipitate. The complex isolated was highly stable to heat and its decompositon temperature is above 300°C. It is also highly insoluble in water. To do the elemental analysis it was digested with concentrated HCl but it precipitates on dilution. This was also observed with all other complexes of cadmium which contain bipyridine. The IR spectrum of this complex, (Fig. 16 a) showed that it is not hydrated. It is reported in the literature[14-21], that cadmium coordinates to one, two or three molecules of the base. However, it was not possible to know how many molecules do coordinated and whether this was the mono or bis or the tris complex.

In two other similar experiments urea and malonamide were introduced as the second ligand. In both cases a white complex was precipitated with similar IR spectra (Fig. 16 b and Fig. 17). This complexes also did not melt up to 300°C. In both isolated complexes, the N-H stretching peak at 3400 cm^{-1} was not observed. Neither was the strong C=O peak at about 1650 cm^{-1}. This is, therefore, a conclusive evidence to rule out the formation of a mixed ligand complex.

In yet other two experiments the concentration of urea and malonamide were increased four folds, but the complexes isolated in these two cases have similar IR spectra (Fig. 18 a and Fig. 18 b) to the above two complexes when the molar ratio was 1:1:1. The conclusion that can be derived here is that an increase of four folds in the concentration of urea and malonamide did not alter the course of the reaction and the urea and the malonamide did not coordinate even when present in relatively higher concentrations.

Cadmium chloride reacts also with phenanthroline similarly and a white precipitate is separated. This complex was also stable to heat as it does not melt up to 300°C. The IR spectrum of this complex (Fig. 19 a) showed that it is not hydrated. Elemental analysis for this complex was not carried out because of the solubility reason mentioned above.

In another experiment urea was added as a second ligand to cadmium chloride and phenanthroline. The reacting substances were added in the molar ratio of 1:1:1. A white complex was isolated. Its IR spectrum (Fig. 19 b) showed that it is not hydrated. The typical N-H and C=O peaks also were not observed. Therefore, the urea did not coordinate. The concentration of urea was then increased ten times and the reaction carried. A white precipitate was formed. The IR spectrum of the complex (Fig. 19 c) showed a very diffused peak at 3500-3400 cm^{-1}. It also showed a sharp peak at 2180 cm^{-1}, a peak that was observed with high urea concentration as in the case of copper complex (page 60).

The synthesis of some of the complexes were then carried out in methanol: ethanol mixture 50:50 (v/v). This solvent system was found out to be a better system as far as yield and isolation were concerned. As the alcohols have a low dielectric constant than water the solute-solvent interaction is less and so the complexes separated were easily isolated from the solvent. In some cases the complexes were isolated during refluxing and in other cases concentration was needed.

The two binary complexes of nickel and copper, $Ni(MA)_2Cl_2$ and $Cu(MA)\ Cl_2.H_2O$ were synthesised according to the procedure described by Aggrawal and coworkers[50] and then the reactions of bipyridine and phenanthroline with these two complexes were investigated.

$Ni(MA)_2Cl_2$ was refluxed with bipyridine in methanol: ethanol system for four hours. After concentration and cooling white crystals cocrystalized with some blue crystals. The blue crystals were washed off with a minimum quantity of ethanol and the white crystals were characterized by melting point determination and NMR to be malonamide. The blue crystals could not be isolated. This may suggest that the malonamide in the original complex was substituted by the bipyridine.

When $Ni(MA)_2Cl_2$ was refluxed with phenanthroline in alcohol mixture, white and blue crystals precipitated. These were separated and the white crystals were characterized to be malonamide. The blue crystals were assigned the formula $Ni(phen)Cl_2.6H_2O$ as the nickel content was 13.68% (cal. 13.8%), chlorine content was 15.4% (cal. 16.9%) and the nitrogen content 5.9% (cal. 6.9%). However, its IR spectrum, (Fig. 20 b) showed a peak at about 1650 cm^{-1}. This may be due to impurities of malonamide.

The synthesis of the binary complex of nickel with urea was also tried in alcohol. After refluxing for six hours, concentration and cooling, the complex was not isolated.

The reaction between $Cu(MA)Cl_2.H_2O$ and bipyridine was investigated. The two reacting compounds were taking in ethanol and refluxed for eight hours. Green crystals separated during refluxing. The formula assigned to this complex is $Cu(bipy)_2Cl_2.H_2O$ on the basis of the copper content 13.92% (cal. 13.66%), nitrogen content 11.4% (cal. 12.04%) and chlorine content 12.92% (cal. 15.27%). The IR spectrum (Fig. 21 b) showed that it is hydrated as there was a strong peak at 3400 cm^{-1}. The strong carbonyl peak at about 1650 cm^{-1} was not seen, which indicates that the malonamide was substituted. The complex is soluble in water and DMSO, but insoluble in $CHCl_3$ and CCl_4.

$Cu(urea)_4Cl_2$ was synthesised in methanol:ethanol mixture by taking copper chloride and urea in the molar ratio 1:2. It is green in color and decompose at 160°C. The IR spectrum (Fig. 22 b) showed a shifted C=O peak at 1580 cm^{-1}. This shift of the C=O peak to lower frequency suggests that the urea coordinates through the oxygen atom. The peaks for the N-H was seen as strong one between 3500 cm^{-1} and 3300 cm^{-1}. The elemental analysis was found to be Cu, 16.08% (cal. 16.95%), N, 29.2% (cal. 29.88%) and Cl, 18.15% (cal. 18.94%), respectively. It is soluble in H_2O, CH_3OH and DMSO, and insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. A complex of copper where four urea molecules are coordinated to the copper ion is not mentioned in the literature. Therefore, this is a newly isolate complex.

$Cd(MA)Cl_2.H_2O$ was synthesised folowing a similar procedure. The reacting substances were taking in a methanol: ethanol mixture and refluxed for eight hours. The crystals were isolated after concentration and cooling. It decomposes at about 200°C. the results of the analysis showed the cadmium content to be 36.12% (cal. 37.02%), chlorine content to be 21.55% (cal. 23.38%) and nitrogen content to be 8.9% (cal.

9.22%). This complex is highly soluble in water and alcohol. The yield was quite high for this complex (94.7%).

$Cd(urea)Cl_2 \cdot H_2O$ was synthesised in methanol from urea and cadmium chloride. The solution was not refluxed but it was heated gently for about three hours. The complex was isolated during heating. The elemental analysis was found to be Cd, 45.17% (cal. 43.05), N, 9.81% (cal. 10.72%) and Cl, 26.99% (cal. 27.19%), respectively. The IR spectrum (Fig. 22 a) showed a strong peak at 3500-3400 cm^{-1} which is due to O-H and N-H stretching vibrations. The C=O peak appeared at 1640 cm^{-1}, and the C-N stretching peak at 1450 cm^{-1}. It is soluble in water and DMSO, slightly soluble in ethanol and insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. In the system $CdCl_2$-urea-methanol and $CdCl_2$-urea-ethanol the existance of complexes in the ratio 1:1 and 1:4 is reported[45] but the isolation of either complexes is not mentioned.

There are several conclutions that can be drawn from the foregoing discussions. The binary complexes of bipyridine and phenanthroline with Ni(II), Cu(II) and Cd(II) are easily formed. Urea and malonamide do not coordinate as a second ligand in the presence of either bipyridine or phenanthroline, as in none of the experiments attempted a mixed ligand was formed.

Comparing the stability of the complexes formed by 2,2-Bipyridine and 1,10-Phenanthroline, in the case of bipyridine there is a free rotation of the central C-C bond in the bipyridine molecule[5], while the phenanthroline molecule has a rigid structure, which is a planar system[5], hence the entropy conditions make the formation of the bipyridine complex slightly less favoured than the rigid prearranged phenanthroline molecule.

Comparing this two bases to malonamide and urea, they have an aromatic ring system, making them stronger pi acceptors with delocalization over an extended carbon frame-work, which is absent in malonamide and urea.

Chelate formation is a factor that contributes to the stability of a complex. Bipyridine and phenanthroline form five membered rings with metal ions while malonamide may form six membered rings. However, bipyridine and phenanthroline form fused rings around the metal ion which seems to confer an even greater stability than the formation of a single ring as in case of malonamide. Moreover, back donation from the metal ion enhances the base-metal bond strength, increasing the stability of the complex.

Urea,H_2NCONH_2, is a bidentate ligand coordinating through the oxygen atom or the nitrogen atom., because if it was to act as a bidintate ligand it would form a four membered ring which would be strained and so unstable. Therefore,the chances for a urea molecule to coordinate in the presence of a strong chelating ligands like bipyridine and phenanthroline is minimum as was observed in this work.

Steric factors also play a role in complex formation. Phenanthroline and bipyridine compared to malonamide and urea are bulky groups, and therefore, it is assumed that they hinder the malonamide and urea molecules from having acces to the metal ion.

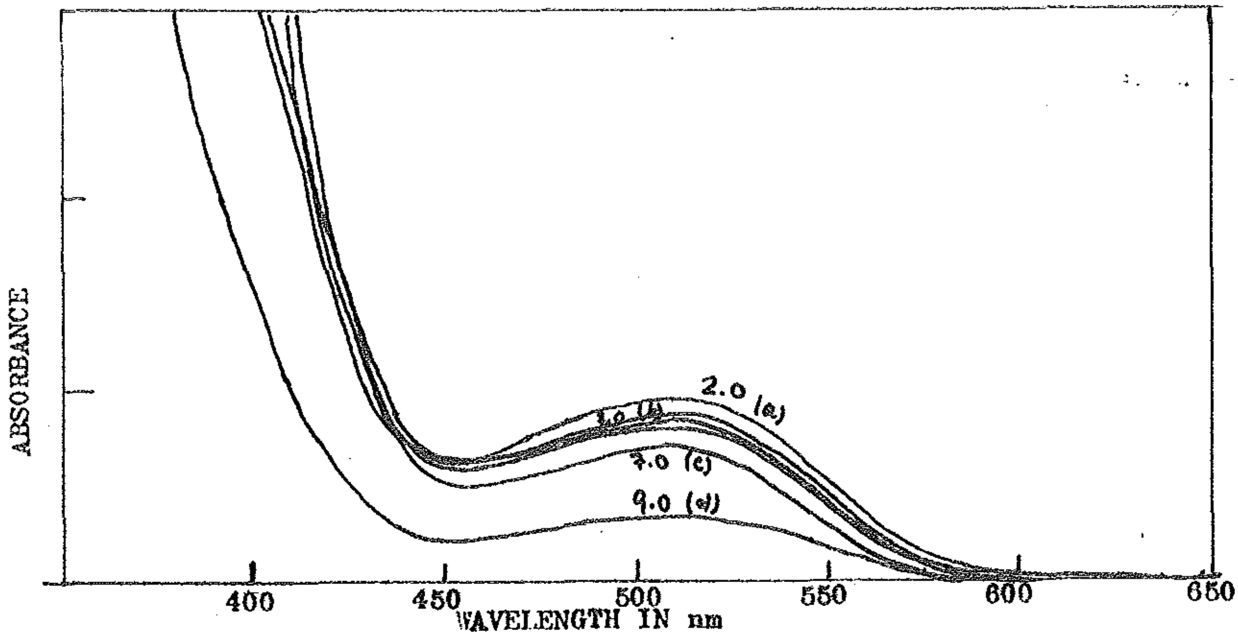


Fig. I Absorbtion spectra of Ni:bipy (I:2) complex at pH
(a) 2.0 (b) 3.0 (c) 7.0 (d) 9.0

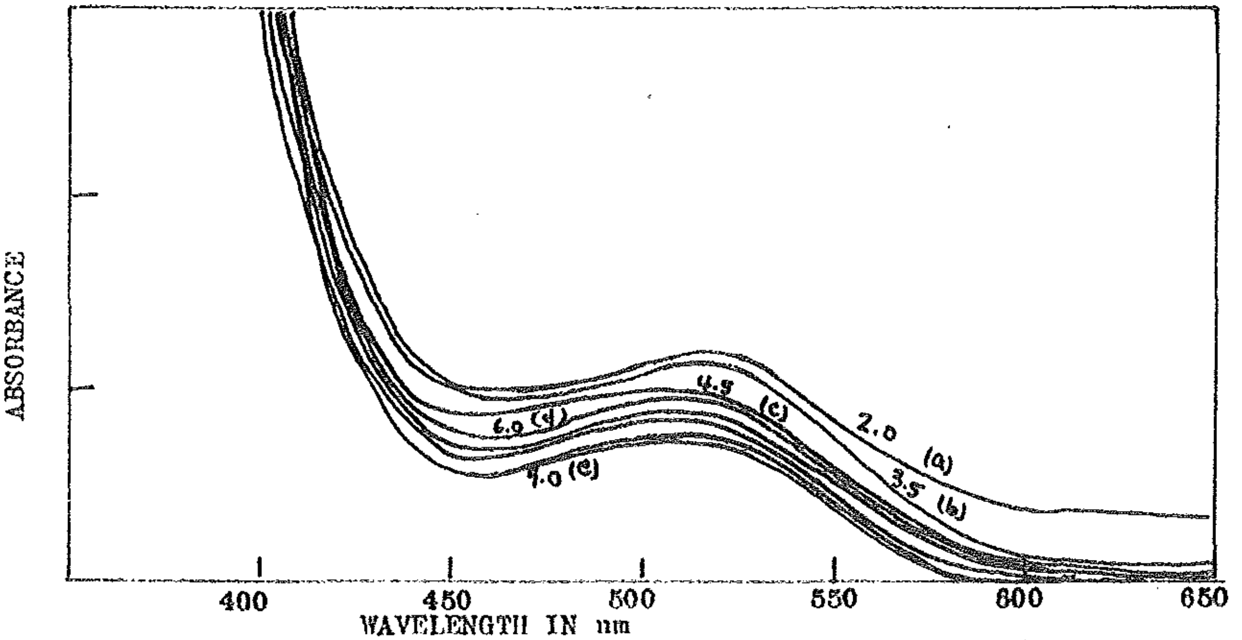


Fig. 2 Absorbtion spectra of Ni:bipy:urea (I:2:I) complex at pH (a)2.0 (b)3.5 (c) 4.5 (d) 6.0 (e) 9.0

