SYNTHESIS AND PHYSICO—CHEMICAL STUDIES OF SOME METAL CHELATES USING MULTIDENTATE LIGANDS IN SOLID & SOLUTION STATES

A THESIS SUBMITTED
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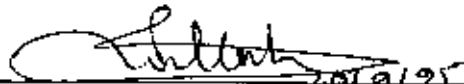MASTER OF PHILOSOPHY (M.PHIL)
IN CHEMISTRY

Presented by

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THESIS APPROVAL SHEET

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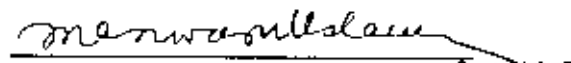Prof. S. E. Haider (Co-Supervisor)
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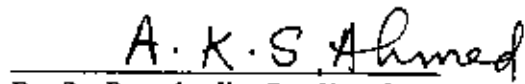
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CHAPTER - I

ABSTRACT

STUDIES IN THE SOLID STATE

Some hexadentate, pentadentate and tetradentate ligand complexes of Co(II), Ni(II), Cu(II) and Cd(II) have been synthesized by the condensation of (i) ethylenediamine and triethylenetetraamine with formaldehyde (ii) 2,6-diacetyl pyridine and triethylene tetraamine (iii) 2,6-diacetyl pyridine and diethylene triammine in the presence of metal ion by template reactions.

The products have been characterized by elemental analysis, spectral studies, conductivity measurement, thermogravimetric analysis and x-ray difraction analysis.

On the basis of the above analysis the complexes have been formulated as

$[Ni(A)]$ $(ClO_4)_2$;   (A = $C_{12}H_{16}N_6$)

$[Cu(A)]$ $(ClO_4)_2$;   (A = $C_{12}H_{26}N_6$)

$[Co(A)]$ $(ClO_4)_2$. $4(H_2O)$;   (A = $C_{12}H_{26}N_6$)

$[Ni(A)]$ $(PF_6)_2$. $6(H_2O)$;   (A = $C_{15}H_{23}N_5$)

$[Cu(A)]$ $(PF_6)_2$. $5(H_2O)$;   (A = $C_{15}H_{23}N_5$)

$[Ni(A)]$ $(PF_6)_2$. $4(H_2O)$;   (A = $C_{13}H_{18}N_4$)

$[Cu(A)]$ $(PF_6)_2$. $4(H_2O)$;   (A = $C_{13}H_{18}N_4$)

$[Cd(A)]$ $(PF_6)_2$. $3(H_2O)$;   (A = $C_{13}H_{18}N_4$)
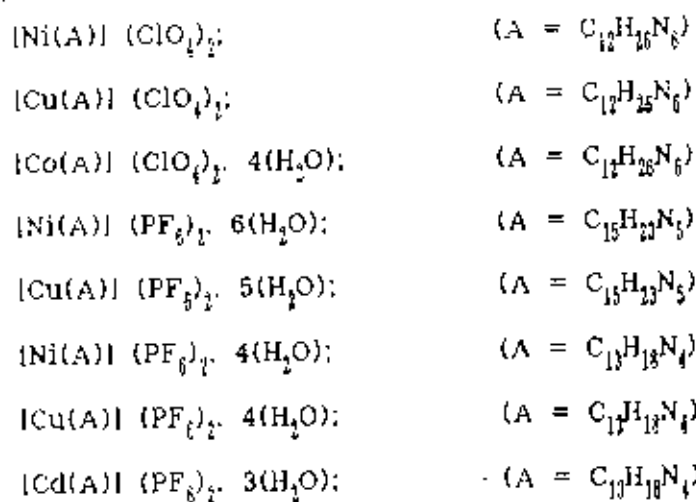
STUDIES IN THE SOLUTION STATE

The stability constants of the ternary complexes |CuAL|, where A refers to oxalic acid (OX) and 2,6-pyridinedicarboxylic acid (DPA) and L refers to glycine (gly), α-alanine (α-ala), phenylalanine (ph-ala) and tryptophyan (Tryp) have been determined potentiometrically using the SCOGS computer program and the order of the stability of the mixed ligand complexes is |Cu-OX-L| > |Cu-DPA-L|. The value of ΔlogK is positive or less negative when A is Oxalic acid. Probable reason for positive or less negative ΔlogK values and the order of stabilization is due to John. Teller effects. The tridentate ligand DPA occupies three equatorial position and the bidentate ligands (amino acids) have to occupy one equatorial and one axial position. So bidentate ligand is strained in occuping one equatorial and one axial position. But in case of |Cu-OX-L| system both ligands are bidentate, therefore no strain is observed.

Again |Cu-DPA-Ph.ala.| and |Cu-DPA-Tryp| complexes are more stable than |Cu-DPA-gly| and |Cu-DPA-α.ala| complexes. This may be due to the intramolecular interligand interaction. The non co-ordinating side group of phenyl alanine and tryptophan come over the pyridyl ring of DPA and thus the noncovalent interaction may cause extra stability.

STUDY IN THE SOLID STATES

1.0 INTRODUCTION

Macrocyclic ligands may be defined as a cyclic compound with nine or more member of heteroatoms and with three or more donar atoms. Metal complexes of macrocyclic ligands occupy a large significant area in modern co-ordination chemistry.

Macrocyclic compounds have a great biological significance such as the Vitamine (B_{12}), which is involved in redox reaction of methionine and in the metabolism of methane producing bacteria[1]. A large number of Macrocyclic ligands already have been synthesised[2] by various workers. The synthetic macrocyclic ligands show other properties which make them suitable for modelling enzymes containing metal ion at the active site. An example is the active site in carbonic anhydrase, the enzymes which catalyses the hydration of carbondioxide.

The distortion of the geometry of co-ordination compounds[3] of copper is reported to reduce the activation for electron transfer reactions and to enhance the redox potential. The tendency for a macrocyclic complex to be more stable with respect to ligand dissociation than a comparable open chain multidentate ligand system, over and above the chelate effect, is well documented[4]. This phenomenon has been termed as the Macrocyclic Effect[5]. Busch and Coworker[6] have proved the enhanced stabilities exhibited in the "Macrocyclic Effect". An enhanced of Macrocyclic Effect has been observed for the Macrocyclic ligand complex by Lehn and Coworkers[7]. The stability is partially due to the ligand rigidity and strong bond energy between metal and donor atoms in macrocyclic complexes

The solvation enthalpies and entropies also play important roles in determining the kinetic stability[6]. A possible route for the formation of the macrocyclic complexes have been shown in Figure(1) which are indicated that the reactions between formaldehyde with ethylenediamine through the coordinated metal ion. Then the amine becomes uncoordinated and triethylenetetramine in octahedral fashions reacts with formaldehyde to yield a tertiaryamine. The resulting macrocyclic ligands contain six nitrogen atoms of which two secondary nitrogen are co-ordinated to the metal ion[38].
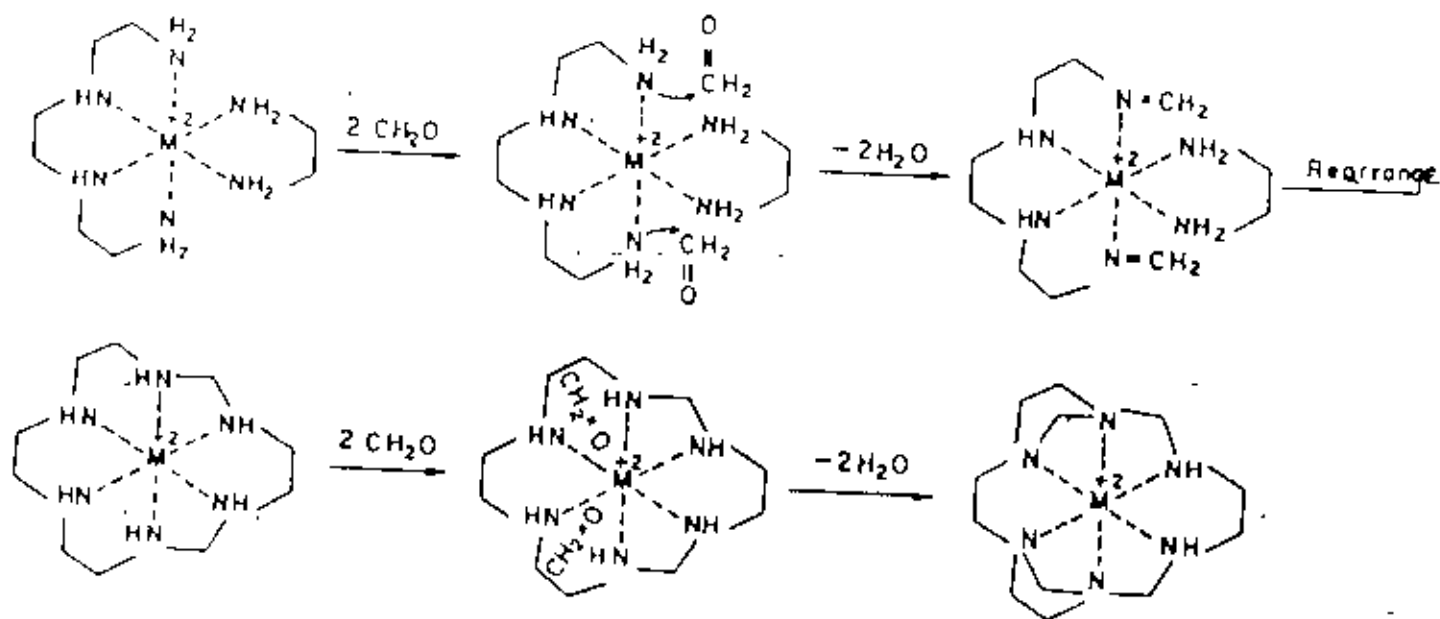
Fig. 1. Proposed mechanism of macrocycle formation by metal template reaction

The redox properties of macrocyclic compounds are of particular interest. because electron transfer may be at either the ligand or the metal sites. E.S.R. studies on the Ni(II) complex of ligand L_1 and L_2 in figure (2) show the electron transfer reactions. where redox processes are essentially localized on the ligand[9].

Thus the macrocyclic compounds are not only of use as models for the naturally occuring compounds but also are of commercial value (e.g. Phthalocyamine dyes such as monastrol blue), practical application (e.g. synthesis of new compounds) and theoretical interest because of structural peculiarities.
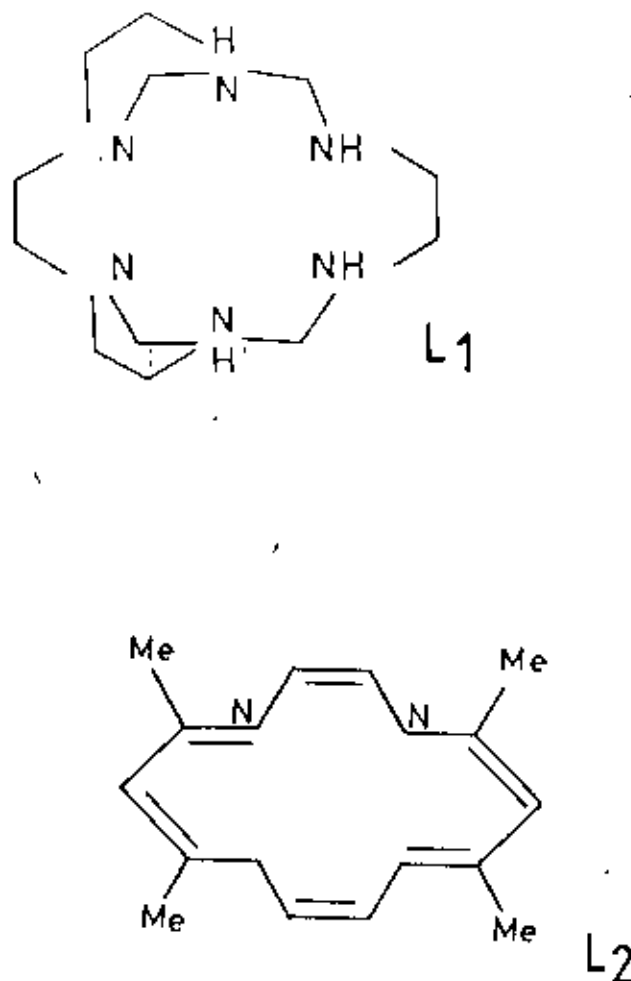
Figure 2.

1.1 TEMPLATE EFFECT IN MACROCYCLIC SYNTHESIS:

There are two kinds of template effect described by BUSCH[6].

(a) Kinetic template effect, where the directive influence of metal ion controls the stepwise reactions.

(b) Thermodynamic template effect, where the metal ion perturbs an existing equilibrium in an organic system and the required product is formed, often in high yield, as its metal complex.

1.1.1 Template Synthesis

Metal template synthesis sometime provide selective routes toward products that are not easily obtainable in the absence of metal ions. It has been shown that template reactions involving formaldehyde and amines facilitate the preparation of saturated polyaza multidentate, macrocyclic, and macro-polycyclic complexes[1-5]. The reactions are simple, straight forward and producing high yields of the products. Previously the synthesis of Ni(II) complexes were carried by the template condensation reactions as described in equations 1-4 [10,11].

$$Ni^{+2} + H_2N\!\!-\!\!\!\diagup\!\!\!\diagdown\!\!\!-\!\!NH_3 + CH_2O + NH_3 \longrightarrow [Ni(L_3)]^{+2} \qquad (1)$$

$$[Ni(L_3)]^{+2} + CH_2O + CH_3NH_3^+ \longrightarrow [Ni(L_4)]^{+5} \qquad (2)$$
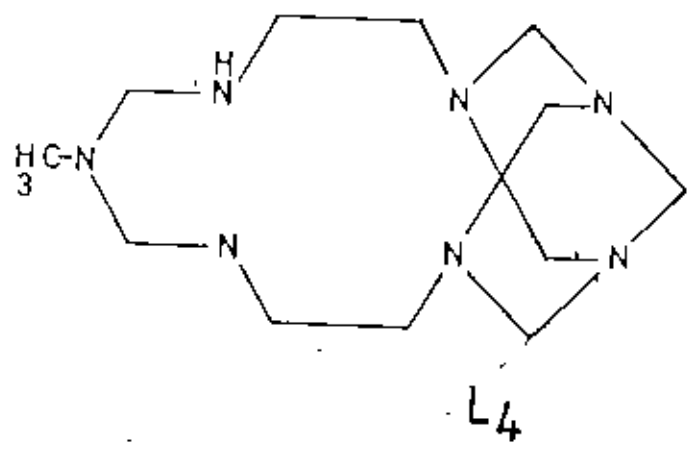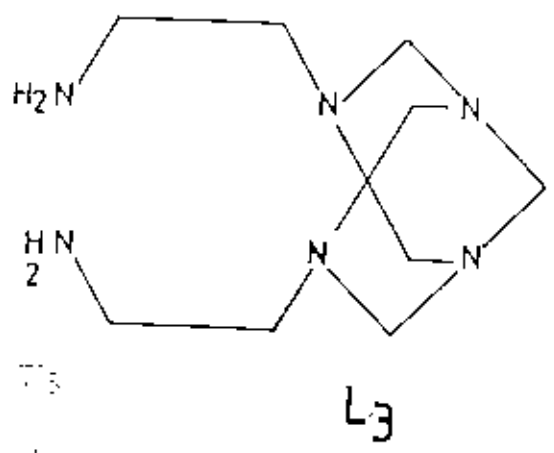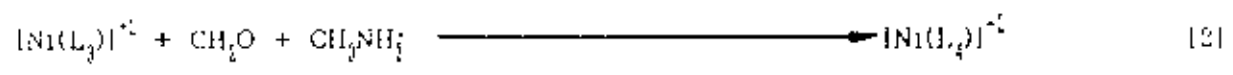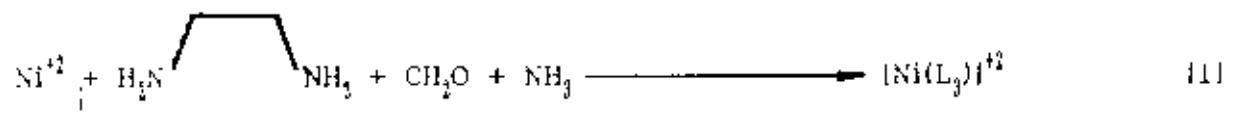
Fig. 3