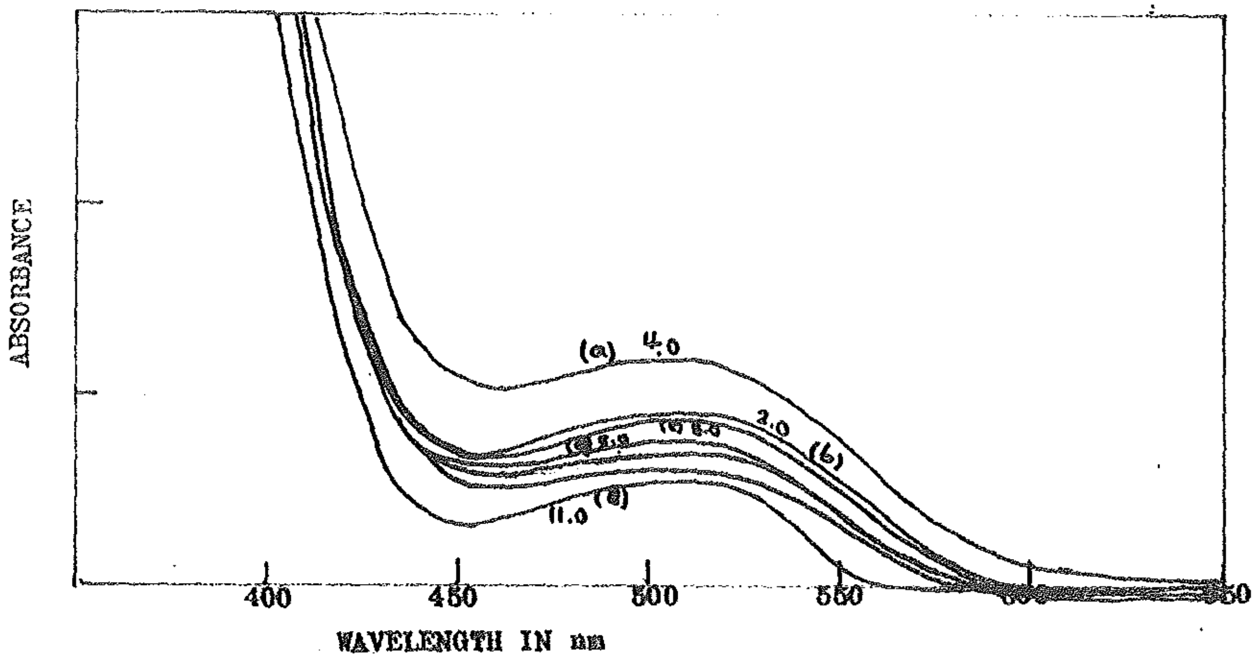


Fig. 3 Absorbtion spectra of Ni:bipy:malonamide (I:2:I) complex at pH (a) 4.0 (b) 2.0 (c)3.0 (d) 5.0 (e) II.0

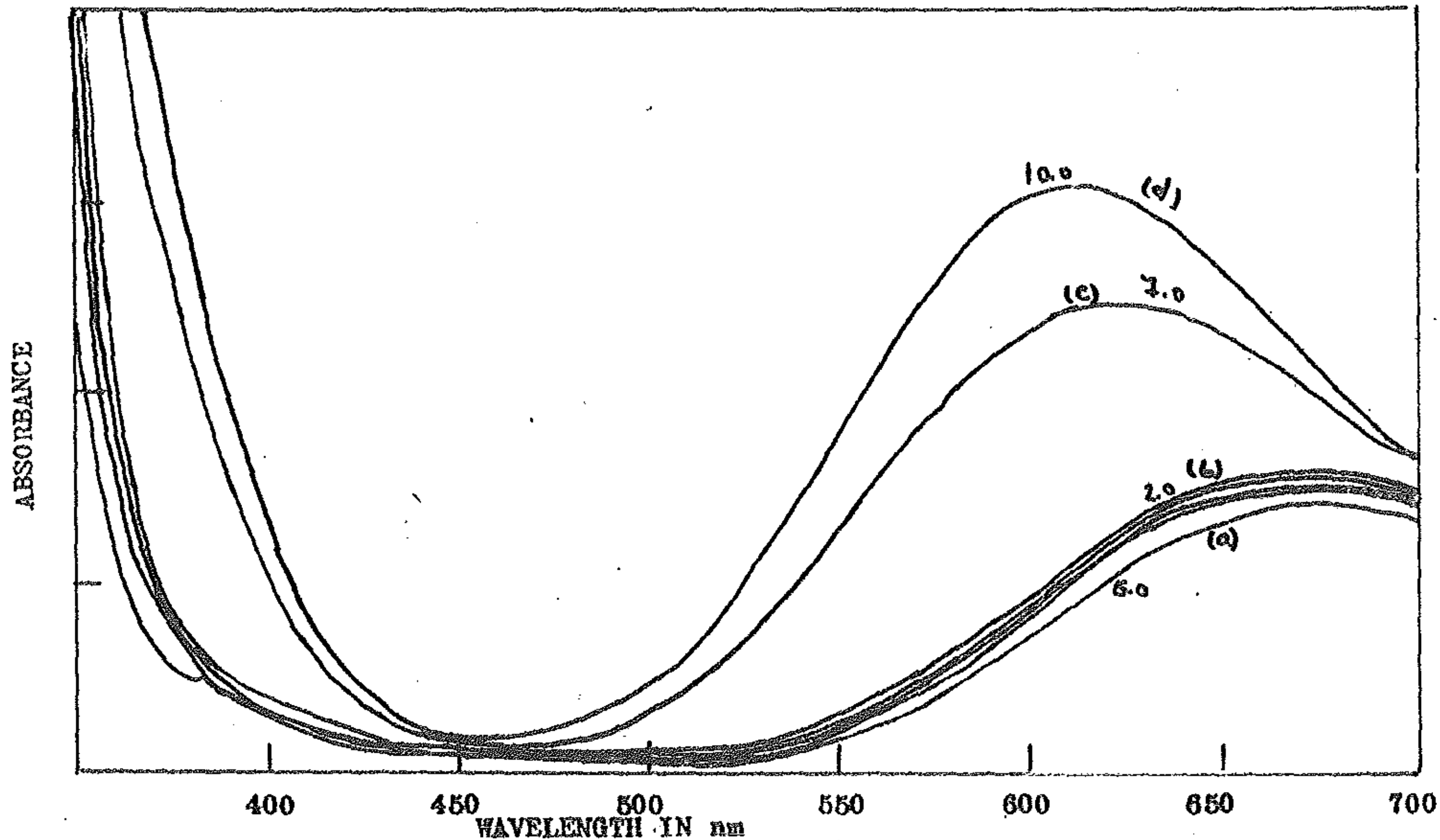


Fig. 4 Absorbtion spectra of Cu:bipy (I:I) complex at pH (a) 5.0 (b)2.0 (c) 7.0 (d) I0.0

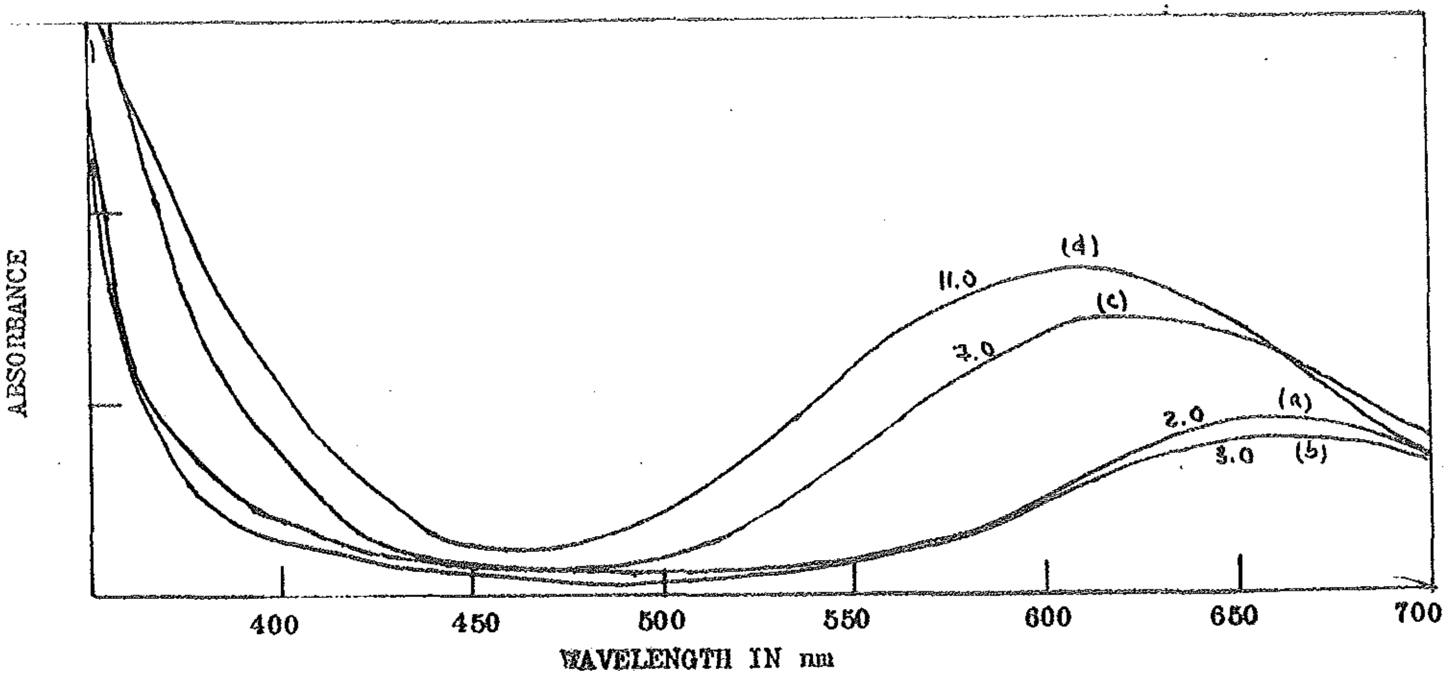


Fig. 5 Absorbtion spectra of Cu:bipy:urea (I:I:I) complex at pH (a) 2 (b) 3 (c) 7 (d) II

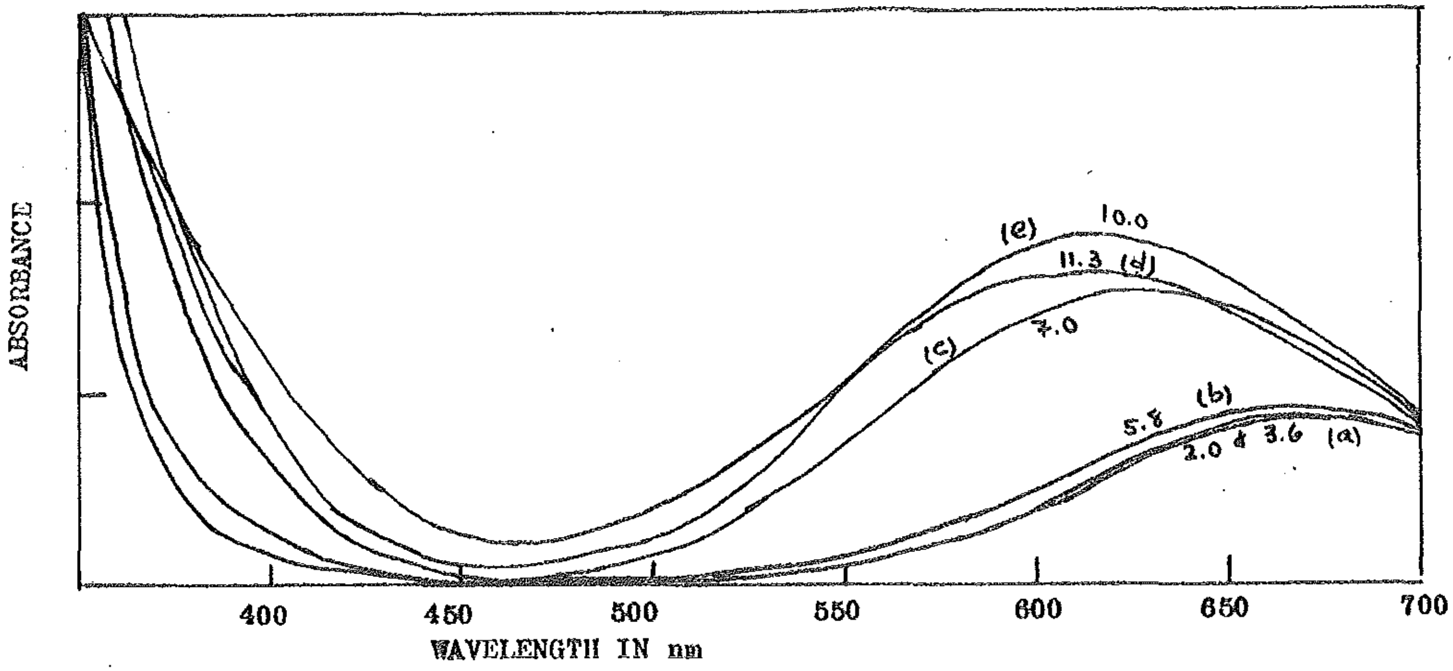


Fig. 6 Absorbtion spectra of Cu:bipy:malonamide (I:I:I) complex at pH (a) 2.0 and 3.6 (b) 5.8 (c) 7.0 (d) II.3 (e) I0.0