For the Ni(II) complexes of ligands shown in figure (3) N—N bite distances involving tetraazabicyclononane were unusually short and the complexes exhibit interesting spectroscopic properties[4].
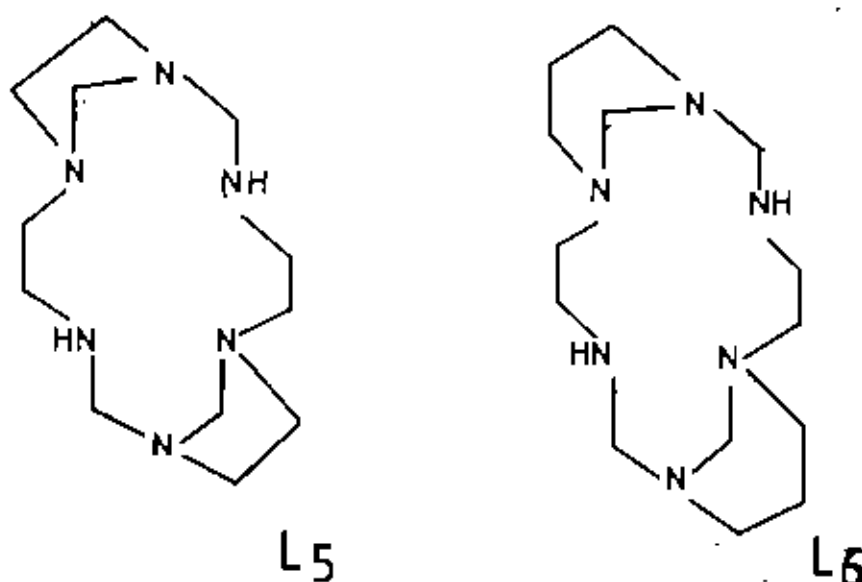
Fig.4

We attemped to synthesize complexes with ligands shown in figure (4) from the reaction of tetraamine, formaldehyde, and ethylenediamine in presence of Ni(II) or Cu(II) ion to see how the spectroscopic properties and structures of the complexes are influenced by having an ethylene moiety substituted for a methylene moiety linking two uncoordinated nitrogens. The possible reactions are shown below.

$$Ni^{+2} + H_2N \diagup \diagdown NH \diagup \diagdown NH_2 + CH_2O \longrightarrow [Ni(L_5)]^{+2} \qquad (3)$$

$$Ni^{+2} + H_2N \diagup \diagdown NH \diagup \diagdown NH_2 + CH_2O \longrightarrow [Ni(L_6)]^{+2} \qquad (4)$$
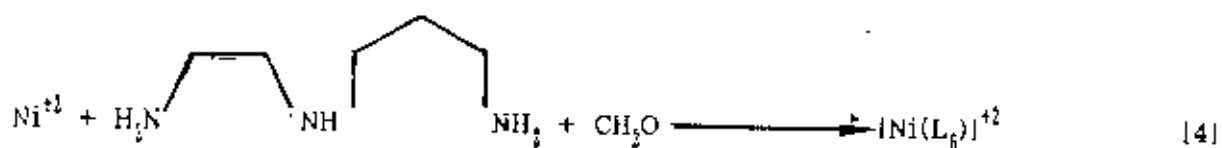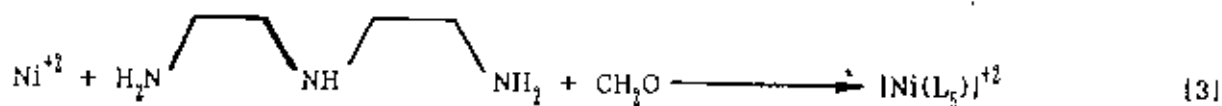
However the reaction yielded complexes of ligand shown in figure (5) by P. Muttan et al.[12-16] instead of ligands shown in figure (4).

1.7.2 Non Template Synthesis:

In non template synthesis, where free macrocyclic ligand is prepared first and then reacted with metal salt to produce a macrocyclic complex. The template ion can not be easily removed from the macrocyclic ring without destruction of the ligand[17]. Non template synthesis of the organic macrocyclic ligand often results in low yield of the desired product. To increase the yield of the macrocycle and reducing polymerization reaction, the step wise synthesis often carried out under high dilution condition. The advantage of this approach is that the macrocyclic ligand may be isolated purified and characterized before the synthesis of metal complex. Often low yield and difficulties in synthesis of the ligands etc are normally observed.
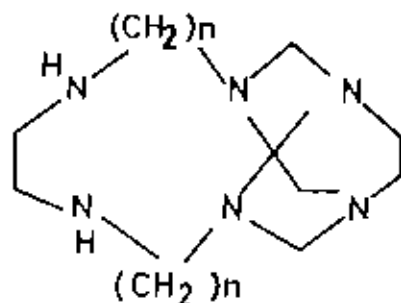
Fig.5: Structure of Ligand.

1.2. PLAN OF THE PRESENT WORK

The present work was undertaken with the objective of synthesizing some (a) hexadentate, (b) penterdentate and (c) tetradentate ligand complexes of Co(II), Ni(II) and Cu(II) by the condensation of (a) ethylene diamine and triethylene tetraamine with formaldehyde, (b) interaction of 2, 6-diacetyl pyridine and triethylene tetraamine, (c) 2-6 diacetyl pyridine and diethylene triamine in the pressence of metal ion by templete reaction. Sometime mineral acid was used to catalyse cyclisation.

The reactions appear to be interesting and significant in view of close similarity of these macrocyclic complexes to certain biological macrocyclic system[18]. Furthermore, these investigations report reveal, that the size of the small ring moieties fused to the macrocyclic ligand significantly affects the metal donors distances as well as indicated by the spectroscopic and electrochemical properties of the complexes. The work also shows that equilibria between square planner and octahedral species of Ni(II) complexes in aqueous solutions are also greathy influenced by the small ring moieties fused to the macrocyclic ligand. Some macrocyclic Ni(II) complexes are known to exist in water as equilibrium mixtures of yellow diamagnetic square planner $[Ni(L)]^{+2}$ and blue (or voilet) paramagnetic octahedral $[Ni(L)(H_2O)_2]^{+2}$ species[19, 20-31].

EXPERIMENTAL

1:3.1 MATERIAL AND METHODS:

The chemicals and solvents used during the preparative and analytical work were standard reagent grade procured from E. Merck of Germany, BDH of England and Aldrich Chemical Company Ltd.

$LiClO_4$ used in the reaction was prepared in the laboratory by the reaction of $LiCO_3$ with $HClO_4$ adopting the usual precautions.

Micro-analytical data for C, H and N were obtained from the Tokyo Institute of Technology, Japan by using Yanagimoto CHN autocorder Type MT-2 and Yazawa Halogen Analyser.

The infrared spectra of the compounds were recorded using JASCO IR 810 spectrophotomer by using KBr Pellets.

The uv-Visible spectra of the compounds were recorded by uv-visible recording spectrophotometer model uv-160 A shimatzu.

Thermogravimetric analysis was done with Rigaku Thermal Analysis Station TAS 100 with Rigaku TG basic unit TG 8110.

X-ray powder diffraction patterns were recorded by using JDX-8P JEOL Ltd, Tokyo, Japan diffraction recorder.

Melting point was determined Fisher John's melting point apparatus.

SYNTHESIS OF THE COMPLEXES:

1.3.2 [Ni(A)] (ClO$_4$)$_2$; (A = C$_{12}$H$_{28}$N$_6$).

82% triethylenetetraamine (4 ml, 1 m mole), 36% aqueous formaldehyde (8 ml) were added to a solution of nickel chloride (6 gm, 1 m mole) in methanol (50 ml). Then ethylenediamine (2 ml, 1 m mole) was added to the mixture which was then refluxed for 12 hrs. A dark orange solution was obtained. The solution was filtered to remove insoluble materials and the filtrate was cooled to room temperature. A saturated solution of LiClO$_4$ (4 ml) was added to the filtrate. It was then allowed to stand in a refrigerator overnight. Orange crystalline products were formed. The crystals were separated by filtration using a sintered glass crucible No. 3 and washed with methanol. The product was crystallized from hot water, dried over silica gel and weighed. 70% yield with respect to the metal was obtained. The melting point recorded was 209^{0}C. The I.R. spectra of [Ni(C$_{12}$H$_{28}$N$_6$)] (ClO$_4$)$_2$ is shown in Figure (6).

1.3.3 [Cu(A)] (ClO$_4$)$_2$; (A = C$_{12}$H$_{28}$N$_6$).

This compound was prepared by a method similar to that for [Ni(A)] (ClO$_4$)$_2$. CuCl$_2$. 2H$_2$O was used as a metal source. The solution mixture was refluxed for 12 hrs. The colour changed to dark violet from blue. It was filtered and a saturated LiClO$_4$ (4 ml) solution was added to the filtrate. The solution was left in a refrigerator until the crystals were formed (1 day). Yield was 65% having m.p. 213°C. The I.R. spectra of [Cu(C$_{12}$H$_{28}$N$_6$)] (ClO$_4$)$_2$ is shown in Figure (6).
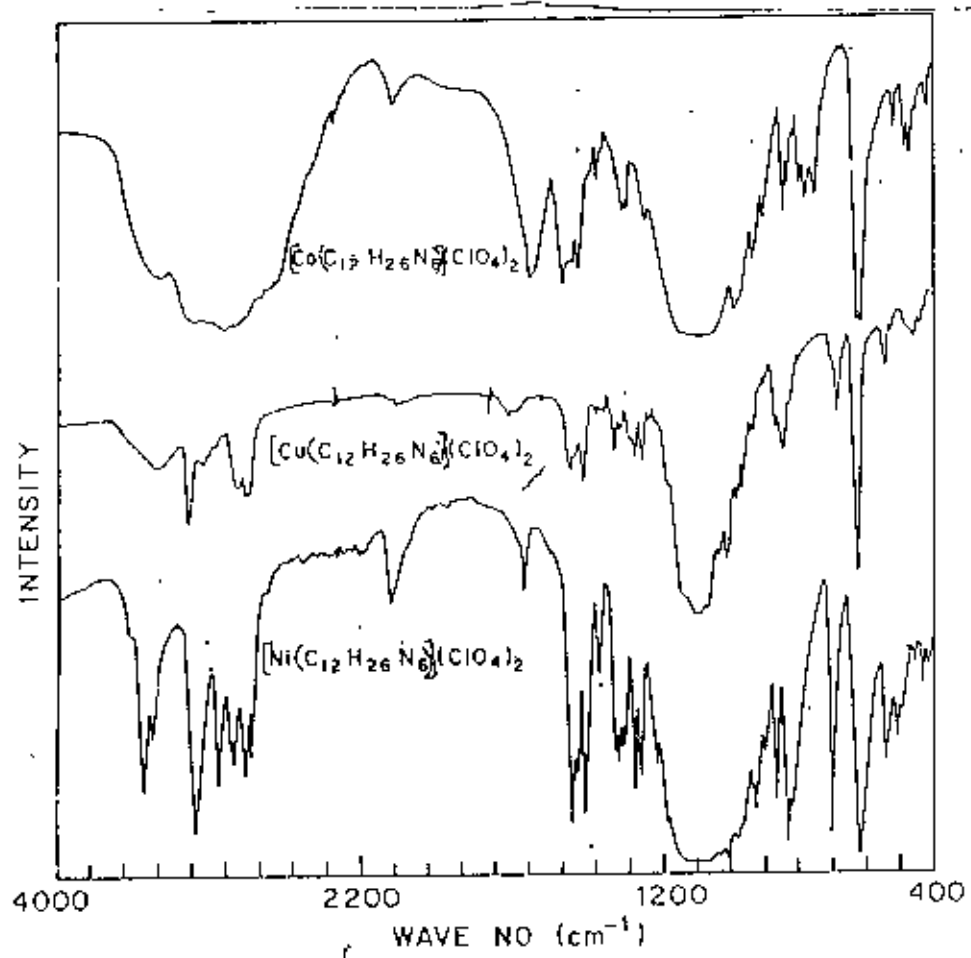
Fig. 6 · I R spectra of the complexes

1.3.4 [Co(A)] (ClO$_4$)$_2$ 4(H$_2$O): (A = C$_{12}$H$_{15}$N$_6$)

This compound was prepared by a method similar to that for [Ni(A)](ClO$_4$)$_2$. CoCl$_2$ 6H$_2$O was used as a metal source. The colour of the solution mixture was changed from violet to dark brown. Yield: 65% yield m.p. 212^{0}C. The I.R. spectra of [Co(C$_{12}$H$_{15}$N$_6$)] (ClO$_4$)$_2$ 4(H$_2$O) is shown in Figure (6).

1.3.5 [Ni(A)] (PF$_6$)$_2$ 6(H$_2$O): (A = C$_{15}$H$_{22}$N$_5$)

Triethylene tetramine (0.15 ml, 1 m mol) and Nickel acetate (1.15 g. 1m mol) were separately-dissolved in 25 ml of D.D Water. In another beaker, 2.6-diacetyl pyridine (0.16 g, 1 ml) was dissolved in 50 ml of methanol. This solution was taken in a round bottle flask and Nickel solution was added to it followed by 2-3 drops of acetic acid. The mixture was refluxed for 30 minutes then triethylenetetraamine solution was added to it. The colour immediately changed from green to reddish brown. The solution was further refluxed for 12 hours. The solution was filtered and concentrated. Then ammonium hexafluorophosphate was added to it. The crystal product was collected by filtration and dried over silicagel in a desiccator and weighed. Yield 60%. Melting point 150°C. The I.R. spectra of [Ni(C$_{15}$H$_{22}$N$_5$)] (PF$_6$)$_2$ 6(H$_2$O) is given in Figure (7).
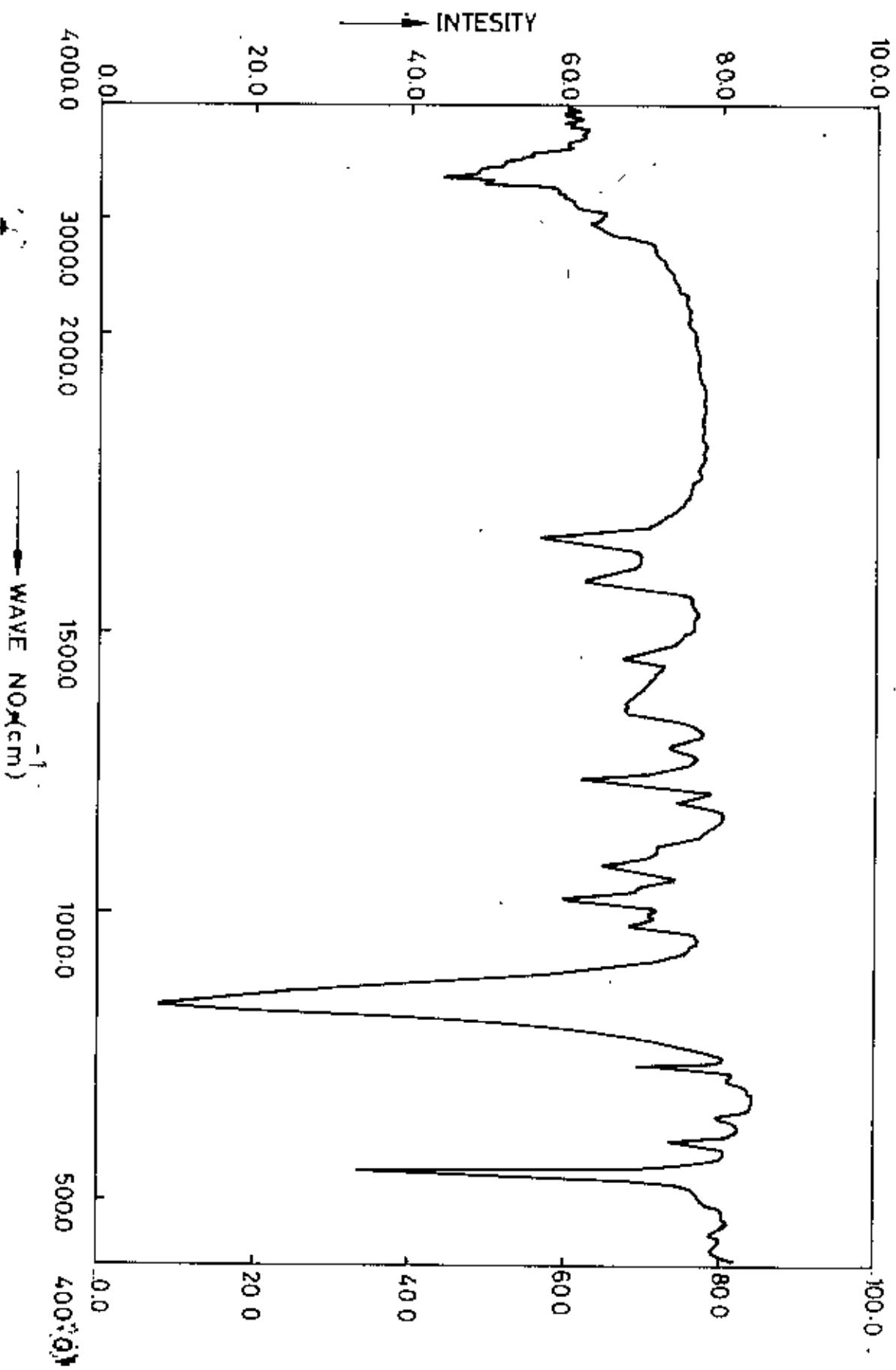
Fig. 7: The I.R. Spectra of the Complex [Ni(C₁₅H₂₃N₅)] (PF₆)₂ 6(H₂O).

INTESITY

WAVE NO.(cm⁻¹)

1.3.6 [Cu(A)](PF$_6$)$_2$. 5(H$_2$O): A = C$_{15}$H$_{21}$N$_5$

This compound was prepared by a method similar to that for [Ni(A)](PF$_5$)$_2$6(H$_2$O). The copper acetate was used as a metal source. The colour of the solution mixture was changed from green to blue. Ammonium hexafluorophosphate was added to it. The crystal was collected by filtration and dried in desiccator. Yield. 55%. Melting point 215°C. The I.R. spectra of [Cu(C$_{15}$H$_{21}$N$_5$)] (PF$_6$)$_2$ 5(H$_2$O) is given in Figure (8).

1.3.7 [Ni(A)] (PF$_6$)$_2$ 4(H$_2$O): A = C$_{11}$H$_{16}$N$_4$

2, 6 diacetyl pyridine (0.3264g, 2 m mol) was dissolved in 75 ml of methanol. Nickel acetate (0.5 g, 2 m.mol) was dissolved in 25 ml of D.D water. These two solutions were taken in a round bottom flask and 2-3 drops of acetic acid was added to it. Then it was refluxed for half an hour. A solution of diethylenetriamine (0 202 g, 2 m mol) in 50 ml of D.D. water was added to the round bottom flask. Then it was refluxed for further 12 hrs. The colour changed from blue to reddish brown. Then the coloured solution was concentrated and some amount of ammonium hexaflorophosphate was added to it. A deep brown powder product was obtained. It was filtered and dried in desiccator. Yield 55%, melting point 299°C. The I.R. spectra of [Ni(C$_{11}$H$_{16}$N$_4$)] (PF$_6$)$_2$ 4(H$_2$O) is shown in Figure (9).

INTESITY

4000.0

0.0

10.8

21.6

32.4

43.2

54.0

3000.0

2000.0

15000

1000.0

500.0 400

0.0

10.8

21.6

32.4

43.2

54

WAVE NO.(cm⁻¹)
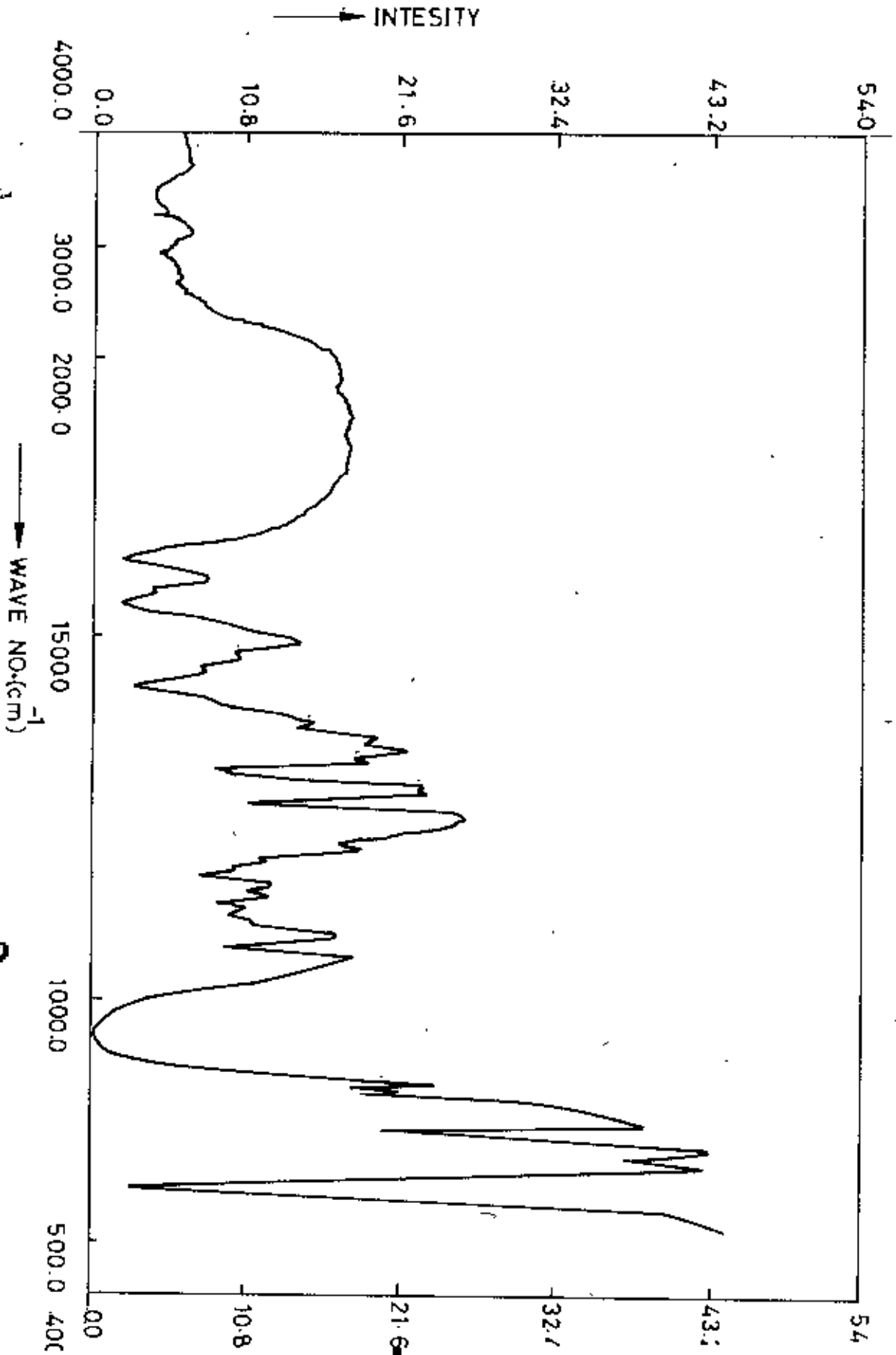
Fig. 8 : The I.R. Spectra of the Complex [Cu(C₁₅H₂₃N₅)] (PF₆)₂ 5(H₂O).
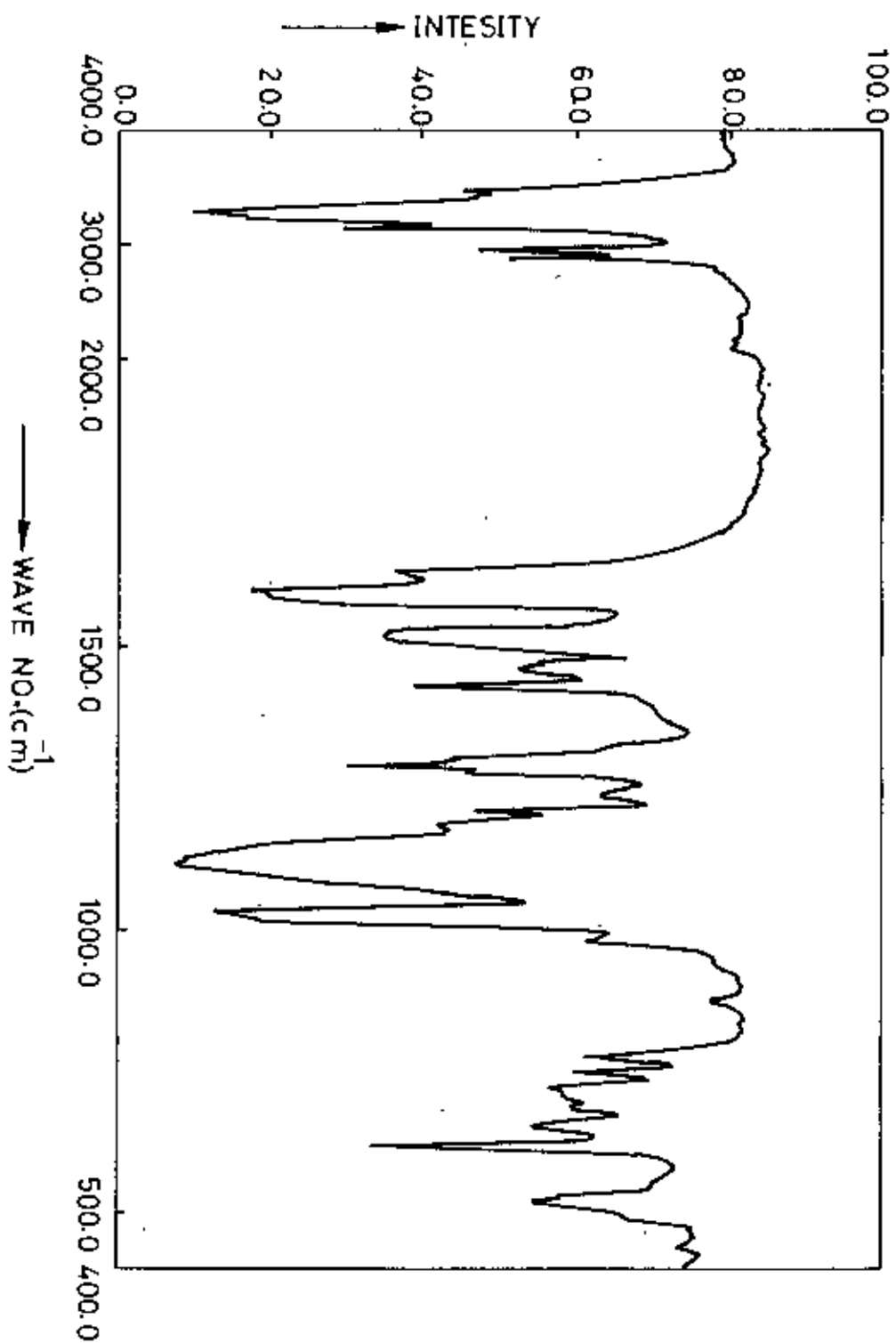
Fig.(6): The I.R. Spectra of the Complex [Ni(C$_{13}$H$_{18}$N$_4$)] (PF$_6$)$_2$ 4(H$_2$O).

1.3.5 $[Cu(A)]$ $(PF_6)_2$ $4(H_2O)$: $A = C_{13}H_{16}N_4$

This compound was prepared by a method similar to that for $[Ni(A)](PF_6)_2 4(H_2O)$ Copper acetate was used as a metal source and the solutions were refluxed for 12 hrs. The colour changed from prussian blue to navy blue. A green powder product was obtained after adding ammonium hexafluorophosphate. The product was collected. Yield: 65%, melting point 260°C. The I.R. spectra of $[Cu(C_{13}H_{16}N_4)]$ $(PF_6)_2$ $4(H_2O)$ is shown in Figure (10).