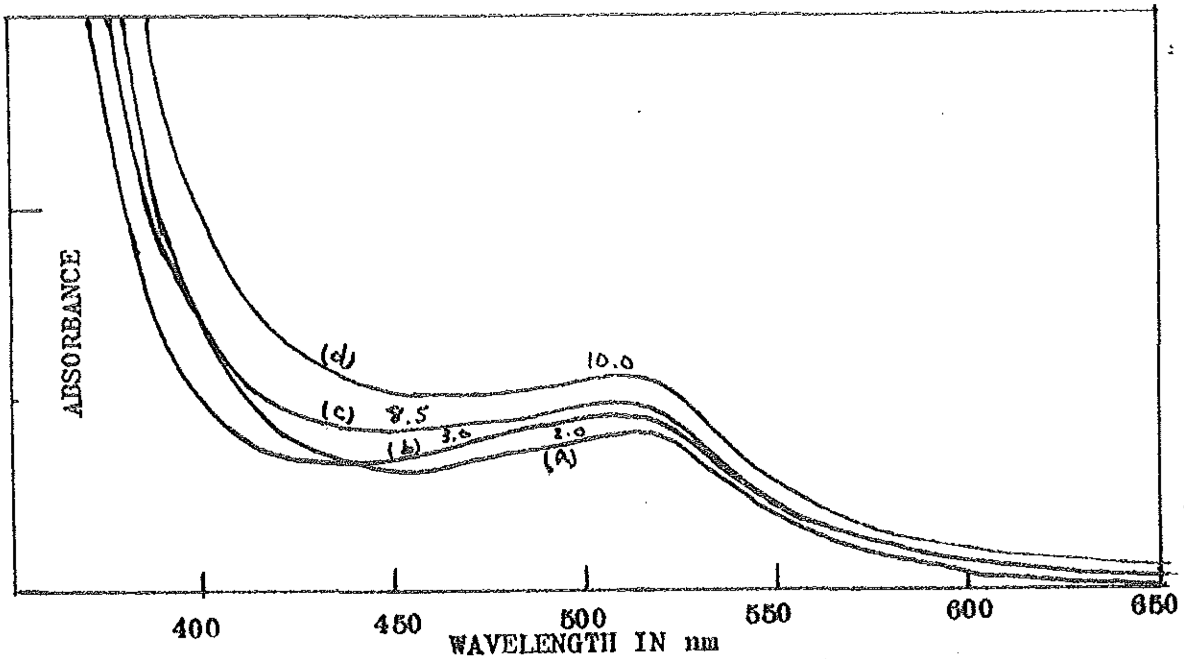


Fig. 7 Absorbtion spectra of Ni:phen (I:I) complex at pH (a) 2.0 (b) 3.0 (c) 8.5 (d) I0.0

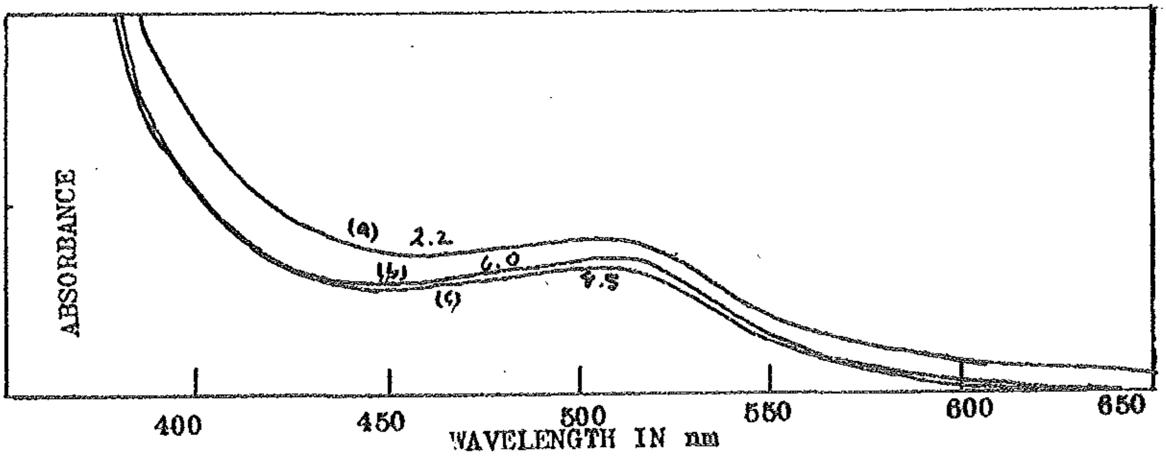


Fig. 8 Absorbtion spectra of Ni:phen:urea (I:I:I) complex at pH (a) 2.2 (b) 6.0 (c) 8.5

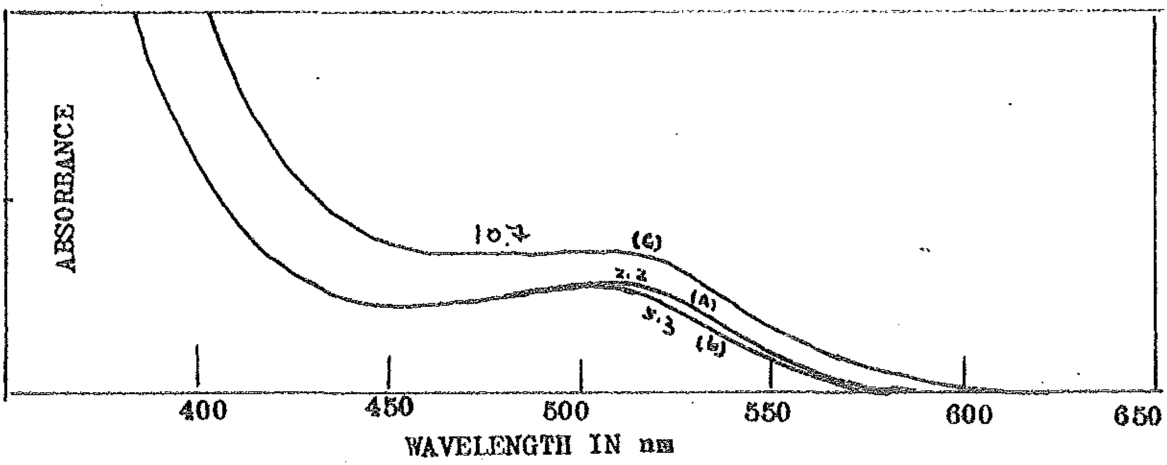


Fig. 9 Absorbtion spectra of Ni:phen:malonamide(I:I:I) complex at pH (a) 2.2 (b)5.3 (c) I0.7

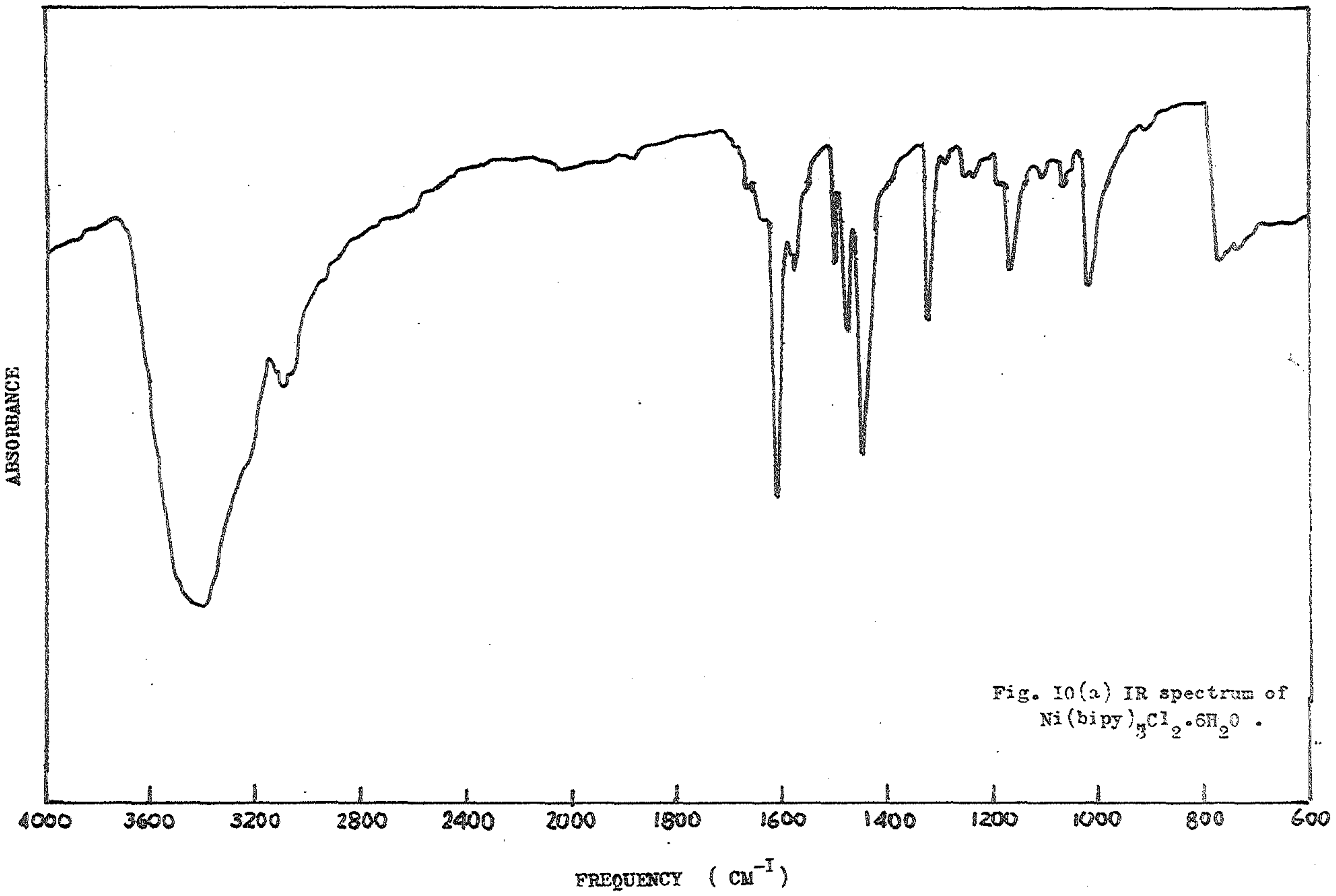


Fig. 10(a) IR spectrum of $Ni(bipy)_3Cl_2 \cdot 6H_2O$.

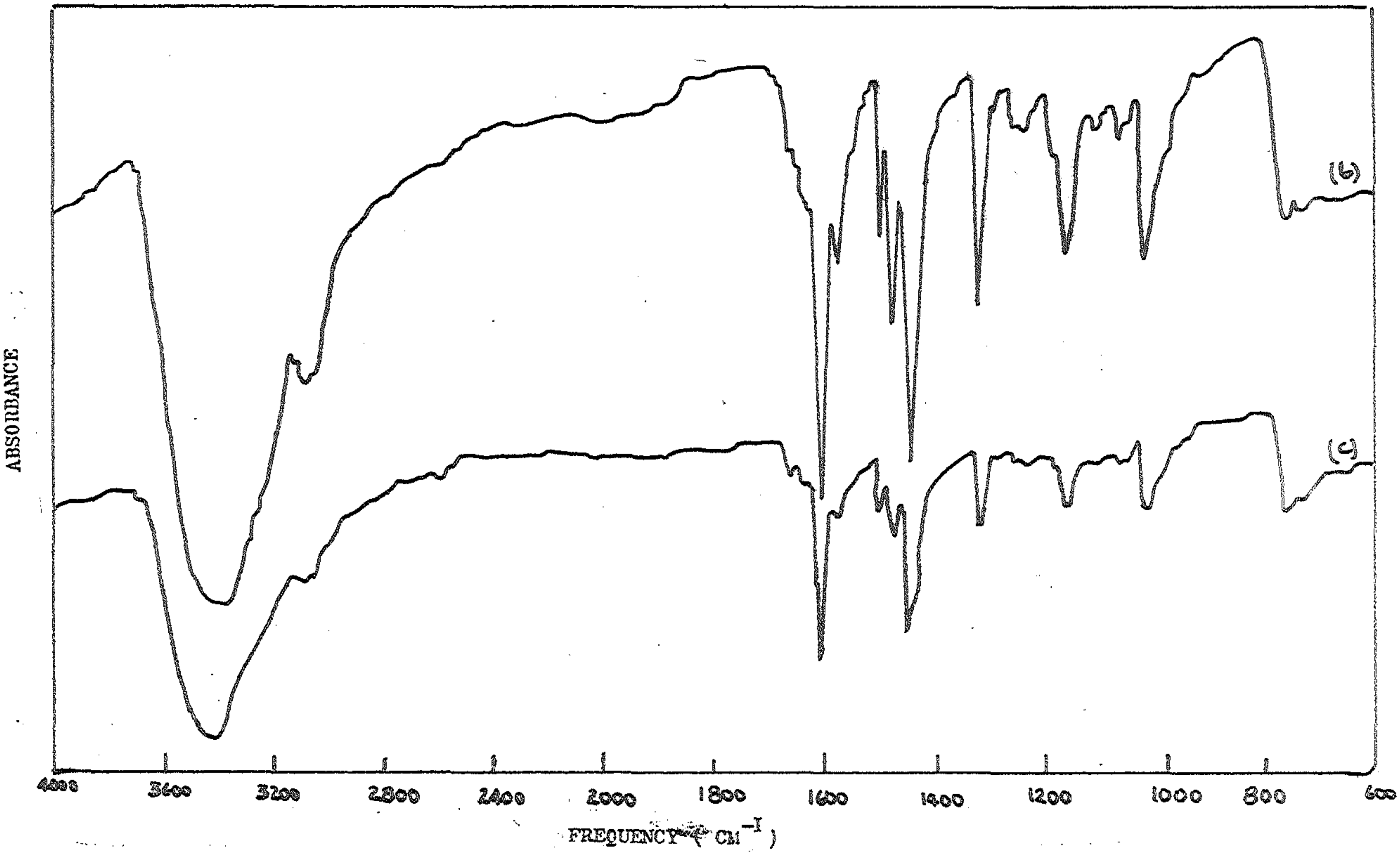
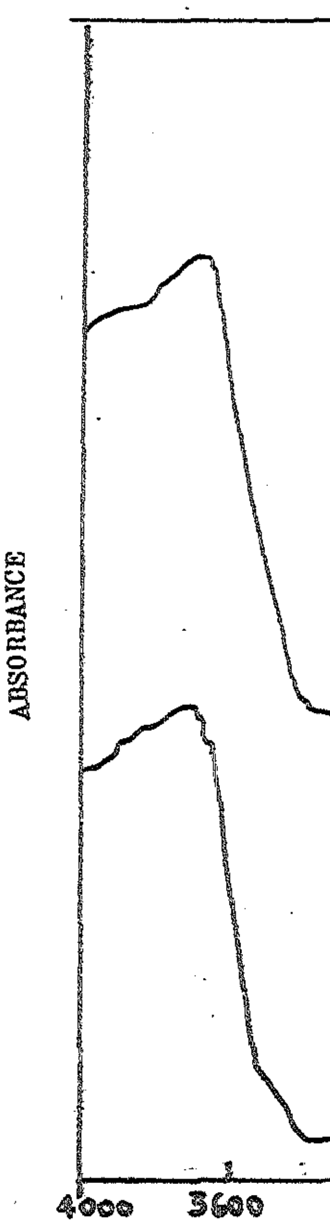


Fig. 10 IR spectra of (b) Ni:bipy:urea (1:2:1), (c) Ni:bipy:malonamide(1:2:1) in KBr.