1.3.9 $[Cd(A)]$ $(PF_6)_2$ $3(H_2O)$: $A = C_{13}H_{16}N_4$

This compound was prepared by a method similar to that for $[Ni(A)](PF_6)_2 4(H_2O)$ The cadmium acetate was used as a metal source. The solution was refluxed for 15 hrs. A colourless solution turned to light orange. After adding of ammonium hexafluorophosphate, orange product was obtained. The product was collected by filtration and dried in desiccator. Yield 50%. The I.R. spectra of $[Cd(C_{13}H_{16}N_4)]$ $(PF_6)_2$ $3(H_2O)$ is shown in Figure (11)
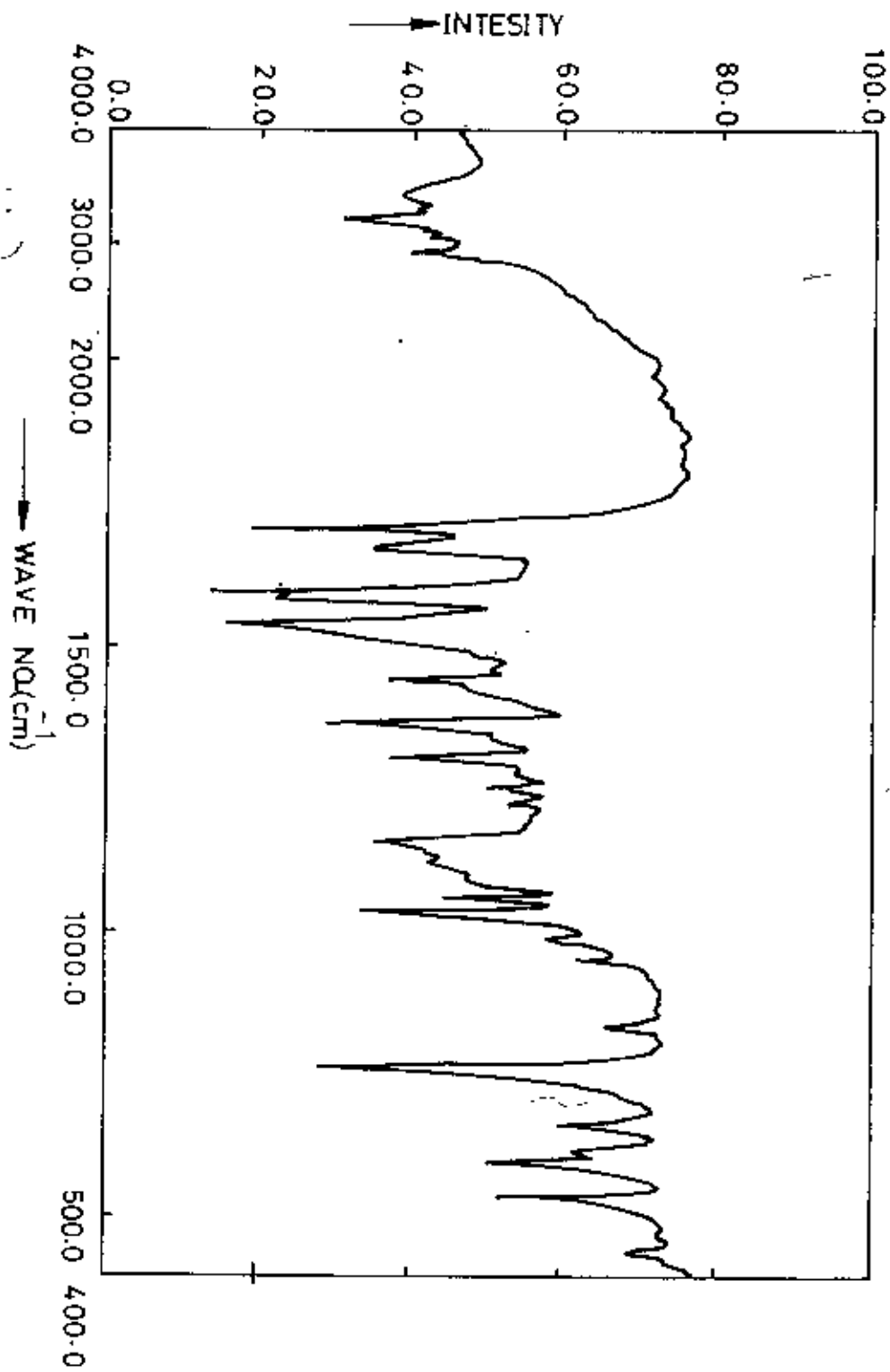
Fig. 10: The I.R. Spectra of the Complex [Cu(C$_{13}$H$_{18}$N$_4$)] (PF$_6$)$_2$ 4(H$_2$O).
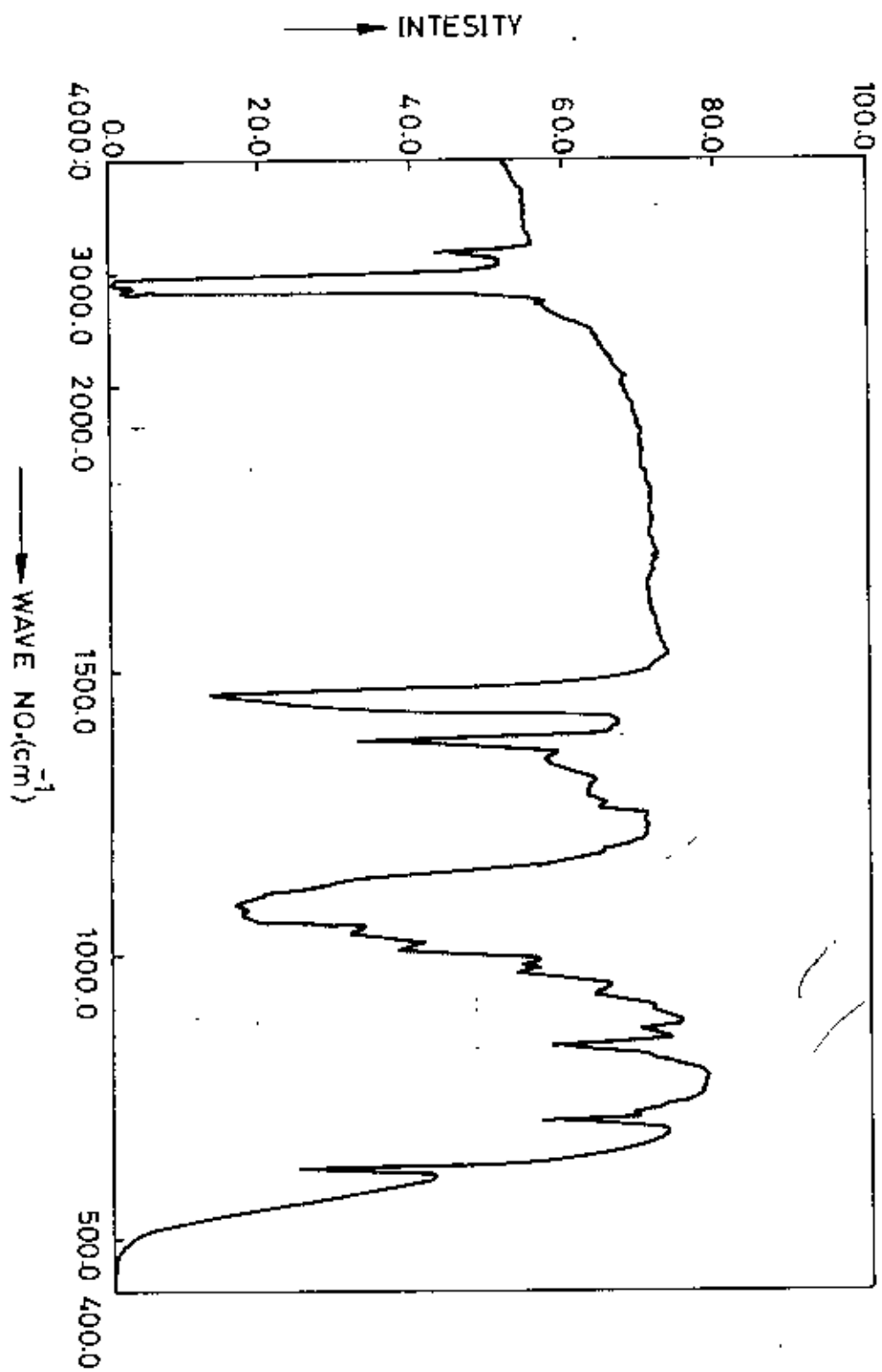
Fig. 11: The I.R. Spectra of the Complex [Cd(C$_{13}$H$_{18}$N$_4$) (PF$_6$)$_2$ 3(H$_2$O)·

CHARACTERIZATION AND PROPERTIES

1.4.1 MELTING POINT:

Melting point indicates an unique property of a substance. The range of melting temperature indicate whether the compound is ionic or nonionic. Generally ionic compound melt at high temperature and nonionic compound melt at low temperature. The purity of the compound is indicated by the sharp m.p. by using Fisher John's melting point apparatus, the melting point of samples were recorded upto 300°C. The results are shown in Table (1).

Table (1). Melting Points of the Complexes.

Compounds	Melting Points (°C)	Colour Change	
		Before Melting	After Melting
$[Ni(C_{12}H_{26}N_6)](ClO_4)_2$	209.00	Dark orange	Ash
$[Cu(C_{12}H_{26}N_6)](ClO_4)_2$	213.00	Violet	Black
$[Co(C_{12}H_{26}N_6)]ClO_4)_2$ 4(H$_2$O)	212.00	Brown	Brown
$[Ni(C_{15}H_{43}N_5)](PF_6)_2$ 6(H$_2$O)	150.00	Reddish Brown	Ash
$[Cu(C_{15}H_{29}N_5)](PF_6)_2$ 5(H$_2$O)	215.00	Blue	Black
$[Ni(C_{13}H_{16}N_4)](PF_6)_2$ 4(H$_2$O)	299.00	Brown	Black
$[Cu(C_{13}H_{16}N_4)]PF_6)_2$ 4(H$_2$O)	260.00	Green	Black
$[Cd(C_{13}H_{16}N_4)]PF_6)_2$ 3(H$_2$O)	186.00	Brown	Red

From the Table (1) the complexes were found to melt accompanied by decomposition together with colour changes.

1:4.2 SOLUBILITY:

The solubility test was done on qualitative basis which indicates where the compound is ionic or covalent. Most of the compounds prepared are easily soluble in organic solvents. This indicated that the compound has covalent character. This test is the excellent agreement with the melting point of the complexes. The solubility data are given in Table (2).

Table (2): Solubility of the Compound. (Qualitative Observations)

Compound	Soluble in	Sparingly soluble in	Insoluble in
$[Ni(C_{12}H_{16}N_6)](ClO_4)_2$	methanol and chloroform	Hot water and DMSO	ethanol, water and diathylether.
$[Cu(C_{12}H_{16}N_6)](ClO_4)_2$	methanol and chloroform	Hot water and DMSO	ethanol, water and diethylether.
$[Co(C_{12}H_{22}N_5)](ClO_4)_2 \cdot 4(H_2O)$	methanol and chloroform	Hot water and DMSO	ethanol, water and diethylether.
$[Ni(C_{15}H_{23}N_5)](PF_6)_2 \cdot 6(H_2O)$	Acetone, methanol and DMF	Hot water	chloroform, ethanol and water
$[Cu(C_{15}H_{23}N_5)](PF_6)_2 \cdot 5(H_2O)$	Acetone, methanol and DMF	Hot water	chloroform, ethanol and water
$[Ni(C_{12}H_{16}N_4)](PF_6)_2 \cdot 4(H_2O)$	Acetone, methanol and DMF	Hot water and DMSO	chloroform, ethanol, water and CCl_4
$[Cu(C_{12}H_{16}N_4)](PF_6)_2 \cdot 4(H_2O)$	Acetone, methanol and DMF	Hot water and DMSO	chloroform, ethanol, water and CCl_4
$[Cd(C_{12}H_{16}N_4)](PF_6)_2 \cdot 3(H_2O)$	Acetone, methanol and DMF	Hot water and DMSO	chloroform, ethanol, water and CCl_4

1.Ø.3 ELEMENTAL ANALYSIS:

This is a unique technique for the characterization of any chemical compound. Elemental analysis for carbon, hydrogen and nitrogen of some of the complexes were obtained from the Tokyo Institute of Technology, Japan by using Yanagimoto CHN Autocorder Type MT-2. Now a days, computerized instrument is usually used for determination of elemental analysis. The results of the elemental analysis are summarised in Table (3).

Table (3): Microanalytical Data of the Complexes.

Sample	% C		% H		% N	
	Found	Cal.	Found	Cal.	Found	Cal.
$[Ni(C_{12}H_{15}N_6)]$ $(ClO_4)_2$	28.12	28.12	5.02	5.11	16.32	16.47
$[Cu(C_{12}H_{25}N_6)]$ $(ClO_4)_2$	27.88	27.86	5.07	5.06	16.33	16.31
$[Co(C_{15}H_{36}N_6)]$ $(ClO_4)_2$ $4(H_2O)$	24.65	24.65	4.57	4.48	14.44	14.43
$[Ni(C_{15}H_{30}N_5)]$ $(PF_6)_2$ $6(H_2O)$	24.52	24.66	4.84	4.83	9.39	9.59
$[Cu(C_{15}H_{27}N_5)]$ $5(H_2O)$	24.99	25.12	4.45	4.60	9.00	9.78

1.4.4 CONDUCTIVITY MEASUREMENT:

Conductance is an additive property of solution and it is indicate whether a compound is ionic or covalent. Under the influence of an electric field, solution of electrolytes conduct an electric current by the migration of ions.

The specific conductance of solution decreases with increasing dilution, so the specific conductance of the complexes were measured, using very dilute solution (0.00001 M). Acetone was used as a solvent and TOA conductometer of model No. CM—5S was used. The molar conductance data was given in Table (4).

The specific conductance of the complexes were measured by the following relationship[32].

Molar Conductance =   Specific Conductance x Volume in which 1 mole is dissolved.

Table (4) molar conductance data for some complexes.

Compound	Concentration of Solution (M)	Molar Conductance ohm^{-1} cm^2 mol^{-1}	No. of ions.
$[Ni(C_{12}H_{26}N_6)](ClO_4)_2$	0.00001	282	3
$[Cu(C_{12}H_{26}N_6)](ClO_4)_2$	0.00001	240	3
$[Co(C_{12}H_{26}N_6)](ClO_4)_2$ $4(H_2O)$	0.00001	261	3
$[Ni(C_{15}H_{23}N_6)](PF_6)_2$ $6(H_2O)$	0.00001	260	3
$[Cu(C_{15}H_{23}N_6)]$ $5(H_2O)$	0.00001	250	3
$[Ni(C_{12}H_{18}N_4)]$ $4(H_2O)$	0.00001	225	3
$[Cu(C_{12}H_{18}N_4)]$ $4(H_2O)$	0.00001	200	3
$[Cd(C_{12}H_{18}N_4)]$ $3(H_2O)$	0.00001	150	2

1.4.5 I. R-SPECTRA

I. R. spectroscopy is a valuable technique for characterization of macrocyclic complexes.

The infra-red spectra of the complexes were recorded on a JASCO IR 810 spectrophotomer by using KBr Pellets.

The tentative band assignment have been made on the basis of standard. Literature[32,33,34].

The infrared absorption peaks of the complexes synthesized during this research are summarised in Table (5) and identification of the absorptions are indicated.

Table (5) I R spectra bands of complexes.

Compound	H_2O	NH	CN	(CH_3)	(PF_6)	(MN)	(ClO_4)
$Ni(C_{12}H_{26}N_6)(ClO_4)_2$	3650	3210 840	1610	1550 2950	-	440	510
$Cu(C_{12}H_{26}N_6)(ClO_4)_2$	3250	3210 840	1440	1610 2830	-	420	510
$Co(C_{12}H_{26}N_6)(ClO_4)_2(H_2O)$	3450	3000 840	1440	1450 2950	-	448	480
$Ni(C_{15}H_{23}N_5)(PF_6)_2 \, 6(H_2O)$	3650 1475	3450 1590	1247 1050	2955 1360	550	450	-
$Cu(C_{15}H_{23}N_5)(PF_6)_2 \, 5(H_2O)$	3670 1470	3500 1590	1150	1370 1450	560	448	-
$Ni(C_{13}H_{18}N_4)(PF_6)_2 \, 4(H_2O)$	1450	3500 1550	1260 1300	1450 1340	550	450	-
$Cu(C_{13}H_{18}N_4)(PF_6)_2 \, 4(H_2O)$	3660 3400	3455 1590	1230 1090	1375 1400	560	490	-
$Cd(C_{13}H_{18}N_4)(PF_6)_2 \, 3(H_2O)$	3650 1470	3200 1590	1040 1090	1200 2900	560	490	-

1.4.6   ELECTRONIC SPECTRA:

Ultraviolet spectra can give qualitative knowledge of electronic properties. The energy absorbed in the u.v. region produced transition. The transition consists of usually non bonding p or bonding orbital to the next higher energy orbital i.e. (antibonding π^* or σ orbital)[35]. For recording the u.v. spectra of the macrocyclic complexes, a double beam u.v. visible spectrophotometer of model No. uv 160 A Shimatzu, Japan was used. The absorption bands of the complexes in the uv region results from the d-d^*, n-π and π-π' electronic transitions. The pattern of the maxima in longer wave length which is due to the metal to ligand charge transfer transition. The u.v.–visible spectra of the samples are shown in Fig. (12–15). The relatively weak absorption band in the region 300–700 usually indicates n-π^* transition and bands to high intensity (240–280 nm) are possible due to n-π' transition. The absorption peaks are presented in Table (6).
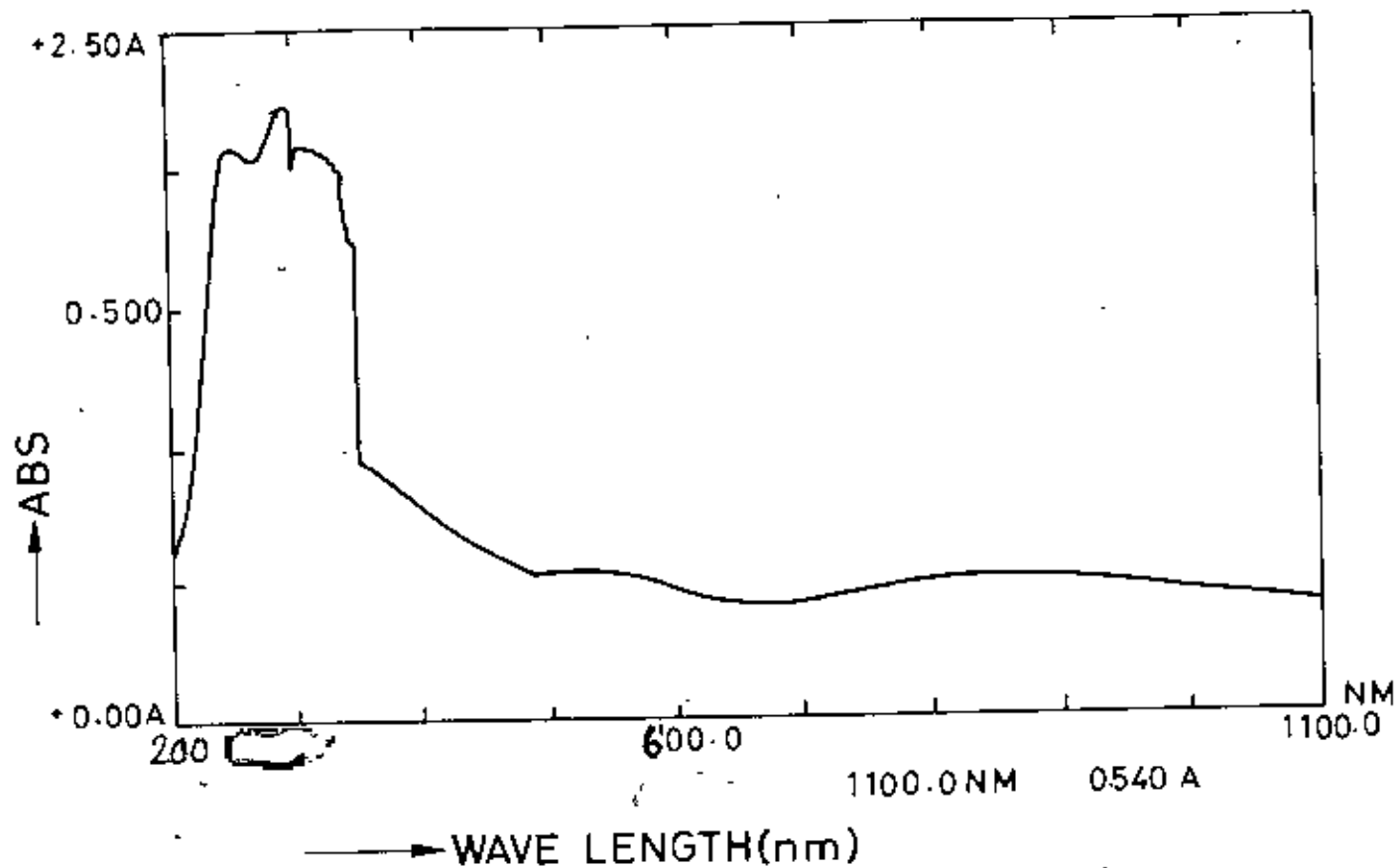
Fig. 12: u.v. Spectra of the Complex Ni[(C$_{12}$H$_{26}$N$_6$)] (ClO$_4$)$_2$.

*** PEAK-PICK ***

--- PEAK ---		--- VALLEY ---	
	ABS		ABS
861.0	0.503	655.0	0.403
309.0	2.106	303.0	1.993
296.0	2.224	268.0	2.035
254.0	2.066		
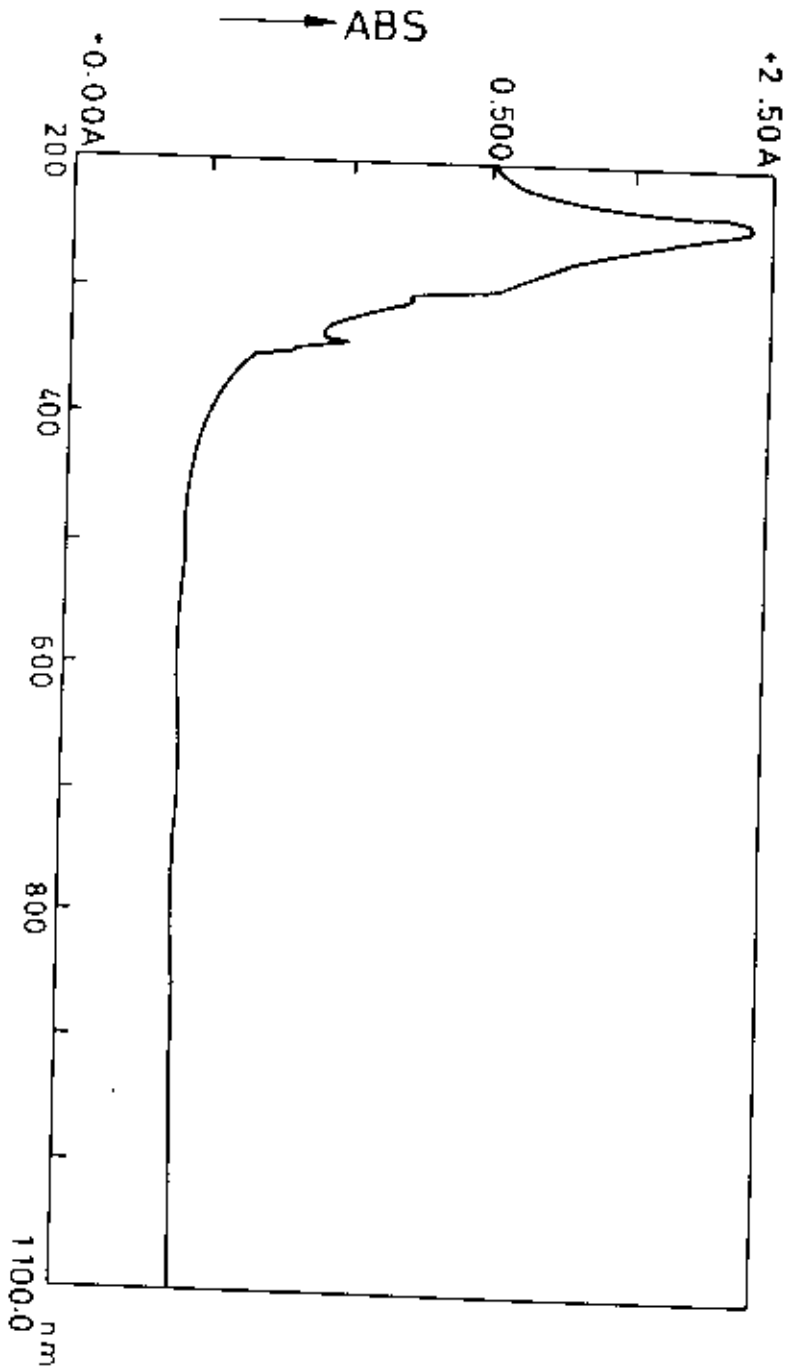
Fig.13: u.v. Spectra of the Complex Cu[(C12H26N6)] (ClO4)2;

→ ABS

→ WAVE LENGTH(nm)

*** PEAK-PICK ***

--- PEAK ---

	ABS
672.0	0.423
341.0	0.951
243.0	2.431

--- VALLEY ---

	ABS
1070.0	0.418
553.0	0.404
334.0	0.902

Fig. 14: u.v. Spectra of the Complex Co[(C₁₂H₂₆N₆)] (ClO₄)₂ 4(H₂O).

*** PEAK-PICK ***

PEAK —   --- VALLEY ---

	ABS		ABS
341.0	1.228	576.0	0.587
299.0	1.444	328.0	1.160
243.0	1.957	290.0	1.430
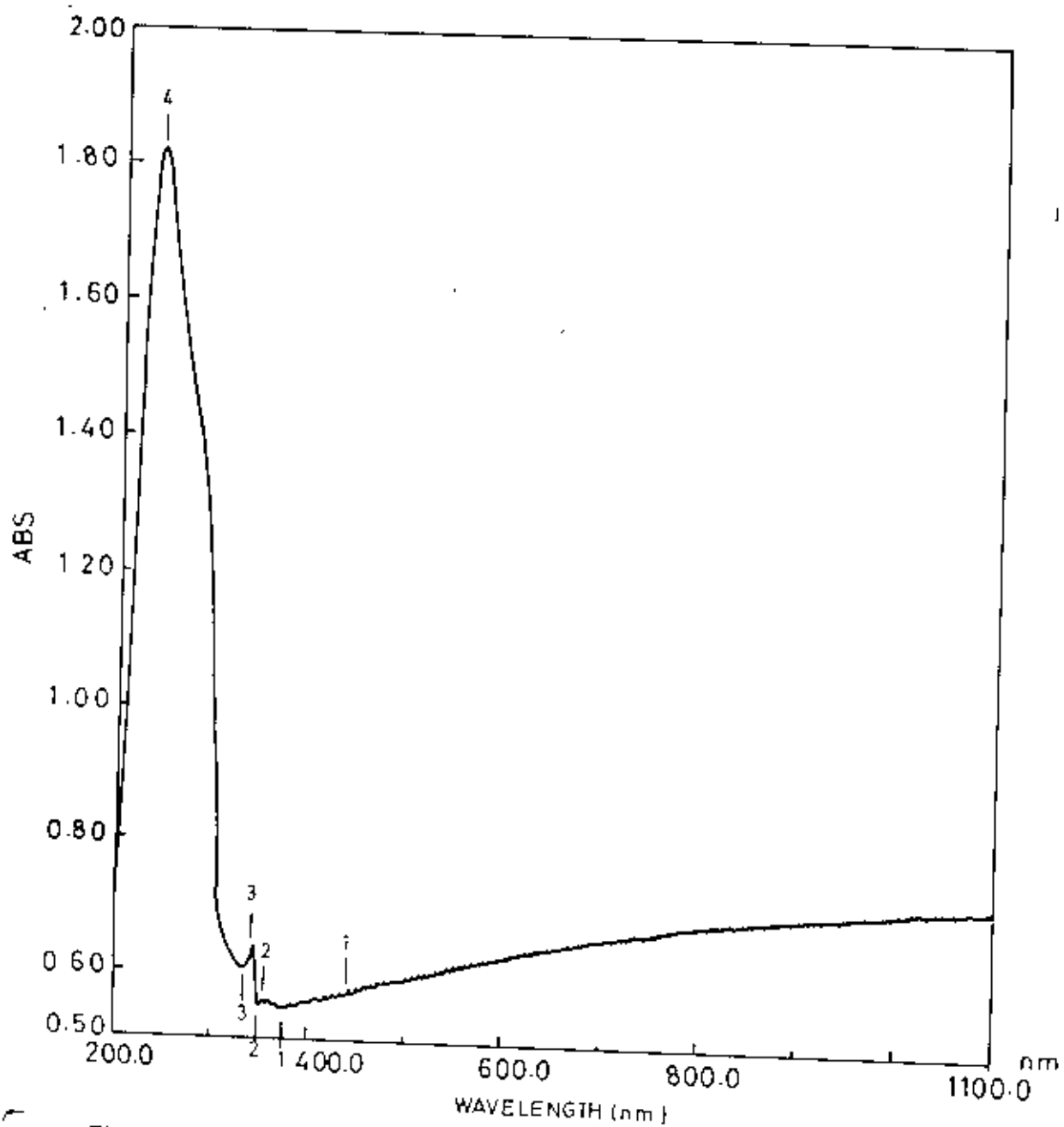
Fig.15: u.v. Spectra of the Triethylenetetram ine.

*** PEAK-PICK ***

--- PEAK ---

	ABS	--- VALLEY ---	
			ABS
443.0	0.576		
357.0	0.560	377.0	0.542
344.0	0.640	350.0	0.547
240.0	1.822	336.0	0.603

Table (6) uv-visible spectral data of some macrocyclic complexes.

Compounds	Maximum (nm)			
$Ni(C_{12}H_{26}N_6)$ $(ClO_4)_2$	861.00	309.00	296.00	254.00
$Cu(C_{12}H_{26}N_6)$ $(ClO_4)_2$	672.00	341.00	243.00	--
$Co(C_{12}H_{26}N_6)$ $(ClO_4)_2$ $4.H_2O$	--	341.00	299.00	243.00
$Ni(C_{15}H_{22}N_5)$ $(PF_6)_2$ $6.H_2O$	458.00	449.50	285.00	236.00
$Cu(C_{15}H_{22}N_5)$ $(PF_6)_2$ $5.H_2O$	--	280.00	--	236.00
$Ni(C_{13}H_{18}N_4)$ $(PF_6)_2$ $4(H_2O)$	763.00	280.00	--	225.00
$Cu(C_{13}H_{18}N_4)$ $(PF_6)_2$ $4(H_2O)$	--	--	221.50	--
$Cu(C_{13}H_{18}N_4)$ $(PF_6)_2$ $3(H_2O)$		290.00	221.00	--
Triethylene tetramine	443.00	357.00	344.00	240.00
diethylene triamine	--	--	238.50	--
2,6-diacetyl pyridine	--	274.00	236.00	220.00

1.4.7 THERMAL ANALYSIS:

Thermal analysis gives an idea about the bond strength of a compound and provides information about bonding nature. In thermogravimetry (TG), a change in the weight of a substance is recorded as a function of temperature with respect to time. Changes in the weight are the result of the breaking or formation of various chemical bonds at evaluated temperature. From this analysis it is also known whether the reaction take place is endothermic or exothermic. Weight loss at lower temperature is due to lattice component or loss of weakly coordinated component which are attached with central metal atom in coordinated complexes.

The thermogravimetric results depend upon the particle size, weight, heating rate, atmosphere of furnace etc. Thermograms of the compounds are taken by RIGAKU thermal analysis station TAS 100 with basic TG unit thermoflux TG 8110 from the HBRT laboratory, Dhaka. The heating rate controlled by the temperature programer panel 15°C/min.

The thermogravimetric analysis indicated that the $Ni(C_{12}H_{18}N_6(ClO_4)_2$ changed composition at 290°C with violent exothermic explosion which is comprehensible due to the presence of perchlorate ion. From the TG of $Cu(C_{12}H_{20}N_6(ClO_4)_2$ it was observed that the compound changed composition at 270°C with violent exothermic explosion, which is comprehensible due to the presence of perchlorate ion. The weight loss could not be computed to any chemical change. The thermogravimetric analysis is given in Fig. (16).