ABSORBANCE
4000
3600

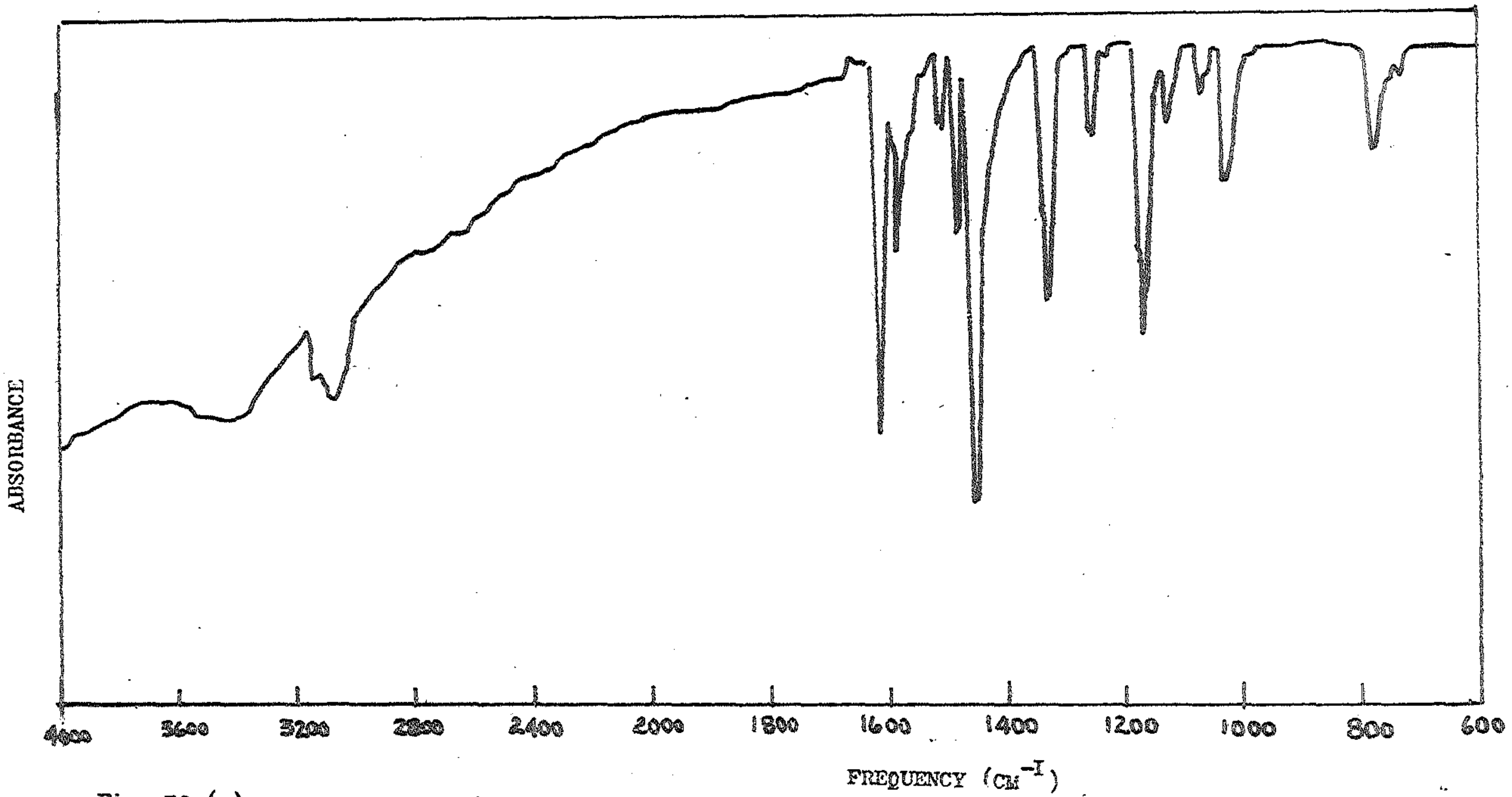


Fig. I2 (a) IR spectra of Cu(bipy)Cl$_2$ in KBr

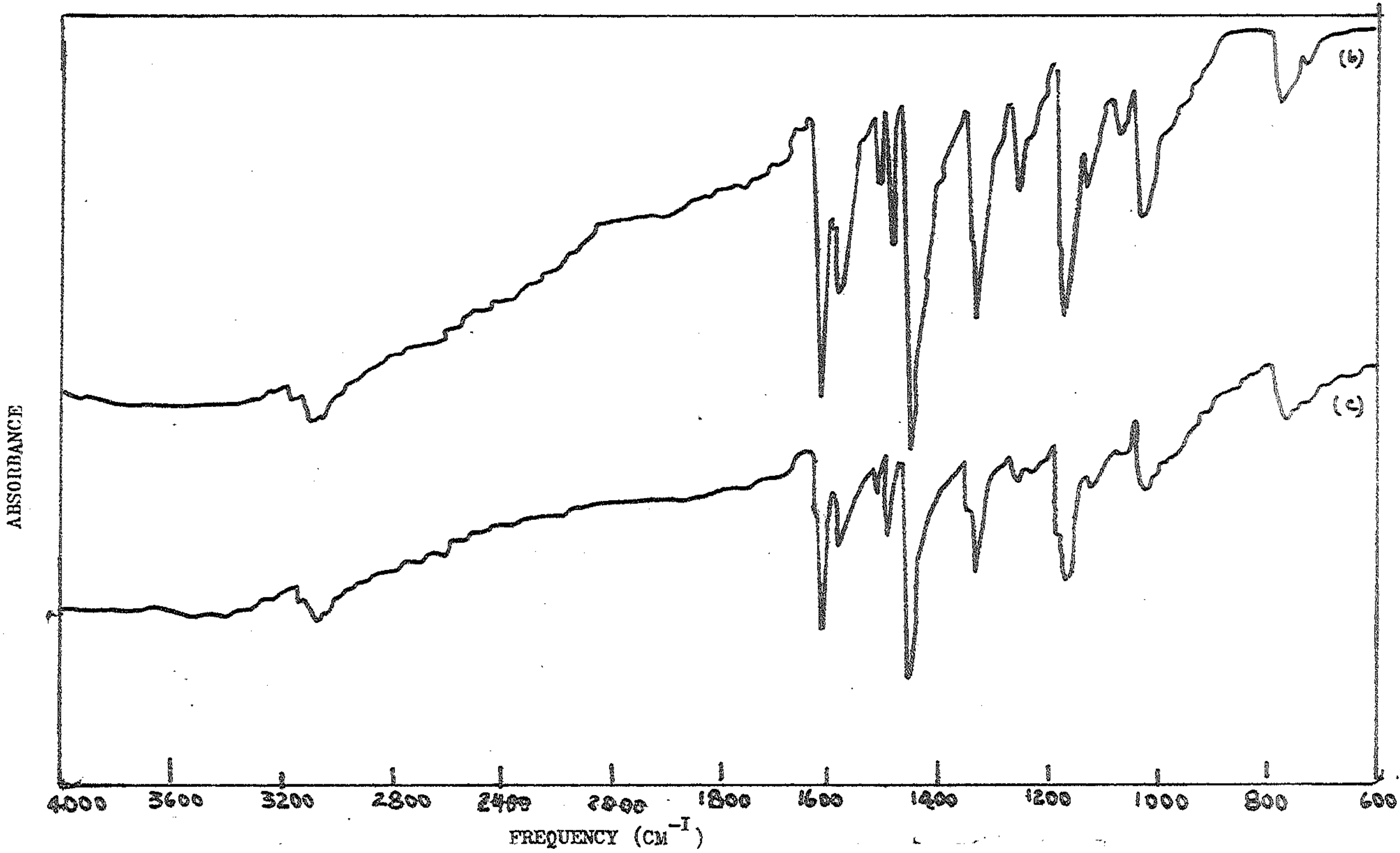


Fig. I2 IR spectra of (b) Cu:bipy:urea (I:I:I) , (c) Cu:bipy:MA (I:I:I) in KBr

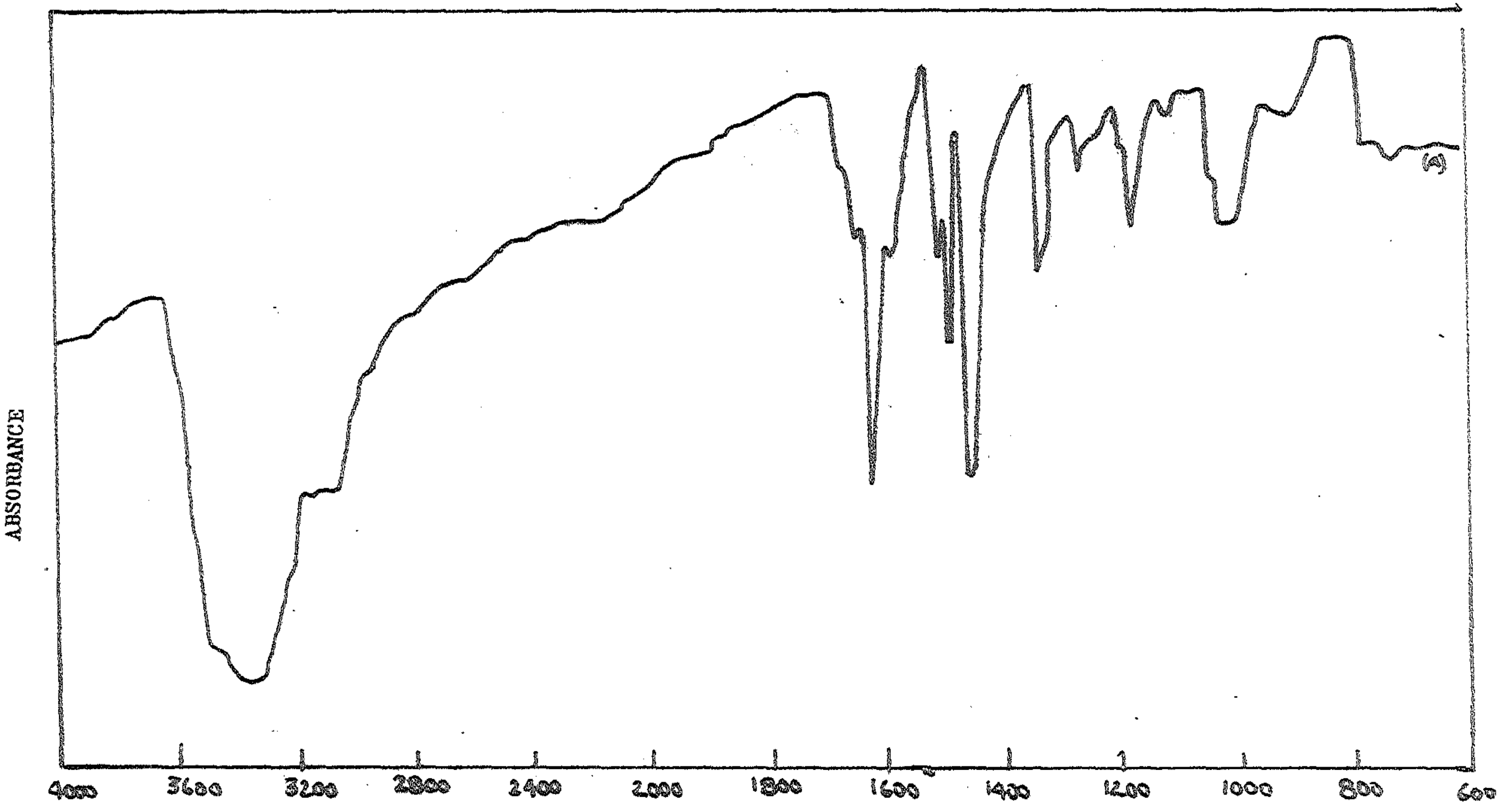


Fig. 13 (a) IR spectrum of Cu(bipy)(OH)Cl.H_2O in KBr

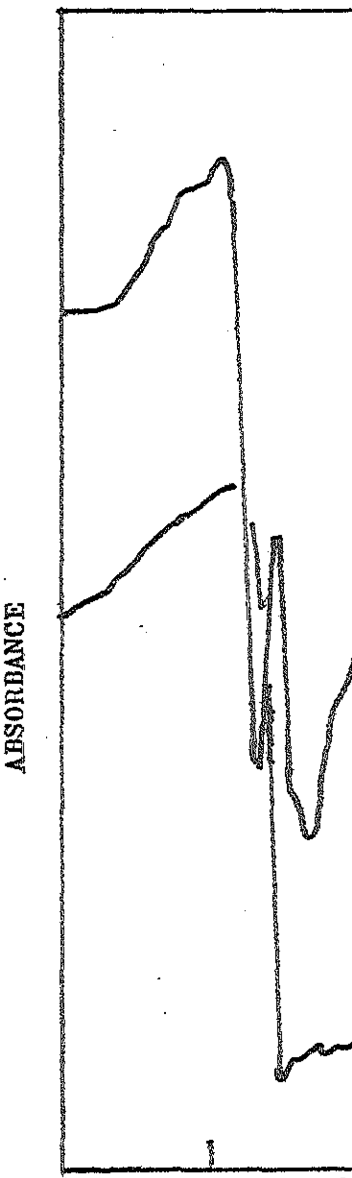
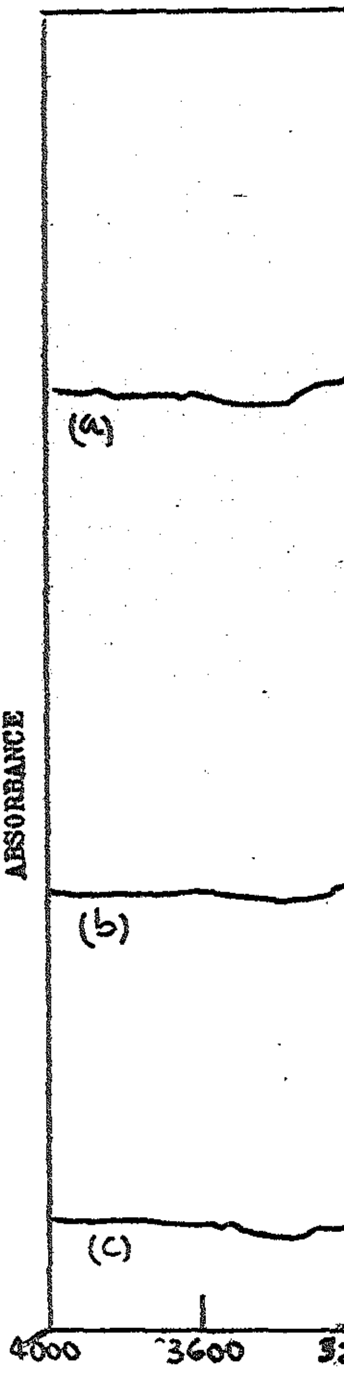


Fig. 13


ABSORBANCE
(a)
(b)
(c)
4000
3600

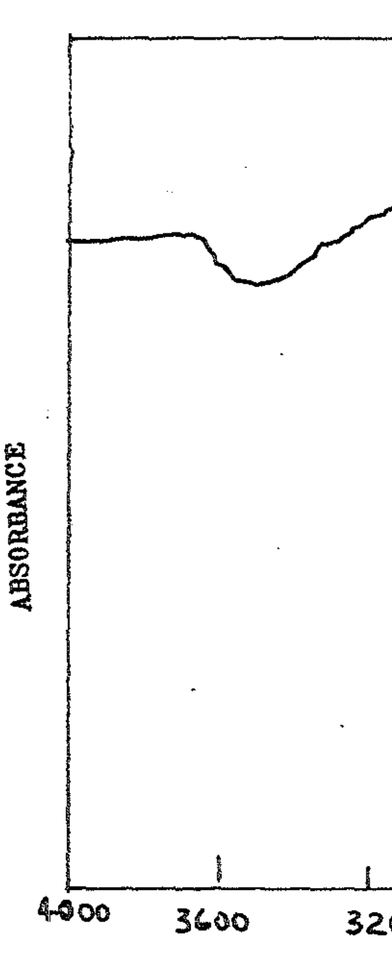


Fig. I5 IR

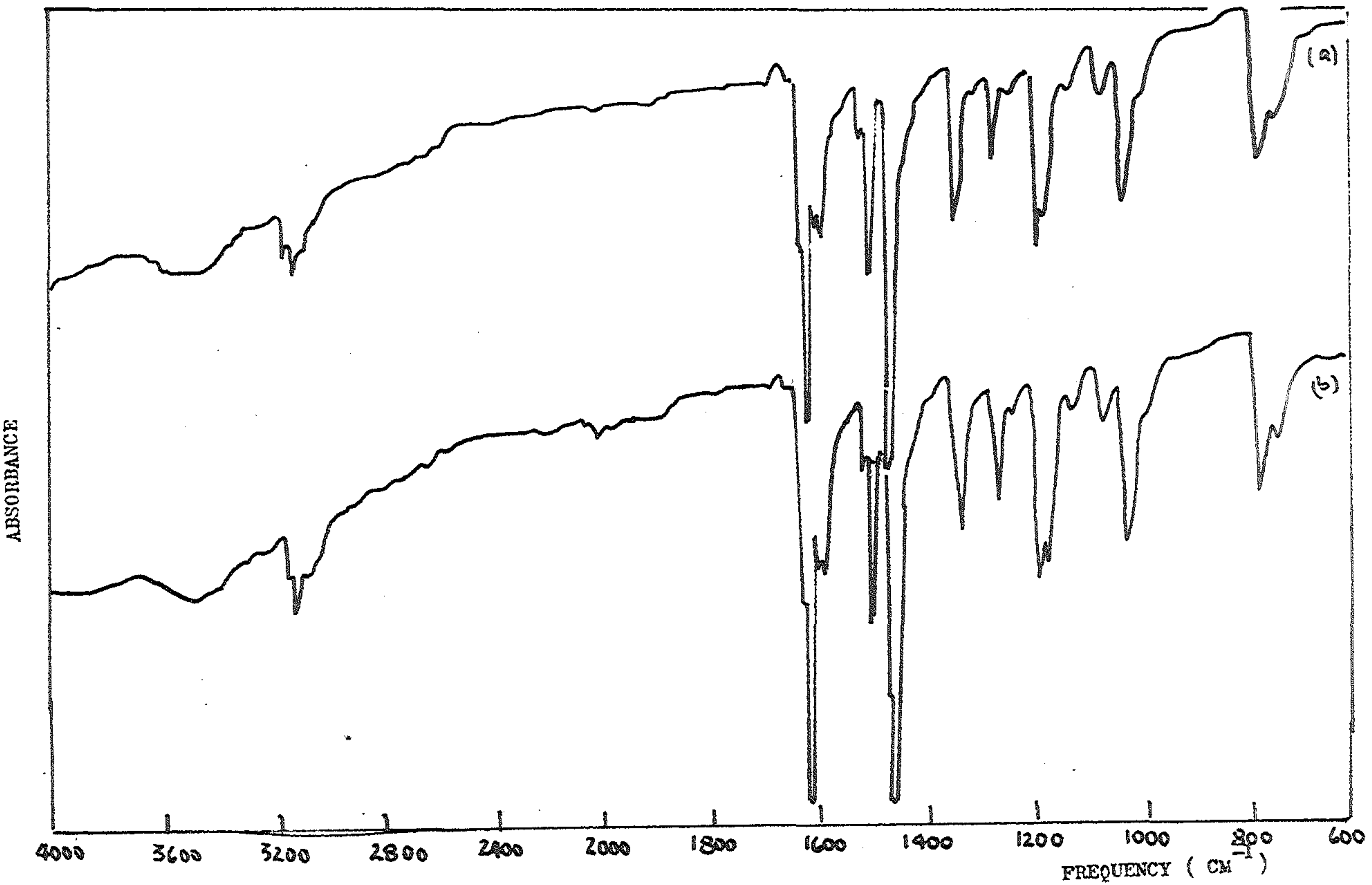


Fig. I6 IR spectra of (a) Cd:bipy (I:I) , (b) Cd:bipy:urea (I:I:I) in KBr

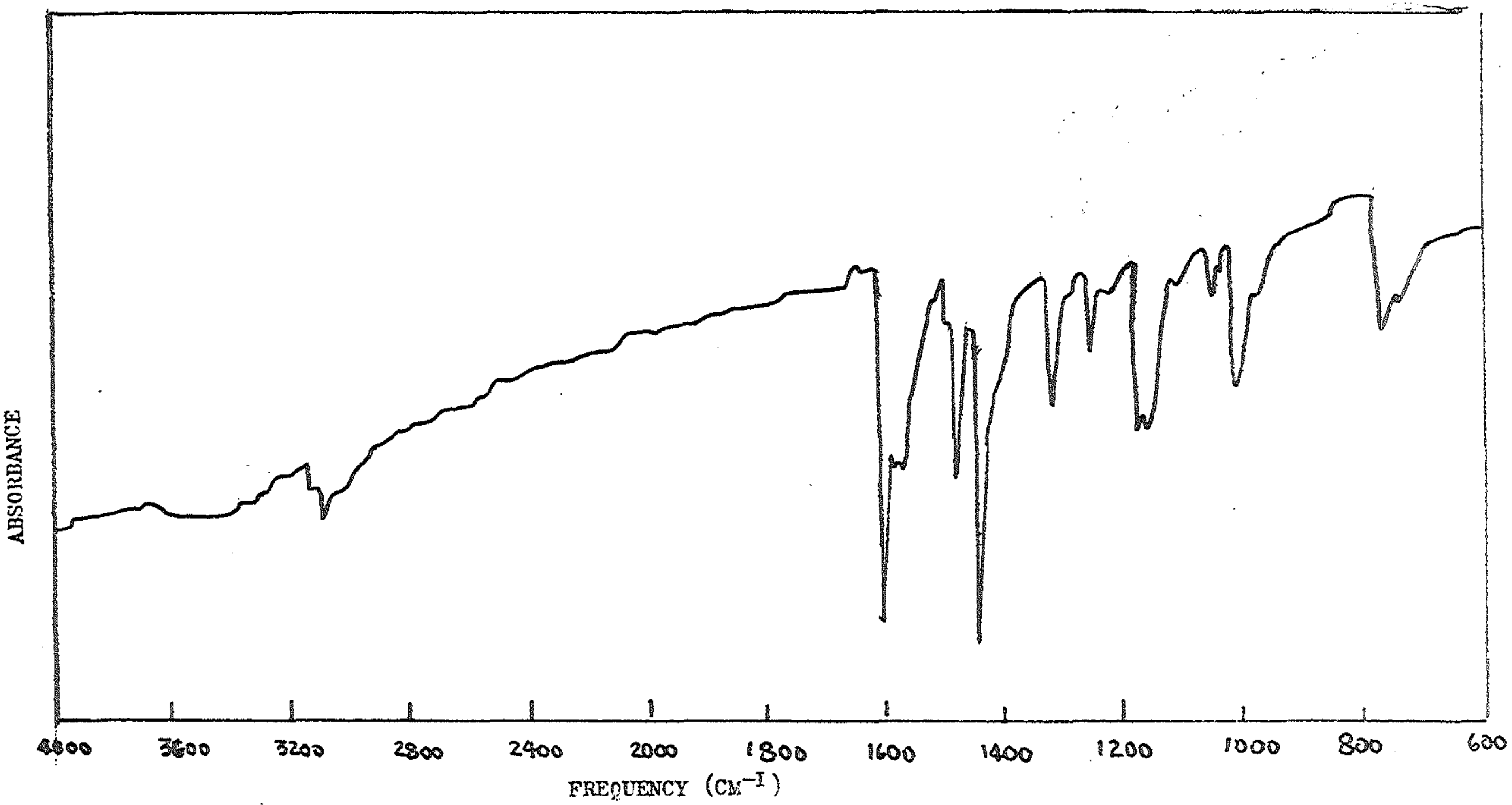


Fig. I7 IR spectrum of Cd:bipy:malonamide (I:I:I) in KBr.