1.4.7.2   THERMAL ANALYSIS OF $Ni(C_{11}H_{18}N_4)(PF_6)_2$ $4(H_2O)$ & $Cd(C_{17}H_{19}N_4)(PF_6)_2$ $3(H_2O)$:

In the case of Ni complex the TG curve shows that the weight loss start at 40°C and continues upto 120°C. But in the Cd complex the weight loss start from 100°C and continue upto 150°C. These weight loss are probably due to the removal of water molecule. The weight loss at 200°C to 325°C and 200° to 400°C corresponding to the explosion of two molecule of hexafluorophosphate. Third step weight loss is possibly due to the removed of 2.6 diacetylpyridine and final step weight loss is due to metal and diethylene triamine for both cases. The TG curve are shown in Fig. (17-18).
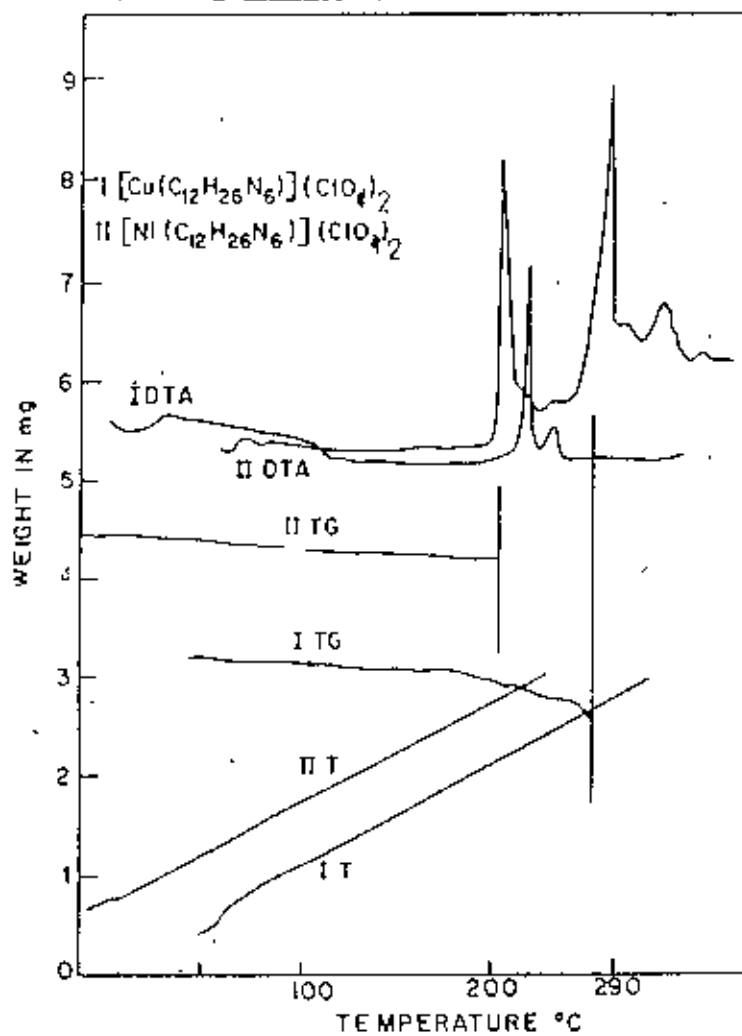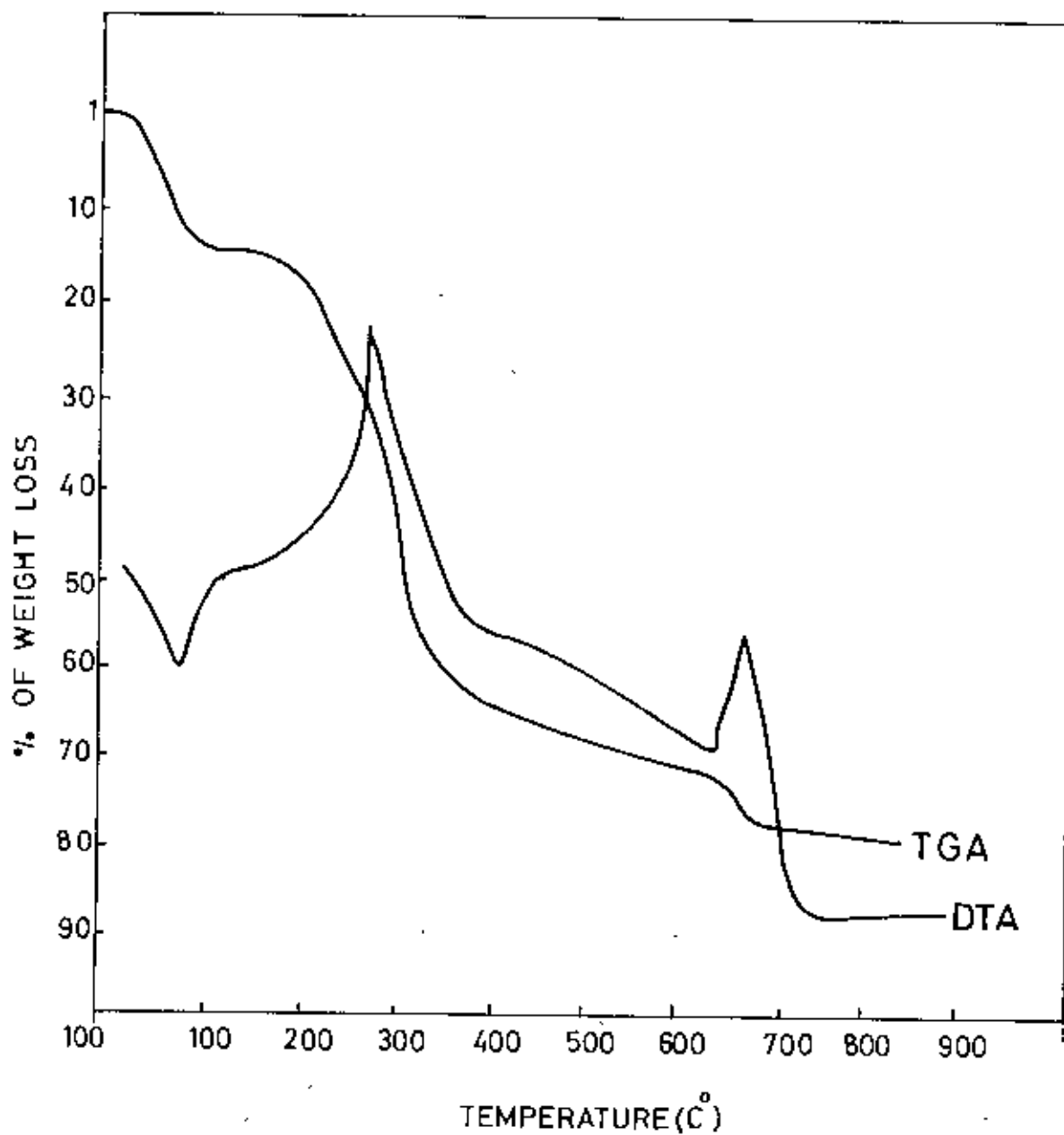
Fig.16. Thermogravimetric analysis of the complexes

Fig.42. The TG and DT Curve of the Complex [Ni(C$_{13}$H$_{18}$N$_4$)] (PF$_6$)$_2$ 4(H$_2$O).
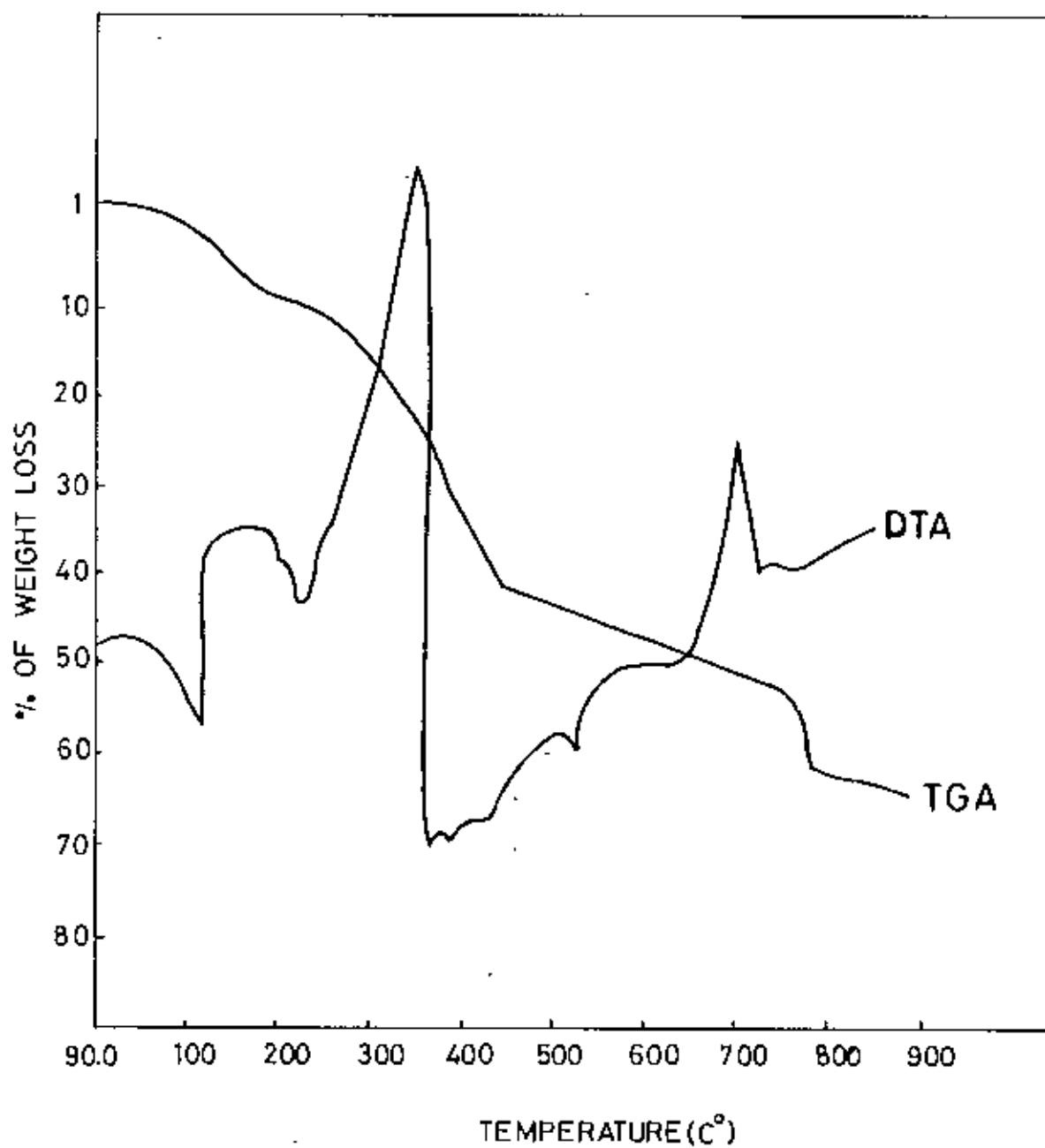
Fig. 18:- The TG and DT Curve of the Complex [Cd(C$_{13}$H$_{18}$N$_4$)](PF$_6$)$_2$ 3(H$_2$O).

1.4.7.3   Thermal Analysis of $Ni(C_{15}H_{13}N_5)(PF_6)_2$ 6(H_2O) & $Cu(C_{15}H_{13}N_5)(PF_6)_2$ 5(H_2O):

In the case of Ni complex the TG curve shows that weight loss start at 50°C and continues upto 250°C. This weight loss is due to removal of water molecules. But in the Cu complex the weight loss start from near 100°C and continue 500°C. The weight loss from 250°C to near 700°C corresponding to the explosion of two molecule of hexafluorophosphate. Third step weight loss within the temperature rang 700°C to 900°C is probably due to removal of 2, 6 diacetylpyridine. The TG curve are shown in Fig. (19-20).

1.4.8   X-Ray DIFFRACTROMETRIC ANALYSIS

The X-ray powder diffraction patterns were recorded by using JDX-8P JOEL Ltd., Tokyo, Japan diffraction recorder.

For X-ray diffractrogram, Cu-K$_\alpha$ radiation and Ni filter was recorded with a scanning speed of 2°/min, chart speed 20 mm/min. Scanning range 5-52° (Cu-K$_\alpha$ = 1.5418A). Only the powder diffractrograms are represented in Fig. (21). The complete x-ray diffraction of single crystal products are under investigation.

Fig.19: The TG and DT Curve of the Complex $[Ni(C_{15}H_{23}N_5)](PF_6)_2$ $6(H_2O)$.
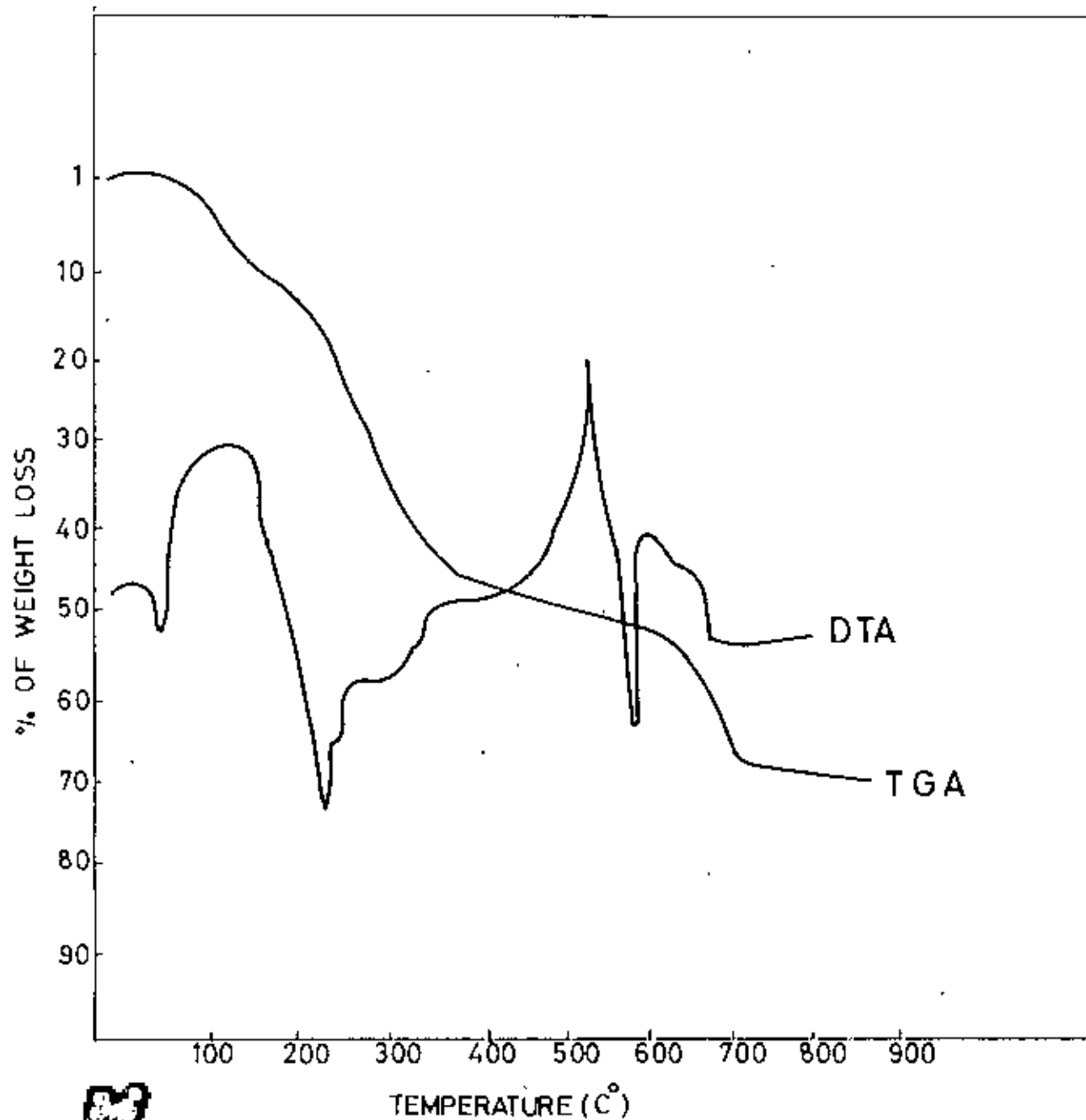
Fig. 20 The TG and DT Curve of the Complex $[Cu(C_{15}H_{23}N_5)]$ (PF_6) $5(H_2O)$.
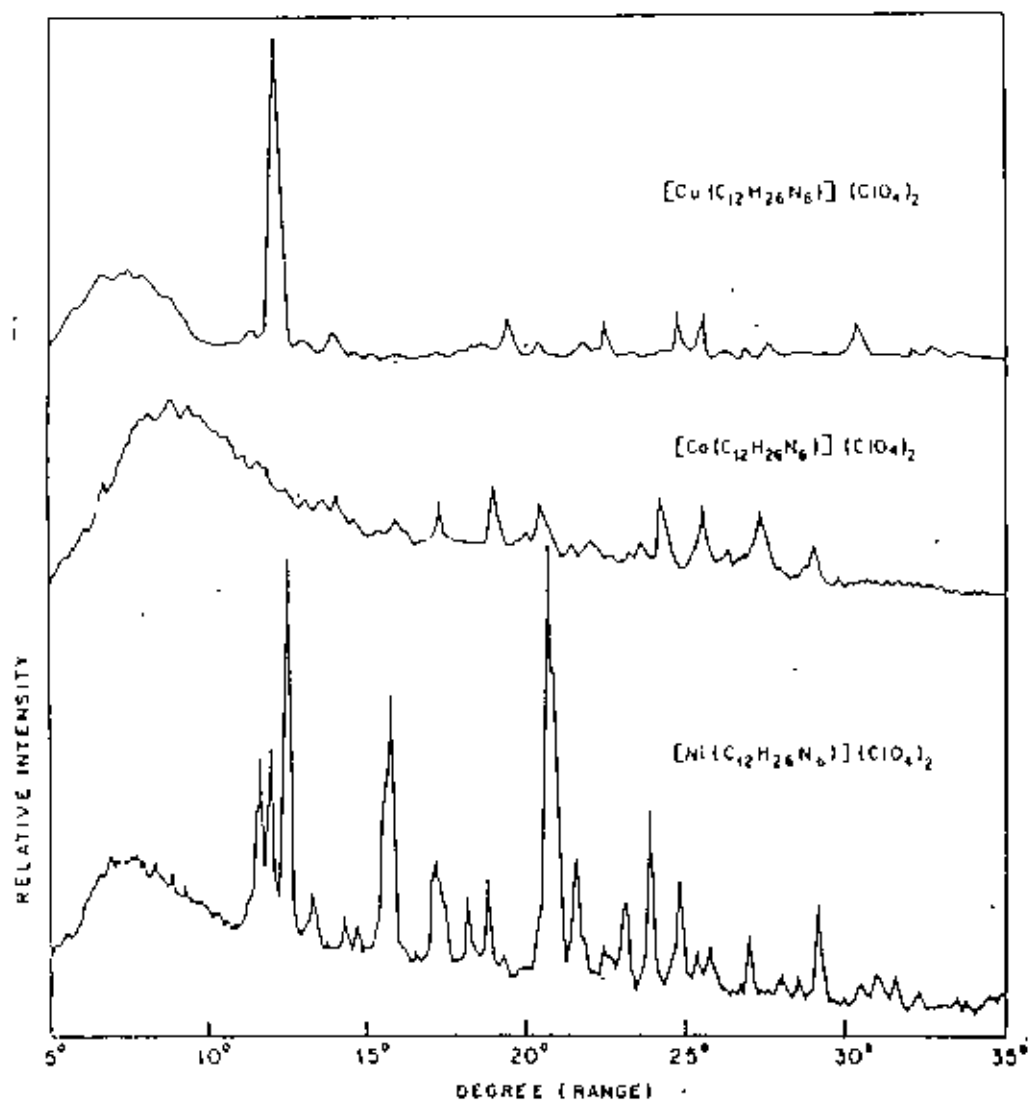
Fig. 21: Comparison of X-ray diffractogram of the complexes

1.6 DISCUSSIONS
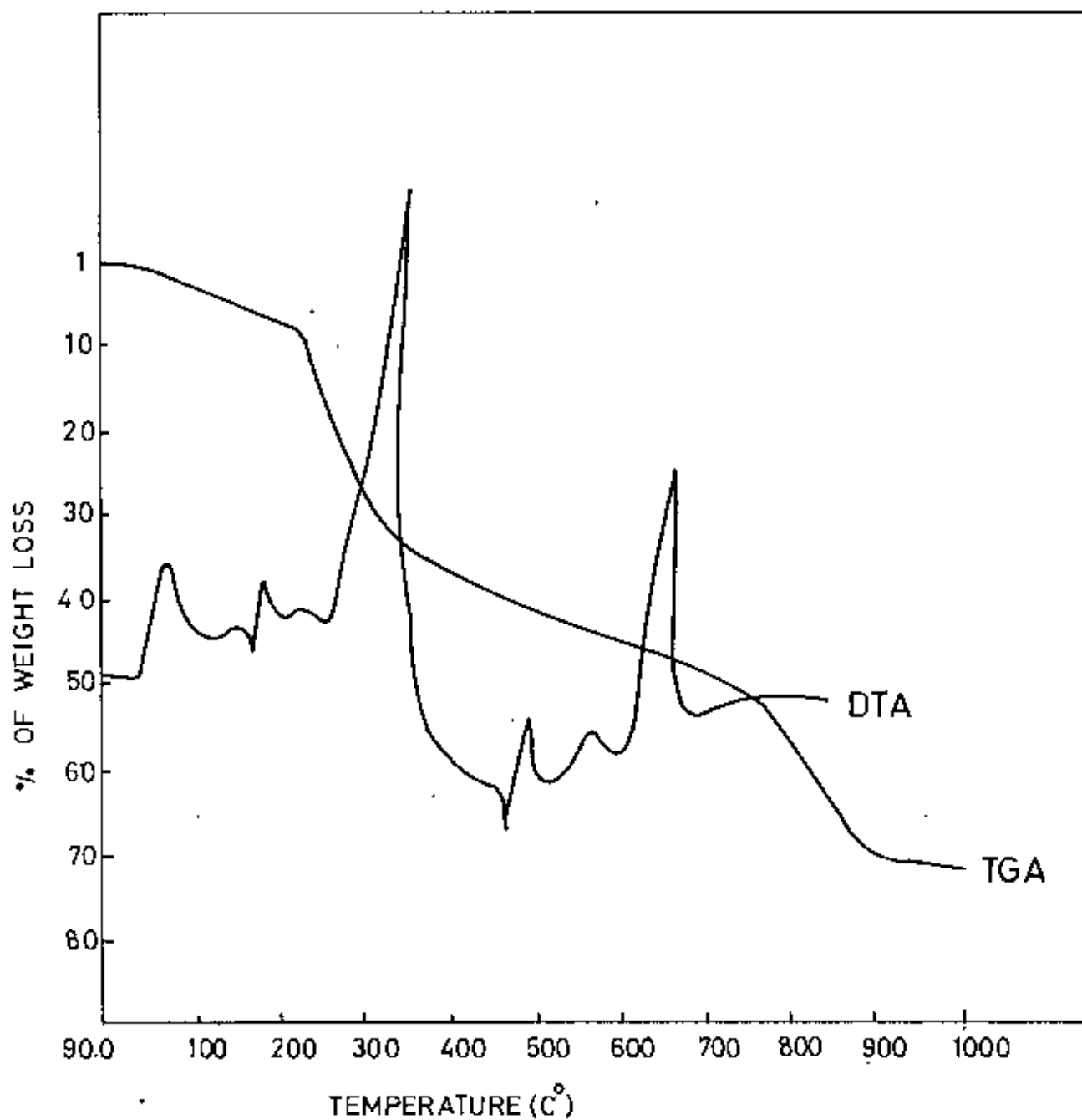
In the present work several metal complexes of hexadentate $(C_{12}H_{26}N_6)$, pentadentate $(C_{15}H_{27}N_5)$ and tetradentate $(C_{17}H_{18}N_4)$ macrocyclic ligand were synthesized by using ethylenediamine and triethylene-tetraamine with formaldehyde, 2,6-diacetylpyride with triethylene tetraamine or diethylenetriamine and metal salts. Aqueous or aqueous-methanol was used as a reaction media. Lithium perchlorate or amonium hexafluorophosphate were used as a counter ion for the formation and precipitation of solid crystalline complexes. For a good yield first row transition metal were used. The formula of complexes are given below:

[Ni $(C_{12}H_{26}N_6)$] $(ClO_4)_2$

[Cu $(C_{12}H_{26}N_6)$] $(ClO_4)_2$

[Co $(C_{12}H_{26}N_6)$] $(ClO_4)_2$

[Ni $(C_{15}H_{27}N_5)$] $(PF_6)_2$ $6(H_2O)$

[Cu $(C_{15}H_{23}N_5)$] $(PF_6)_2$ $5(H_2O)$

[Ni $(C_{17}H_{18}N_4)$] $(PF_6)_2$ $4(H_2O)$

[Cu $(C_{17}H_{18}N_4)$] $(PF_6)_2$ $4(H_2O)$

[Cd $(C_{17}H_{18}N_4)$] $(PF_6)_2$ $3(H_2O)$
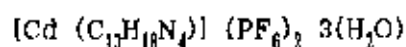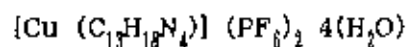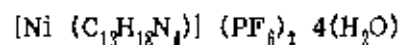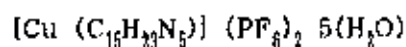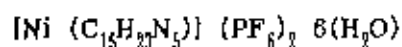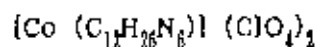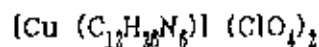
In this reaction a metal ion coordinates a tetraamine and an ethylenediamine in octahedral fashion. Formaldehyde combines with two cis coordinated amine moieties for the cyclization, yielding methylenediamine linkages[5-8]. Uncoordinated secondary amines involving methylenediamine linkages react further with formaldehyde to become tertiaryamine. The resulting macrocycle ligands contain six nitrogen atoms, of which four nitrogen are tertiary, either coordinated or uncoordinated, while the remaining two are secondary and coordinated to the metal ion.

Microanalytical results of complexes for C, H and N for some complexes are in good agreement with the calculated values corresponding to the macrocyclic complex formations. Complexes have sharp m.p. indicating the purity of the complexes. The ready solubility of the complexes also suggest that the desired macrocyclization proposed has taken place leading to the formation of the macrocyclic complexes.

The I.R. spectra of the complexes are discussed together with the characteristics bands. The peaks of various vibration modes are listed in Table (5) for comparative study. The $> C = N-$ bands appear at 1610 cm^{-1} for the complexes indicating the macrocycle formation. The N-H of NH$_2$ and $>C =$ groups generally vibrate at $3350-3150$ and $1850-1700$ cm^{-1}, respectively. Since the Schiff base condensation reaction takes place between a diamine and a dicarboxyl, the absorption due to the free N-H and $>C = O$ group disappear. The peaks at around 4000 cm^{-1} may be an indication of the presence of those of $>$ N-H group. The absorption bands at around 3600 cm^{-1} are due to the presence of lattice water. The invariation appear at around 500 cm^{-1} is due to the M-N band. The identity of the infrared spectra of the complexes also suggest that these complex possess complicated structures. The complexes show a number of intense absorption bands in the u.v. region. From the shape, position and intensity, these bands are within the assigned $\pi-\pi'$ transitions. Conductivity measurement of some complexes are carried out using acetone as solvent. It is show that except for the Cd complex the number of ion is 3. For the Cd complex, the no. of ion is 2 and the electrolyte type is 2:1.

The results of the thermogravimetric analysis of Ni and Cu complexes in Fig. (16) indicate the explosive nature of the complexes. From Fig. (24–25), it is observed that the complexes studied start weight loss at low temperature indicating the removal of water molecule. Macrocyclic complex to be more stable with respect to ligand dissociation than open chain must possess multidentate ligand site system. X–ray diffractogram of the complexes $Ni(C_{12}H_{16}N_6)$ $(ClO_4)_2$ $Cu(C_{12}H_{26}N_6)$ $(ClO_4)_2$ and $Co(C_{12}H_{26}N_6)$ $(ClO_4)_2$. $4(H_2O)$ are shown in Fig. (27) for the purpose of comparison only. However, further work for the determination of the complete structure using single crystal x–ray diffractometer is in progress.

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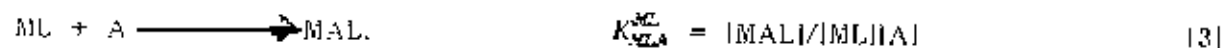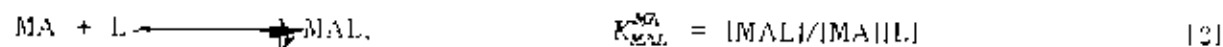   J of Bangladesh Academy of Science, Vol. 16, No. 1, 99-103, 1994.

CHAPTER - II

2.0 INTRODUCTION

In a complex, where two or more ligands of the same type are bonded with a metal ion is called a binary ligand complex and if different types of ligands are present, then the complex is said to be ternary complex or mixed ligand complex.

In a living tissue and fluid, strong co-ordinating transition metal ions and potential co-ordinating sites of organic molecules are responsible for biochemical reactions[1]. In such cases the mixed ligand complex formation is to be observed[2,3]. In a biochemical system the ternary complexes[4-8] expected to be formed. Taking everything together one is not surprised any more about Woods' conclusion[9], "if you think that biochemistry is the organic chemistry of living system, you are misled; biochemistry is the co-ordiation chemistry of living system". The biochemical reactions are nothing but models of ternary complex forming[10-13] systems. The synthetic ternary complexes are formed when metal ion bonded with two different carrier ligands and substrate [14,15,14-19]. The stabilities of the ternary complexes and associated binary complexes[6,7,10-13,20-27] have been reported.

The formation of ternary complex can be expressed in three different ways as follows

$$M + A + L \longrightarrow MAL, \qquad \beta_{MAL}^{M} = [MAL]/[M][A][L] \qquad [1]$$

$$MA + L \longrightarrow MAL, \qquad K_{MAL}^{MA} = [MAL]/[MA][L] \qquad [2]$$

$$ML + A \longrightarrow MAL, \qquad K_{MLA}^{ML} = [MAL]/[ML][A] \qquad [3]$$

Hence

$$\log \; K^{MA}_{MAL} \;\; = \;\; \log \; \beta^{M}_{MAL} \;\; - \;\; Log \;\; K^{M}_{MA} \tag{4}$$
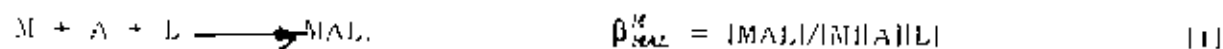
$$\log \; K^{ML}_{MLA} \;\; = \;\; \log \; \beta^{M}_{MLA} \;\; - \;\; Log \;\; K^{M}_{ML} \tag{5}$$

There are two common methods to express, on a quantitative basis the stability of ternary complexes[5,28,29]. Firstly it can be expressed[30] in terms of

$$\Delta \log K = \log \; K^{MA}_{MAL} \; - \log K^{M}_{ML} \; = \log \;\; K^{ML}_{MLA} \; - \log \; K^{M}_{MA} \tag{6}$$

i.e. the difference in the tendency of a ligand (A or L) to bind with free metal ion and with the metal ion already bound to another ligand (L or A). It is evident that from the relationship eq. (6) that the influence of both ligand is mutual and both ligands are either stabilized or destibilized in their co-ordination to the metal ion equally.

ΔlogK must be a constant because it is the result from substraction of two constant logK is a constant corresponding to the equilibrium constant of the reaction indicated in equation [7].

$$MA \; + \; ML \; \xrightarrow{\hspace{2cm}} MAL \; + \; M \tag{7}$$

$$logK = log \frac{[MAL] \; [M]}{[MA] \; [ML]} \tag{8}$$

From statistical consideration ΔlogK is expected to be negative. This is because when the first ligand (A) combines with a given multivalent (hydrated) metal ion, it has more co-ordination position available for bonding than when it combines

with metal already bound to another ligand (L). Hence, the order Log K_{ML}^{M} >

Log K_{MLA}^{ML} usually holds and one expects to observe negative values for $\Delta logK$.

The stabilization factor governing $\Delta logK$ depends on the coordination number of the metal ion and the denticity of the ligand.