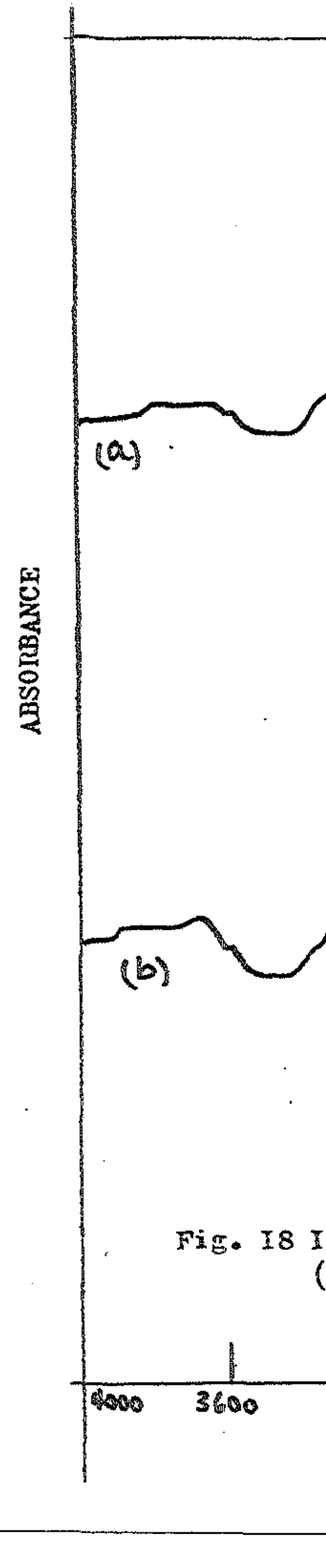
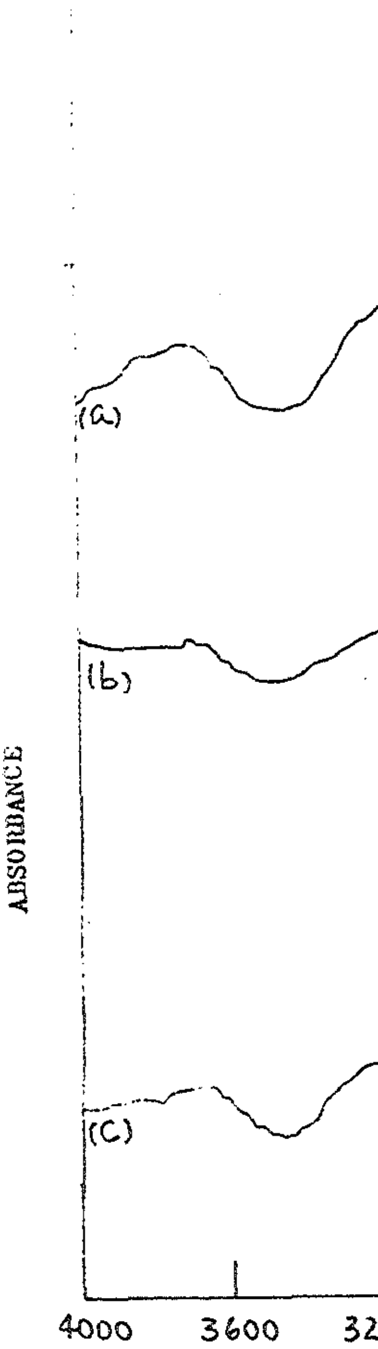
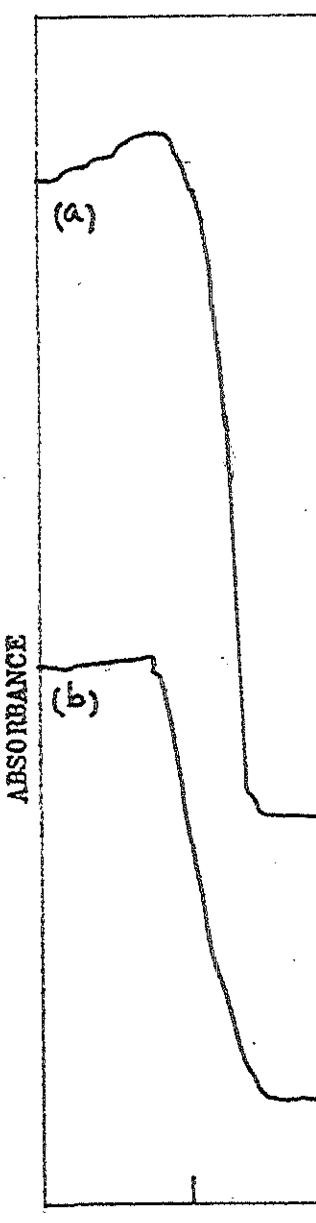
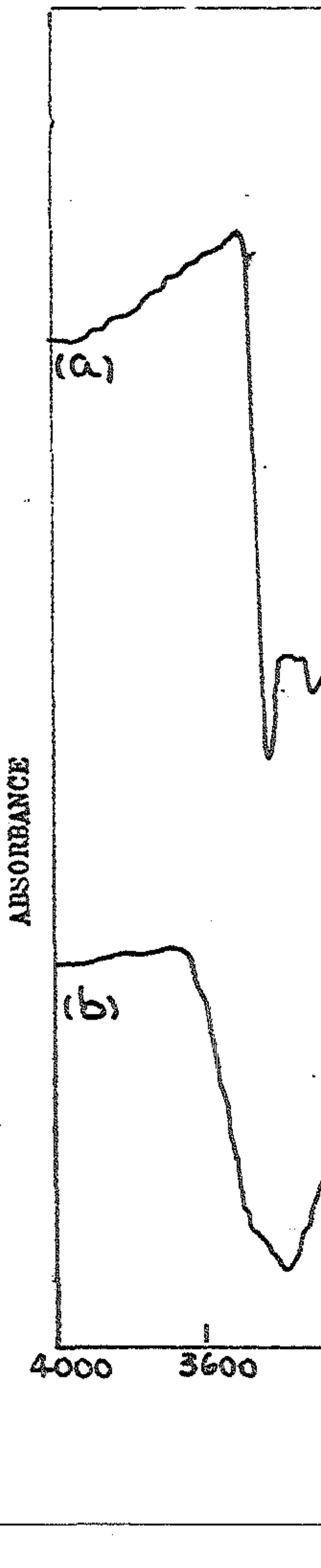
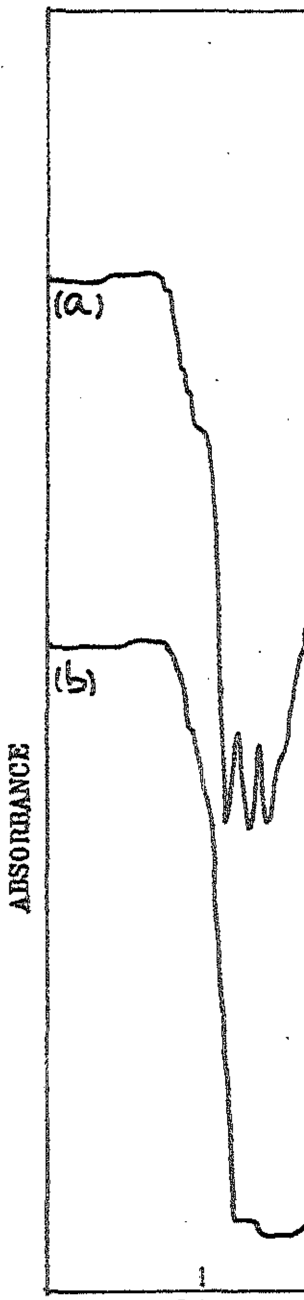


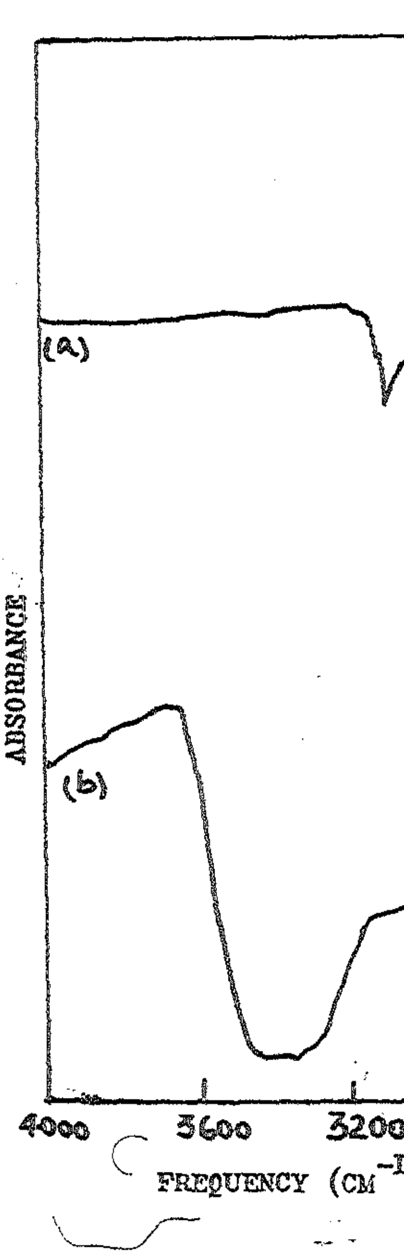
Fig. I8 I
(


ABSORBANCE
(a)
(b)
(C)
4000
3600
32


(a)
(b)
ABSORBANCE
4000
3600


ABSORBANCE
(a)
(b)
4000
3600


(a)
(b)
ABSORBANCE
4000
3600


(a)
(b)
ABSORBANCE
4000
3600
3200
FREQUENCY (CM^{-1}

Tab

	Comp
1	Cu(bip
2	Cu(ure
3	Cu(MA)

* M

Table I.

	Compound
4.	$Cu(urea)_4$
5.	$Cd(MA)Cl_2$
6.	Cd(urea)Cl

*

Table 2.

	Compou
I.	Cu(bipy)
2.	Cu(urea)
3.	$Cu(MA)_2$
4.	Cu(urea
5.	Cd(urea

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valine)[25] are reported. Ternary complexes of Cu(II) and Ni(II) with bipyridine and substitued salicylic acid were studied by potentiometric technique.[26]

Uncharged complexes of the type $M(phen)_2(NCS)_2$, (M=Ni(II) and Cu(II))have been prepared both from aqueous and non-aqueous system.[27]

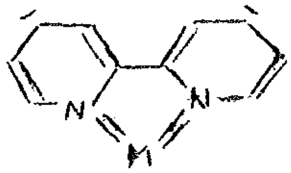
The mixed complexes of $[Ni(phen)(N\text{-}R\text{-}Salicylaldimine)_2]$,$Ni(phen)_2(Salicylic\ acid)_2 \cdot 3H_2O$ and Ni(phen) (Salicyläldimine) (Sal)$\cdot 3H_2O$ were synthesised in benzene.[28]

The mixed ligand complexes MAL (M = Ni(II); Cu(II); Zn(II) or Cd(II); A = bipyridine or phenanthroline and L = ethylene diamine or propolyne diamine) were studied in solution by Parikh and Bhattacharya.[29]

The mixed ligands $[Ni\ (phen)_2][Ni(CN)_4]\cdot 4H_2O$ and $Ni(phen)_3(CN)_2\cdot\ H_2O$ are reported by Schilt.[30]

The major factor for electron pairing and strong covalent bonding with many of the bipyridine and phenanthroline complex was syggested by Nyholm[31-32] to be the formation of double bonds, and suggested that structures (III) and (IV) contribute to the resonance hybride.

(III)



(IV)

Similar structures can be written for the phenanthroline compounds. Thus, the double bonds are indicated to account for the stability of some bipyridine and phenanthroline complexes.

Bipyridine reacts slower than does phenanthroline, but this difference only in small degree accounts for the lower stability of bipyridine complexes.[33]

Since bipyridine and 1,10-phenanthroline are bidentate ligands it might be reasonable to assume the complex formation with a metal ion to proceed in a step wise fashion, one nitrogen-metal bond forming in each step, with the replacement of one coordinated water molecule. Usually this stepwise replacement of water molecules by a chelate formation would be expected to follow in rapid sequence with no way of distinguishing the individual steps. However, it is possible to postulate an acid catalysis where the intermediate formed by the replacement of one water molecule goes to product faster by elemination of hydronium ion.[34]

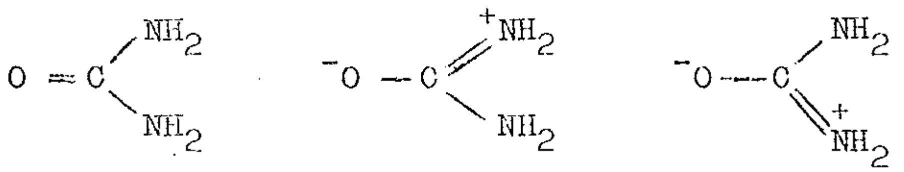
2.2 Complexes of Urea and Malonamide

Urea is the amide of the carbonic acid and therefore it is sometimes called carbamide. Urea, $CO(NH_2)_2$, is both a weak acid and a weak base, the basic dissociation constant

$$CO(NH_2)_2 + H_2O \rightleftharpoons H_2NCONH_3^+OH^-$$

is about 10^{-14}, similar to that of water.[35] Urea forms rather weak complexes in water. Urea has two possible sites of coordination, namely the amine nitrogen and the carbonyl oxygen.

Vaughan and Donohue[36] considered the structure of urea to involve resonance between the three following structures, the observed values of the interatomic distance indicating 30% double bond



character for the carbon-to-nitrogen bond leaving 40% for the carbon-to-oxygen bond. The donor atom with Cu(II) and Zn(II) is the oxygen atom.[37] However, in some instances urea coordinates through the nitrogen atom with Pt(II) and Pd(II). Hence, by observing the presence or absence of a carbonyl IR band near 1700 cm^{-1}

and by the presence or absence of shifted NH_2 peaks, the urea complexes have been divided into two groups, one with nitrogen and the other with oxygen as the donor atom.

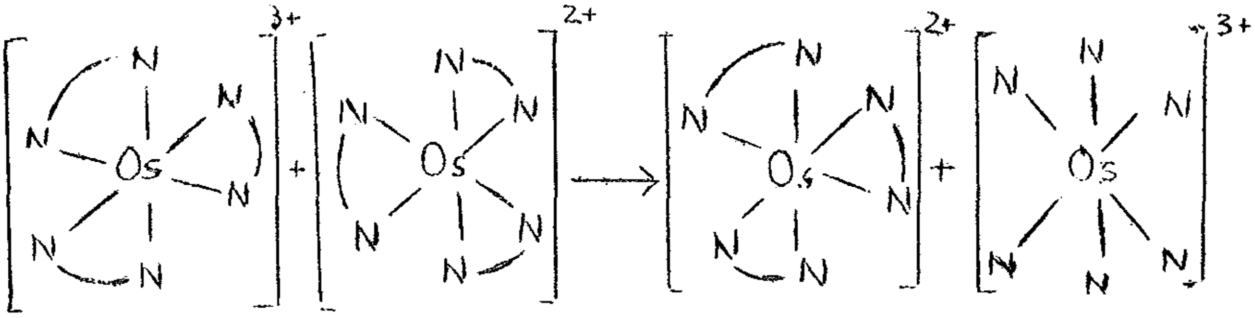
Stable complexes formed from metal salts with 2,4, or 6 moles of urea are known. Complexes of urea with nickel, copper, zinc and cadmium are reported in the literature.[38-43] In the system urea-$CuCl_2$ and urea-$NiCl_2$, the complexes detected were $CuCl_2 \cdot 2CO(NH_2)_2$; $NiCl_2 \cdot 2CO(NH_2)_2$ and $NiCl_2 . 10CO(NH_2)_2$. The spectrum of $CuCl_2 \cdot 2CO(NH_2)_2$ showed that the urea coordinates through the oxygen atom.[44] As it was observed that the C-O stretching vibration decreases by 50-60 cm^{-1}. In the system $CdCl_2$- urea in aqueous medium, the cadmium coordinates to six urea molecules.[44] But in the system $CdCl_2$-urea-methanol and $CdCl_2$-urea-ethanol the existence of complexation in the ratios 1:1 and 1:4 was established.[45]

Malonamide or propanediamide, $CH_2(CONH_2)_2$, is the derivative of malonic acid. Complexes of malonamide are not widely reported in the literature. Copper coordinates with only one or two molecules of malonamide forming $CuCl_2L_2$ (L = Malonamide)[46]. Nickel chloride forms $NiCl_2L_2$ and the stability of the coordinate bond decrease in the series $Fe < Co < Ni < Cu$.[47-48] The ligand coordinates through the oxygen atom. The complex CdX_2L_2 (X = Br, NCS; L = malonamide) is also reported[49] and it is known that the malonamide coordinates through the oxygen atom. Aggarwal and coworkers[50] also reported the synthesis and characterization of the complexes $NiLCl_2$ and $CuLCl_2 \cdot H_2O$ in alcoholic medium (L = malonamide).

2.3 Reaction Mechanism of Complex Compounds[51-52]

There are several mechanisims for complex compounds. They are generally classified as (i) electron transfer reactions (ii) substitution reactions (iii) molecular rearrangment and (iv) reaction of coordinated ligand.

(i) Electron transfer reactions are those reactions termed as oxidation reduction reactions in which there is a change in the formal oxidation state of the reacting substances involved. However, there are two types of reactions that fall within the scope of the redox process; reactions involving simple electron transfer and reactions that can be considered as atom transfer reactions both with or without electron transfer. The two reactions can be illustrated by the following two reactions.[53]



Where N͡N is 2,2'-bipyridine. The two chiral reactants do not themselves racemize, but when they are mixed, electron transfer leads to a rapid loss of optical activity.

$NO_2^- + OCl^-$ --------> $NO_3^- + Cl^-$

The oxidation state of nitrogen changes from + 3 to +5 while chlorine changes from 1 to -1. Electron transfer reactions may occur by either or both of the two mechanismes known as outer sphere and inner sphere. Outer sphere mechanism involves electron transfer from reductant to oxidant, with the coordination spheres of each staying intact. Inner sphere mechanism on the other hand, is one in which the reductant and oxidant share a ligand in their inner or primary coordination sphere, the electron being transfered across a bridiging group.

(ii) Substitution reactions are reactions where the ligand-metal bond is broken and a new one is formed instead. The mechanism of substitution reactions are thoroughly studied for square planar complexes like those formed by Pt(II) and other d^8 systems. Though Ni(II) belongs with Pt(II) to the same group, more often it forms tetrahedral complexes and it is found that it can undergo substitution reactions 10^6 times more rapidly than Pt(II) complexes.

In such reactions usually the factors influencing the reactivity of the complex are the nature of the entering groups, the position (cis or trans) of other groups, the nature of the incoming group and, of course, the nature of the central metal ion.

The majority of complexes formed by transition metals are, however, octahedral, so their substitution reactions are extremely important. Reaction at square planar centres occur by association addition but in octahedral complex this is not possible because additional coordination positions are not available and so substitution occurs by dissociative activation.

Studies on octahedral complexes have been largely limited to two types of reactions:

i. Replacement of coordinated solvent e.g.

$$[Ni(H_2O)_6]^{2+} + bipy \longrightarrow [Ni(H_2O)_5\ (bipy)]^{2+} + H_2O$$

ii. Hydrolysis: e.g.

$$[Co(NH_3)_5(OSMe_2)]^{3+} + H_2O \dashrightarrow [Co(NH_3)_5(H_2O)]^{3+} + Me_2SO$$

There is significant contribution to the activation energy in substitution reactions by the change in the energy of the d orbitals on going from the ground state to the transition state. Any loss in energy is presumed to be proportional to the activation energy. The kinetic lability or innertness of a complex depends on the struture preference energy, SPE, of the octahedron and a transition state; if the structure preference energy is less than some arbitrary value, the complex is predicted to be labil, but if the structure preference energy is less than that value, the complex will be inert.[51]

(iii) Molecular rearrangement reactions are reactions in which the ligands of the first coordination sphere remain attached to the central metal ion but rearrangement of these ligands occurs.[51] This may lead either to cis-trans isomerization or to a change in chirality, or both. The possibility of rearrangement obviously has a bearing on the synthesis of coordination compounds.

(iV) Reactions of coordinated ligands are reactions that occur at the coordinated ligands themselves.[51] A metal ion should be able to influence strongly the reaction at the coordinated ligands, as compared to the uncoordinated ligand. This is caused by changes in in intra-ligand charge distribution, by both sigma withdrawal and by pi donation or withdrawal.

Coordination of ligands to metal ions also place them in the correct geometry for their later union, thereby, the course of their reaction is changed.

2.4 Solvent Effect

The nature of the metal is the foremost factor that affect the stability of complex ions, but the nature of the donor group and the solvent are also influential. Since most reactions are carried out in the liquid phase the effect of the solvent has a determining effect in the the path way of a reaction. The way in which the rate constant vary may depend in the nature of the solvent. In many reactions, the solvent plays an important role by participating intimatly in the rate controlling step of the reaction.

The solubilization of a solute will occur when the attraction force between the solvent molecules and solute molecules are greater than those between the solvent molecules themselves and between the solute molecules themselves. These solvent-solute attraction may be non specific (van deer Waals and dipolar) or specific (with an identifiable acid-base interaction between solute and solvent). The terms specific and non specific suggest solvation by a specific donor orbital-acceptor orbital interaction or by more general way intermolecular attraction respectively.

The heterolytic cleavage of solute bonds to form ionic species in solution is another very important aspect of the solvent solute interaction. This requires efficient ion separation and solvation. Therefore, the type of species that form in solution are largely determined by the properties of the solvent.

One characteristic of a solvent that is of a great importance in causing ion formation by a solute is the dielectric constant of the solvent. The dielectric constant is defined in terms of the medium ability to weaken the forces between two ions:

$$F = (q_1 q_2/r^2)\ (1/\varepsilon)$$

where ε is the dielectric constant of the medium. The conclusion is then that a high solvent dielectric constant tend to support a high degree of solute ionization. Hence the solvent choice for synthetic work is of paramount importance. As an example for donor ligands, a suitable solvent would be one that makes the ligand more basic or less acidic.

2.5 Donor Acceptor Properties[54]

Few concepts have been so enduring as the concept of acids and bases. In the modern concept acids are molecules with a relatively low energy LUMO and fairly high - lying HOMO. The HOMO depends on the base, but most often is an sp^n lone pair.

The amines and ammonia are among the most commonly recognized and generally the strongest of the nitrogen donors. As a class the pyridines are of intermediate basicity.

Many examples of oxygen as a donor can be sited, e.g. water, ethers, ketones, phosphine oxides, etc.

Metal cations, on the other hand, are widely known to act as acids, because they accept electrons from the donor atoms into their d orbital systems or in higher orbitals. This is, then, the basis for a great deal of transition metal ion chemistry.

In the electrochemical series, where the ligands of MD_6 (M = metal ion, D = ligand) are arranged in order of increasing Δo (Δo = splitting energy) a rough single scale of metal-ligand interaction is possible. Bipyridine and phenanthroline come higher than pyridine and ammonia in the serries.

... Pyridine $\sim NH_3 <$ en $<$ bipy $\sim$ phen

The higher positions of bipyridine and phenanthroline are believed to be due to the weaker Pi donor character and stronger Pi acceptor nature of the more delocalized amines. In bipyridine and phenanthroline, the delocalization over an extended carbon frame tends to lower the energy of both π - HMO and π - LUMO.

The stability of a complex is also affected to a great extent by steric factors. The clashing of groups on one or two coordinating ligands results in distortion of bond angles and a decrease in stability. The substituted 2-methyl-1,10-phenanthroline forms weaker complexes with the ferrous ion[55]. This is due to steric hindrance to coordination which increases with further substitution to such an extent that the 2,9-dimethyl phenanthroline does not form complexes with iron. Similarly, the same effect is observed in 6,6'-dimethyl 2,2'-bipyridine which has a low coordinating ability compared to the unsubstituted 2,2'-bipyridine.[56] According to the literature survey done it was found that binary complexes of bipyridine and phenanthroline with the metal ions Ni(II), Cu(II) and Cd(II) are reported. Similarly the binary complexes of these metal ions with urea and malonamide are also reported. However, mixed ligand oomplexes of these metal ions with bipyridine: urea, bipyridine: malonamide, phenanthroline: urea and phenanthroline: malonamide are not reported. Hence, the objective of this investigation is to attempt the synthesis of such mixed ligands complexes.

To effect the synthesis of these complexes, the visible spectra of solutions of the metal ions with the ligands in different molar ratios at different pH will be invistigated. The effect of thermal treatment will also be invistigated spectrophotometrically. The results of such investigations will give a clue as to the optimum conditions to carry about the actual synthesis in the aqueous medium.

As solvents have an effect on the course of chemical reactions the synthesis will also be attempted in alcoholic medium. Suitable procedures of synthesis will also be adapted from the literature.

For the charactrization of the isolated complexes, the metal content, nitrogen content and chlorine content will be analysed. IR and NMR spectra will be recorded. On the basis of these, molecular formulas will be assigned for the isolated complexes.

3. EXPERIMENTAL

3.1 General

All the complexes were stable to oxidation and hydrolysis and were handled in air and synthesised in aqueous midium at pH between 2.0 and 5.0. As bipyridine and phenanthroline are insoluble in water, they were first dissolved in a minimum quantity of ethanol and then water was added. In the synthesis in alcoholic medium the methanol and ethanol were taken in the ratio (v:v) 50:50.

3.2 Reagents and Equipments

All solvents used were purified before use. The ligands used were 1,10-phenanthroline (Sigma, AnalaR), 2,2'-bipyridine (BDH, AnalaR), urea (reagent grade) and malonamide that was synthesised from diethylmalonate and concentrated ammonia solution in the ratio 1:3 by volume as described in the literature.[57]

The metal halides used were $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $CdCl_2.2H_2O$ which were all of reagent grade.

The IR spectra of the compounds were measured over the range 4000 cm^{-1} to 600 cm^{-1} on an IR-spectrometer Perkin Elmer 727 B in KBr. The visible spectra were recorded on a Beckman Model spectrophotometer.

The 'H NMR were recorded on a 60 MHz Varian T-60 A proton nuclear magnetic resonance spectrometer. The pH of solutions were adjusted by a BECKMAN Chem-Mate pH Meter. In the determination of chlorine Philips PW 9418 pH meter was used.

3.3 Elemental Analysis

Nitrogen was determined by the Kjeldahl method.[58] In all cases 0.2 g of commercial Kjeldahl catalyst containing $CuSO_4$ and 5.0 g of potassium sulfate were added and the sample digested with concentrated sulfuric acid.

Nickel was determined gravimetrically by precipitation with dimethylglyoxime.[59] Copper was also determined gravimetrically by precipitation as a complex of benzoin-α-oxime.[60] Cadmium was determined gravemitricaly by precipitation with pyridine and ammonium thiocyanate.[61] Complexes that were not soluble in water were first digested in concentrated HCl, diluted and then the analysis attempted.

Chlorine was determined with a chloride sensitive electrode.[62] A series of KCl solutions in 10^{-2}M KNO_3 solutions were prepared and the potential reading for each solution was recorded from which a calibration graph of potential versus pCl was drawn. Known concentrations of the samples were prepared and the potential of each solution recorded. From the calibration graph, the concentration of the chloride ions were determined, and from this the chlorine percentage in the samples was calculate.

3.4 Preliminary Spectroscopic Studies of Bipyridine Complexes

3.4.1 Ni: bipy (1:2) Different solutions of $NiCl_2.6H_2O$ and bipyridine in the molar ratio 1:2 were prepared by mixing 2.5 ml of 0.002M solution of nickel chloride solution with 5 ml of 0.002M solution of bipyridine, and the pH of the solutions were adjusted to 2.0, 3.0, 4.0, 5.0, 7.0 and 9.0 using diluted HCl and diluted NaOH solution. The visible spectra of these solutions were recorded in the range 700 to 400 nm. All the solutions were found to absorb at 515 nm. and the highest absorbance was observed for the solution with pH 2.0. For the other solutions the absorbance decreased with increasing pH; the color of the solutions was pink. The spectra appears as Fig. 1.

3.4.2 Ni: bipy: urea (1:2:1) Different solutions of nickel chloride, bipyridine and urea in the molar ration 1:2:1 respectively, were prepared as in the above case (3.4.1). The pH were adjusted to 2.0, 3.5, 4.5, 6.0, 7.0, 8.0 and 9.0. The visible spectra were recorded and all the solutions were found to absorb at

520 nm. The absorbance was highest for the solution with pH 2.0. The color of the solutions was pink. The spectra is given as Fig. 2.

3.4.3 Ni: bipy: malonamide (1:2:1): Six solutions of nickel chloride, bipyridine and malonamide in the molar ratio 1:2:1 were prepared. The pH were adjusted to 2.0, 3.0, 4.0, 5.0, 6.2, 7.5 and 11.0. The visible spectra was recorded. A broad peak at about 510 nm was observed for all solutions, with the solution of pH 4.0 having the maximum absorbance. It was also observed that the absorbance decreased with increasing pH, the solution with pH 11.0 having the lowest absorbance. The spectra is given as Fig. 3.

The solution with pH 4.0 was then heated for one hour at 80°C and the spectrum was taken again. However, no change in the λ_{max} was observed.

3.4.4 Cu: bipy (1:1) Solutions of $CuCl_2 2H_2O$ and bipyridine in the molar ration 1:1 were prepared by adding 5 ml of 0.01 M solution of $CuCl_2.2H_2O$ to 5.0 ml of 0.01 M bipyridine and the pH adjusted to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 10. The visible spectra were taken. Solutions with pH less than 7.0 absorbed at 660 nm; for solutions with pH 7.0 and above the absorbance shifted to shorter wave length. The solution with pH

7 absorbed at 625 nm and the solution with pH 11 absorbed at 610 nm. For solutions with pH less than 7.0, the highest absorbance was for solution with pH 2.0. The color of all the solutions range from light blue to dark blue. The spectra are given as Fig. 4.

3.4.5 <u>Cu bipy: urea (1:1:1)</u> Four solutions with pH 2.0, 3.0, 7.0 and 11.0 were prepared in the manner described above. The color of the solutions was blue. The visible spectra were taken. The addition of urea to the Cu:bipy solution broadened the band; otherwise the value of λ_{max} are the same. These solutions were then heated for one hour at 80°C in which case the peak for the solution with pH 11 broadened very much. But no change was observed in the other peaks. The spectrum is shown as Fig. 5.

3.4.6 <u>Cu: bipy: malonamide (1:1:1)</u> Six solutions of identical concentrations were prepared by mixing 5 ml of 0.01 M solution of $CuCl_2 \cdot 2H_2O$, bipyridine and malonamide. The pH of the solutions were adjusted to 2.0, 3.6, 5.8, 7.0, 10.0, and 11.3. The color of solutions was blue. Solutions with pH less than 7.0 have similar spectrum and absorb at 670 nm. For solutions with pH greater than 7, the wavelength shifts to shorter wavelength. Solutions with pH 7 absorbs at 625 nm. Solution with pH 10 absorbs at 610 nm. Solution with pH

11.3 absorbs at 610 nm, but the band is broad. The spectrum is given as Fig. 6.

3.5 Preliminary Spectroscopic Studies of 1,10-Phenanthroline Complexes

3.5.1 Ni: Phen(1:1). Five solutions of nickel chloride and phenanthroline were prepared by mixing 10 ml of 0.01 M, $NiCl_2.6H_2O$ and 10 ml of 0.01 M phenanthroline. The pH of the solutions were adjusted to 2.0, 5.0, 8.5 and 10.0. The solutions were light pink in color. The maximum wavelength at which all the solutions absorb was 515 nm. For solutions with higher pH i.e. 8.5 and 10.0, however, the band broadens. The pink color of the solution disappeared leaving a colorless solutions when the solutions were left overnight. In the two solutions with pH greater than 7.0 a bluish suspension was formed. The spectrum is given as Fig. 7.

3.5.2 Ni:Phen: urea (1:1:1) Four solutions of nickel chloride, phenanthroline and urea in the molar ration 1:1:1 were prepared by mixing 5 ml of 0.01 M of each. The pH was adjusted to 2.2, 6.0, 8.5 and 11.0 and the visible spectra were recorded. All four solutions absorb at 515 nm and with increasing pH the band becomes broad. The solutions were pink in color. The spectrum is given as Fig. 8.

3.5.3 Ni: Phen: malonamide (1:1:1) Three solutions were prepared as described above. So were the pH adjusted to 2.2, 5.3 and 10.7 and the visible spectra were taken. All the three solutions absorb at λ_{max} 515 nm with a broad band. The three solutions have a pink color. The spectrum is given as Fig. 9.

4. SYNTHESIS IN AQUEOUS MEDIUM

4.1 Nickel Complexes

4.1.1 Ni: bipy (1:1) A 0.01 mole of $NiCl_2.6H_2O$ was reacted in water with 0.01 mole bipyridine dissolved in 10 ml ethanol and 20 ml water. The solution was first pink. Then changed to blue on heating. After concentration and cooling no crystals were isolated. The visible spectrum was recorded and was found to absorb at 560 nm.

In another experiment the same stoichiometric quantities were refluxed for three hours; however, the product was the same, and the complex remained in solution.

In another experiment 0.01 mole $NiCl_2.6H_2O$, 0.01 mole bipyridine and 0.04 moles urea were then mixed and the solution was refluxed for three hours. The result obtained was the same as the one above.

Similarly the reaction between $NiCl_2.6H_2O$, bipyridine and malonamide was also investigated, and the result were the same.

4.1.2 Preparation of Dichlorotris (bipyridine) nickel(II) hexa-hydrate: $Ni(bipy)_3Cl_2.6H_2O$

0.2377 g of $NiCl_2.6H_2O$ (0.001 moles) was dissolved in

30 ml distilled water and mixed with 0.3124 g of bipyridine (0.002 moles) dissolved in 10 ml ethanol and 20 ml water. The color of the solution was pink. The pH of the solution was adjusted to 2.0 with diluted HCl. The solution was slowly concentrated by evaporation and then cooled. After cooling overnight pink crystals were formed. The yield was 0.15 g (32%). Melting point: at 175°C changes to green and does not melt up to 300°C. Elemental analysis: found % (calculated%) Ni: 9.97 (8.31); N: 10.82 (11.89), Cl: 10.60 (10.05); Visible spectrum λ_{max}: 515 nm.; IR spectrum: given as Fig. 10 (a).

3400 cm^{-1} (O-H str.), 3100 cm^{-1} (C-H str.)
1600 cm^{-1} (C=N str.;), 1480 cm^{-1}; (C-H bending)
1020 cm^{-1} (ring vibr), 760 cm^{-1} (C-H out of plane def.)

Solubility: It is insoluble in CH_2Cl_2, $CHCl_3$, and CCl_4, but soluble in CH_3OH, H_2O, DMSO. Water loss: 16.01% (cal. 15.29%).

4.1.3 Attempt to prepare Dichlorobis(bipyridine) mono urea nickel(II)·$[Ni\ (bipy)_2(urea)]Cl_2$

1.188 g $NiCl_2.6H_2O$ (0.005 moles) and 0.3003 g urea (0.005 moles) dissolved in 50 ml distilled water was mixed with 1.562 g bipy (0.01 moles) dissolved in 10 ml ethanol and 20 ml water, and the mixture refluxed for three hours, after adjusting its pH to 2.0. The solution was concentrated by evaporation and cooled overnitht. It gave pink crystals. Yield: o.7 g (30.4%) melting point: at about 172°C changes to green. Elemental analysis: found %(calculated%); Ni: 9.35 (8.31); Cl: 12.72 (10.05); N: 9.64(11.89). Visible spectrum: λ_{max}: 520 nm. IR spectrum: given as Fig. 10 (b). The spectrum is similar to that of 4.1.2 Fig. 10 (a). Solubility: insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4. Soluble in CH_3OH, H_2O and DMSO. The isolated complex was established to be $Ni(bipy)_3Cl_2.6H_2O$.

4.1.4 Attempt to prepare Dichloro bis(bipyridine) monomalonamide nickel(II) $[Ni(bipy)_2MA]Cl_2.NiCl_2.6H_2O$

bipyridine and malonamide in the molar ratio 1:2:1 were reacted as described above. Pink crystals were isolated. Yield: 0.52 g (22.6%). Melting point: at 170°C changes to green. Elemental analysis: found% (calculated%); Ni: 4.3 (8.31); N: 10.35 (11.89), Cl: 10,14 (10.05%); Visible spectrum: λ_{max} = 510 nm.; IR spectrum: given as appendix Fig. 10(c). The spectrum is similar to that of 4.1.2. Fig. 10 (a). Solubility: insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4, but soluble in CH_3OH, H_2O and DMSO. The complex isolated was established to be $Ni(bipy)_3Cl_2.6H_2O$.

4.1.5 Attempt to prepare Nickel: urea complex Solutions of 2.377 g $NiCl_2.6H_2O$ (0.01 moles) and 0.6006 g urea (0.01 moles) were mixed and the pH adjusted to 2.0. The solution was then refluxed for three hours. After concentration and cooling no crystals were isolated. The color of solution remained throughout green.

In another experiment the amount of urea was increased four times and the solution refluxed for four hours, but result obtained were the same as above.

4.1.6 Attempt to prepare nickel: malonamide complex

2.37 g $NiCl_2.6H_2O$ (0.01 moles) and 1.0209 g malonamide (0.01 moles) were dissolved in 60 ml distilled water, and the bright green solution was refluxed for three hours. On concentration and cooling white crystals were isolated. The crystals were filtered off. The white crystals were established to be malinamide on the basis of melting point and 'H NMR spectrum. The concentration of the malonamide was then increased four times and the experiment repeated, but this did not show any effect on the product.

The reaction between $NiCl_2.6H_2O$, malonamide and urea were also investigated in the same manner described above. No mixed complex was, however, isolated.

4.1.7 Attempt to prepare Dichloro bis(1,10-phenanthroline) nickel hexahydrate: $Ni(Phen)_2Cl_2.6H_2O$. 0.47 g $NiCl_2.6H_2O$ (0.002 moles) dissolved in 30 ml distilled water was added to 0.39 g phenanthroline (0.002 moles) dissolved in 10 ml ethanol and 20 ml water. The pH of the solution was adjusted to 2.5. The color of the solution was purple which changed to bright blue on heating. On cooling however, no crystals were isolated.

4.1.8 Attempt to prepare Dichloro bis(1,10-phenanthroline) mono urea nickel(II): $[Ni(phen)_2-(urea)]Cl_2$. $NiCl_2.6H_2O$ and phenanthroline in the molar ratio 1:1 were mixed as described above. To this solution was added drop wise 0.1201 g urea dissolved in 30 ml distilled water while heating and stirring. The volume of the solution was then reduced to 15 ml, and after long standing for several days 0.15 g of blue crystals were obtained. Yield: 0.15 g (25.4%), Melting point: at about 140°C changes to green. Elemental analysis: found% (calculated%). Ni: 8.02% (9.81%); Cl: 11.5% (11.87%). Visible spectrum: $\lambda_{max} = 585$ nm. IR spectrum: given as Fig. II (a). 3350 cm^{-1} (O-H str.). 1620 cm^{-1} (C=C, C=N str.). 1440 cm^{-1} (C-H bend), 870 (C-H out of plane def.). The complex isolated was established to be $[Ni(phen)_2Cl_2].6H_2O$. Solubility: it is insoluble in CH_2Cl_2, $CHCl_3$, CCl_4 but soluble is CH_3OH, H_2O, and DMSO.

The concentration of urea was increased four times, so that the molar ratio of nickel chloride, phenanthroline and urea was 1:1:4, respectively. Blue crystals were obtained, which have similar decomposition temperature and IR spectrum to the one above.

4.1.9 Attempt prepared Dichloro bis(1,10-phenanthroline monomalonamide nickel(II) 0.47 g $NiCl_2 \cdot 6H_2O$ (0.002 mole) was dissolved in 30 ml distilled water and mixed with 0.39 g phenanthroline (0.002 moles)dissolved in 5 ml ethanol and 20 ml water. 0.2 g malonamide (0.002 moles) dissolved in 30 ml water was added drop wise to the above solution while heating and stirring. After adding all the amide solution and refluxing for three more hours, the blue solution was concentrated by evaporation. 0.16 g (27.1%) blue crystals were obtained. Melting point: at 140°C changes to green; Elemental analysis: found% (calculated%). Ni: 8.70% (9.81%); Cl: 11.20% (11.87%). Visible spectrum: λ_{max}: 585 nm. The formula was established to be $Ni(phen)_2Cl_2 \cdot 6H_2O$. IR spectrum: is given as Fig. 11 (b).

It is similar to that of 4.1.8 Fig. 11 (a). Solubility: it is insoluble in CH_2Cl_2, $CHCl_3$ and CCl_4, but soluble in CH_3OH, H_2O and DMSO.

4.2 Preparation of Copper Complexes

4.2.1 Preparation of Dichloro mono (bipyridine) copper(II) Cu(bipy) Cl_2:

1.56 g bipyridine (0.01 moles) dissolved in 10 ml ethanol and 20 ml water was mixed with 1.70 g $CuCl_2 \cdot 2H_2O$ (0.01 moles) dissolved in 30 ml distilled water, and the pH of the solution was adjusted to 4.5. The green solution was heated and then concentrated by evaporation. On cooling green crystals were separated. Yield: 0.41 g (14.13%), melting point: at 280°C changes color to black, elemental analysis: found% (calculated%). Cu: 21.13% (21.85%), N: 10.1% (9.63%). Cl: 24.17 (24.46%). Visible spectrum λ_{max}= 660 nm. IR spectrum: given as Appendix Fig. 12 (a). 3050 cm^{-1} (C-H str.); 1600 cm^{-1} (C=C str.), 1500 cm^{-1} (C=N str.), 780 cm^{-1} (C-H out of plane def.). Solubility: it is insoluble in CH_2Cl_2, $CHCl_2$, $CHCl_3$ and CCl_4 but soluble in H_2O and DMSO.

4.2.2 Attempt to prepare Dichloro mono(bipyridine) mono urea copper(II): $[Cu(bipy)(urea)]Cl_2$

0.0025 moles of each of the reacting substances were dissolved in 30 ml water and the three solutions were mixed. The pH of the resulting solution was adjusted to 2.2. The solution was then heated while continuously stirring and then concentrated by evaporation.

On cooling green crystals were isolated. Yield: 0.60 g (20.6%). Melting Point: at about 300°C changeed to dark green. Elemental analysis: found% (calculated%). Cu: 21.52 (21.85), N: 8.07 (9.63), Cl: 16.26 (24.42). Visible spectrum: λ_{max} = 660 nm. IR spectrum: given as Fig. 12 (b). It is similar to the spectrum of 4.2.1 Fig. 12 (a). The isolated complex was established to be $[Cu(bipy)Cl_2]$.

In another experiment the concentration of the urea was increased ten times but the crystals isolated were the same as those above on the basis of the similarity of their IR spectra and decomposition temperature.

4.2.3 Preparation of Monochloro monohydroxo mono(bipyridine)copper(II) trihydrate: $Cu(bipy)(OH)Cl.H_2O$

0.0025 moles of each of copper chloride, bipyridine and urea were each dissolved in 30 ml of distilled water and the three solutions were mixed. The pH of the resluting solution was adjusted to 7 with dilute NaOH solution. The color of the solution was deep blue. The solution was then heated while continuously stirring for one hour. It was then concentrated by slow evaporation until the volume was about 30 ml. On cooling blue crystals were isolated. The yield was 0.67 g (74.4%). The complex does not melt and at 165°C its color changes to black.