The difference, $(logK_{MAL}^{M} - logK_{MA}^{M}$ is generally about -0.5 to -0.8 log units for monodentate ligands and about -1 to -2 log unit for bidentate ligands[31]. In the case where A and L are bidentate ligands, there are twelve edges of a regular octahedron[oh] available for the first entering ligand, but only one five for the second[20] i.e. the statistical factor is 5/12 and accordingly $-\Delta log K_{oh} = -0.4$. For square plane (sp) a factor of 1/4, i.e. $\Delta logK_{sp} = -0.6$ is obtained. However for the distorted octahedron (do) of Cu^{+2} the statistical value is more difficult to assess. Considering the John–Teller inversion to be rapid[31], there are eight (or even twelve) equivalent attacking positions for the first ligand while the value for the second ligand can vary from one to four (or never five) depending on the relative rates of inversion. Hence, the statistical value is between 1/8 (or 1/12) and 4/8 and $\Delta log K_{do} = -0.9$ (or -1.1) to -0.3. In case of Cu^{+2} and the ligands that introduce a strong ligand field, the statistical expression $\Delta log K_{do/Cu} = -0.9$ is considered to be most appropriate one[7]. Hence an experimentally determined value of $\Delta logK$, more or less negative them -0.9, indicates that in equation (7), the tennary complex is favoured less or more, respectively. So the value of $\Delta logk$ is

affected by the nonstatistical factors depending on the natures of the ligands A and L and structure of the metal ion in some cases[12].

The other approach to express the stability of tennary complex on a quantitative basis is based on the "disproportionation constant" K_{reprop} as defined by the following equation.

$$MA_2 + ML_2 \rightleftharpoons 2MAL$$
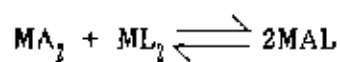
$$K_{reprop} = \frac{[MAL]^2}{[MA_2][ML_2]} \qquad [9]$$

$$\log K_{reprop} = 2\log\beta_{MAL}^M - (\log\beta_{A_2}^M + \log\beta_{L_2}^M)$$

From statistical consideration the value of K_{reprop} is expected to be 4. Under purely statistical considerations the mixed ligand complex MAL is formed by two path ways (eqs. 2 and 3), whereas MA_2 and ML_2 are formed by one path way each. Hence there is a possibility of 50% formation of [MAL], while binary complexes MA_2 and ML_2 are formed to the extent of 25% each. Hence the value of K_{reprop} should be equal to 4 as shown below.

$$K_{reprop} = \frac{[MAL]^2}{[MA_2][ML_2]} = \frac{50^2}{25 \times 25} = 4$$

or, $\log K_{reprop} = 0.6$

Hence log K_{reprop} will be 0.6 if only statistical factors were responsible for the formation constant. If for electrostatical reasons the stability of MA_2 or ML_2 complex is less, more of MAL is formed and the value of $logK_{reprop}$ is higher than 0.6.

Thus the stability of the ternary complexes can be evaluated either based on the values of $\Delta logK$ or $logK_{reprop}$. Each of the above two methods has its own merit and demerits[7,18] and preference to either approach has to depend on the kind of study. The main advantage of consideration of $\log K_{reprop}$ is in its firm statistical basis. It does not depend on the co–ordination number of the metal ion or the denticity of the ligand. This advantage is lost while using $\Delta logK$ formulation, since the statistical value depends upon the co–ordination number of the metal ion and the denticity of the ligand. Log K_{reprop} does not indicate absolute stability of the complex, but its relative stability with respect to the complexes MA_2 and ML_2. In a mixed ligand complex containing a neutral ligand A or a negatively charged ligand L, $\Delta logK$ is not affected by the electrostatic or entropy factor. But steric hindrance between the two ligands in a MA_4 or ML_2 complex results in the distortions from a tetragonal geometry[32,33].

In the present chapter the formation constant of ternary complexes [MAL], where M = Cu(II), A = oxalic (OX) acid or 2, 6–pyridinedicarboxylic acid (DPA), L = Glycine, or α.alaline, or phenylelanine or tryptophan have been determined and the values of $\Delta logK$ have been calculated. The protonation constants and formation constants for binary complexes have been reported earlier[34, 35, 26], and present work has used those of previous constant.

EXPERIMENTAL

2.4.3 APPARATUS

All glasswares used were of pyrex glass. The microburette was calibrated to 0.01 ml by the method described by vogel[37]. The measuring flask of various capacities, pipettes etc. were calibrated by using a standard burette.

Chemicals:

All reagents are AR grade and their standard solutions were prepared by directly dissolving the weighed quantity of them, in known volume of aqueous solution. Copper perchlerate was prepared from analytical pure copper carbonate by treatment with 70% perchloric acid (AR). The resulting solids were washed with ethanol till free from excess acid and recrystallized several times from ethanol. Copper perchlorate are partially soluble in alcohol. Stock solution of copper perchlorate, perchloric acid, sodium hydroxide and sodium perchlorate were all prepared in carbonate free double distilled deionized water. Copper perchlorate solution was also standardized by iodometric titration[38]. Carbonate free sodium hydroxide solution was prepared according to the literature method[39] standardized by standard oxalic acid solution. Standard perchlonic acid solution was prepared from AR 70% acid by proper dilution and titrate with standard alkali.

2.1.2 POTENTIOMETRIC DETERMINATION OF STABILITY CONSTANT

Irving Rossotti titration technique[40,41] has been used to determine the formation constants of the ternary complexes using SCOGS (stability constants of Generalized species) computer programme[42,43].

The activity coefficient of H^+ under experimental condition has been considered to be equal to 0.78 and the value of the ionic product of water 14.167 has been used.

For the determination of formation constants all solutions were titrated potentiometrically against standard (0.02M) sodium hydroxide solution. In all the cases acid concentration was kept 2.00×10^{-2}M and the total ionic strength (1) of the solution was maintained at 0.2M.

For the determination of the formation constants of the ternery complexes (MAL), the following solution (50 cm^3) having M:A:L in the ratio 1:1:1 were prepared.

1. 0.02M $HClO_4$, 0 002M metal perchlorate, 0.002M ligand (A), 0.002M ligand (L) and 0.174M $NaClO_4$ this set was titrated against standard alkali. All the titrations were carried out in aqueous medium and the temperature was maintained at 30°C ± 1°C during the progress of titration. Titration were carried out by using TOA pH-METER HM-20S, having an accuracy of ± 0.01 pH unit. The glass electrode was calibrated using buffer solution of pH 4.01 and 6.86. Hence the stability constants calculated are stochimetric constants[44]. The calculation were carried out by computer, EPSON, PCA X3S/20.

A model input data required for the calculation of formation constant in the ternary system requires the following details.

1. No. of jobs to be calculated.

2. No. of experiments in the set of experiments under study.

3. No. of ligands (two), no. of metals (one) and the no. of complex species formed (including protonated forms of ligand, hydrolyzed metal species etc.).

4. Composition of each species has to be described along with its approximate formation constants as the logarithm to base 10.

5. No. of displaceable protons on ligand (1) and ligand (2).

6. Title of the experiment.

7. Initial concentrations of the metal, ligands, mineral acid ($HClO_4$), titrant base and total initial volume concentrations are expressed in moles/lit and volume in ml.

8. For each titration reading bearing values of titre of base, of pH and INDEX (a quantity which is zero for all but the last reading of experiment when INDEX = 1).

9. Then return to item 6 to read data for next experiment and repeat until data for all the experiments, as indicated by item (2), have been read.

10. Logarithm to base 10 of the ionic product of water, and the coefficient of hydrogen ion under the condition of experiment. (e.g. at 30°C and I = 0.2).

11. The no. of constant to be refined and no. of calculation cycles to be repeated to get convergency in the formation constant values.

12. The particular constant to be varied, given with serial no. as in (4) and the logarithm increment or decrement to be applied to the formation constant in the numerical differentiation.

The reported[34,35,36] protonation constant and formation constant were used as fixed parameters for the refinement of the formation constants of the ternary complexes. The porton ligand formation constant of binary complexes are shown in Table (1). The species considered for the calculation of formation constants of the ternary complexes were A. AH, AH_2, L, LH_2, MA, MA_2, ML, ML_2. The values of formation constant for the ternary complexes. $\Delta logK$ have been presented in Table (2). p^H. Titration curve have been presented in Fig. 1.1 to 1.8 for the ternary complexes. (MAL-system) are shown in Fig. 1.9 to 1.10. Representative species distribution curves as a function of p^H in the solution containing M, A and L have been presented in Fig. 1.11 to 1.18.
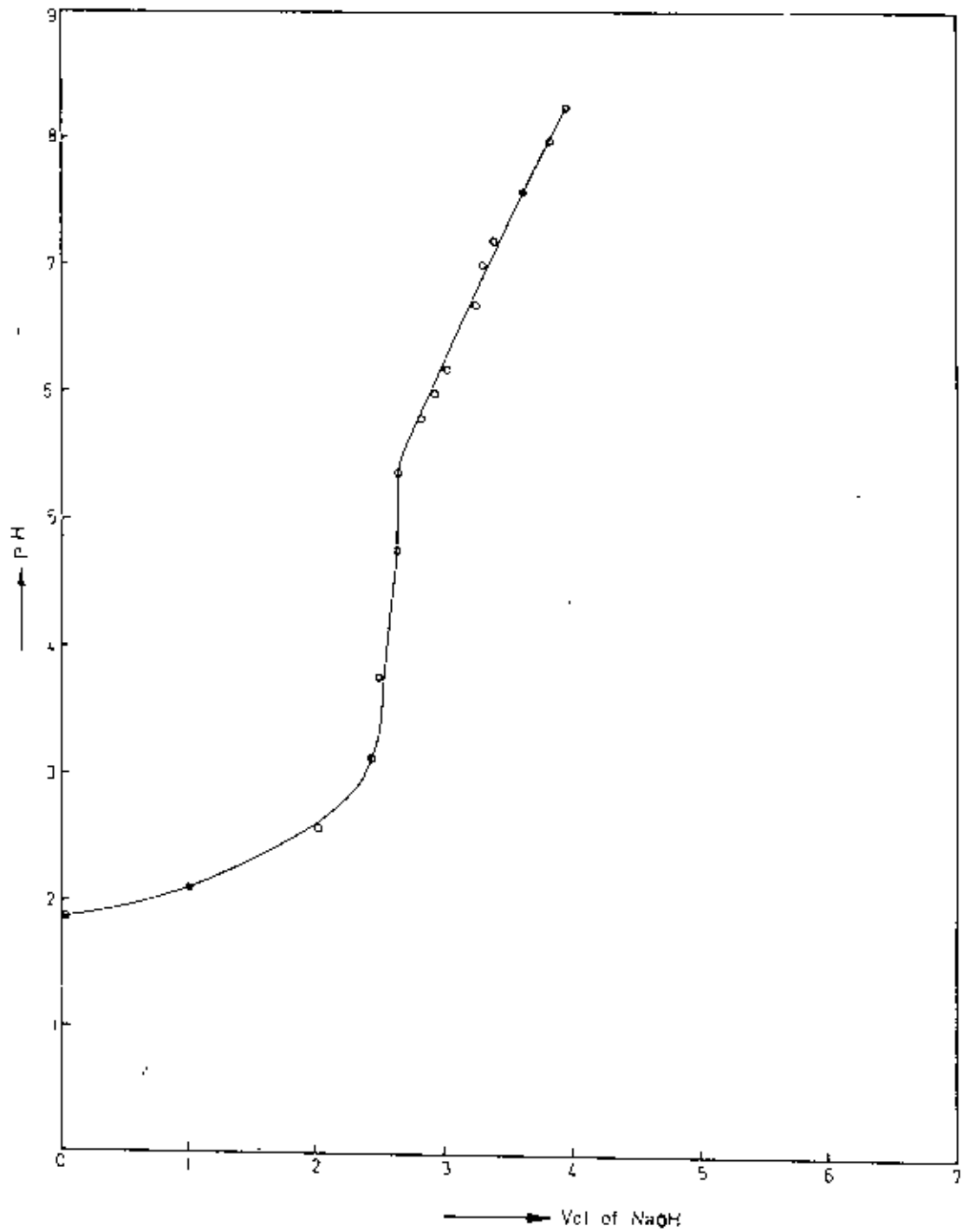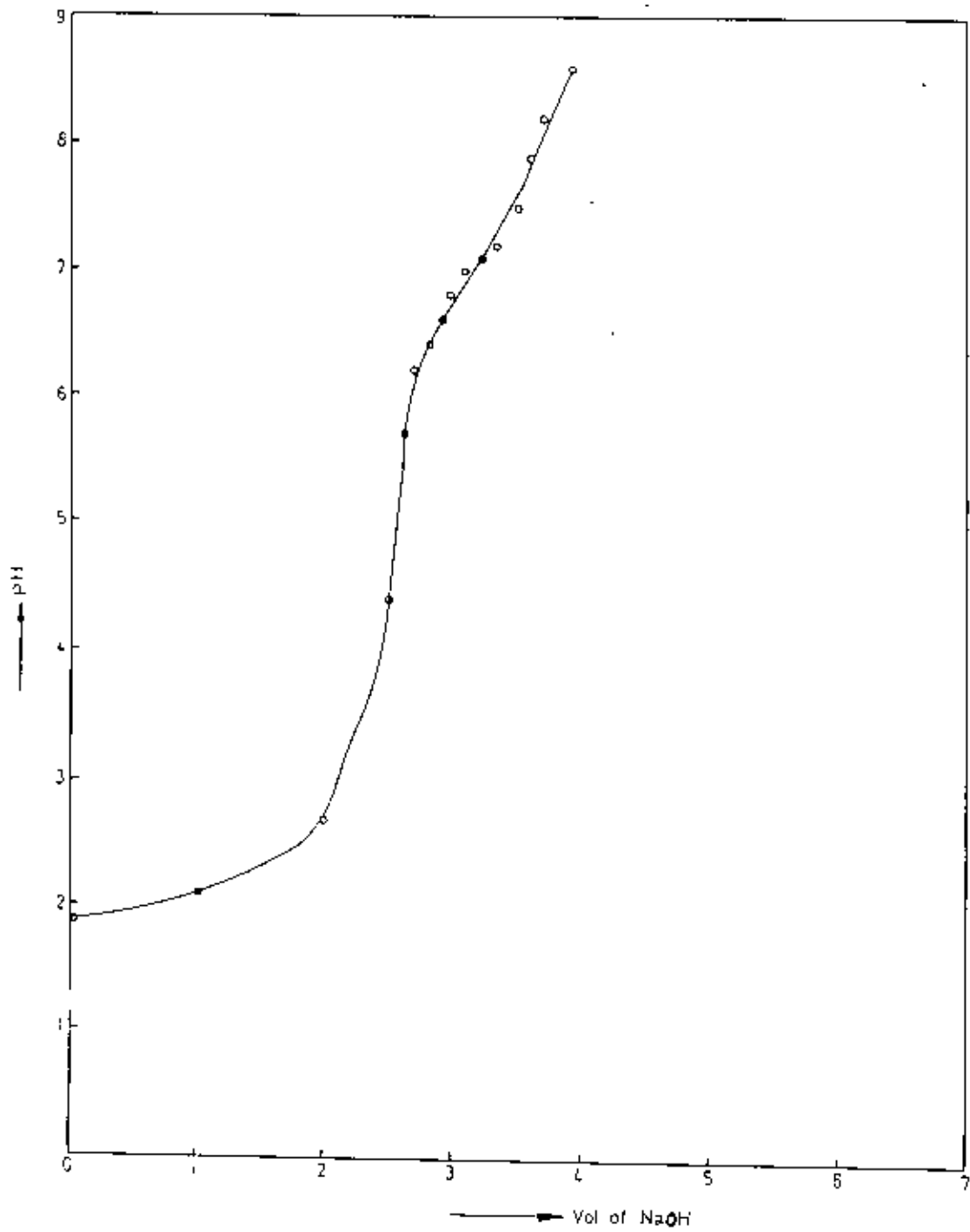
Fig. 3.1: Potentiometric titration curves of aqueous solution containing metal ion, OX and L (each 2.0 X 10⁻³M) curve, where metal ion = Cu²⁺, L = Phe-ala.

Fig. 1.2 Potentiometric titration curves of aqueous solution containing metal ion, OX and L (each 2.0 X 10⁻³M) curve, where metal ion = Cu²⁺, L = Glycine.
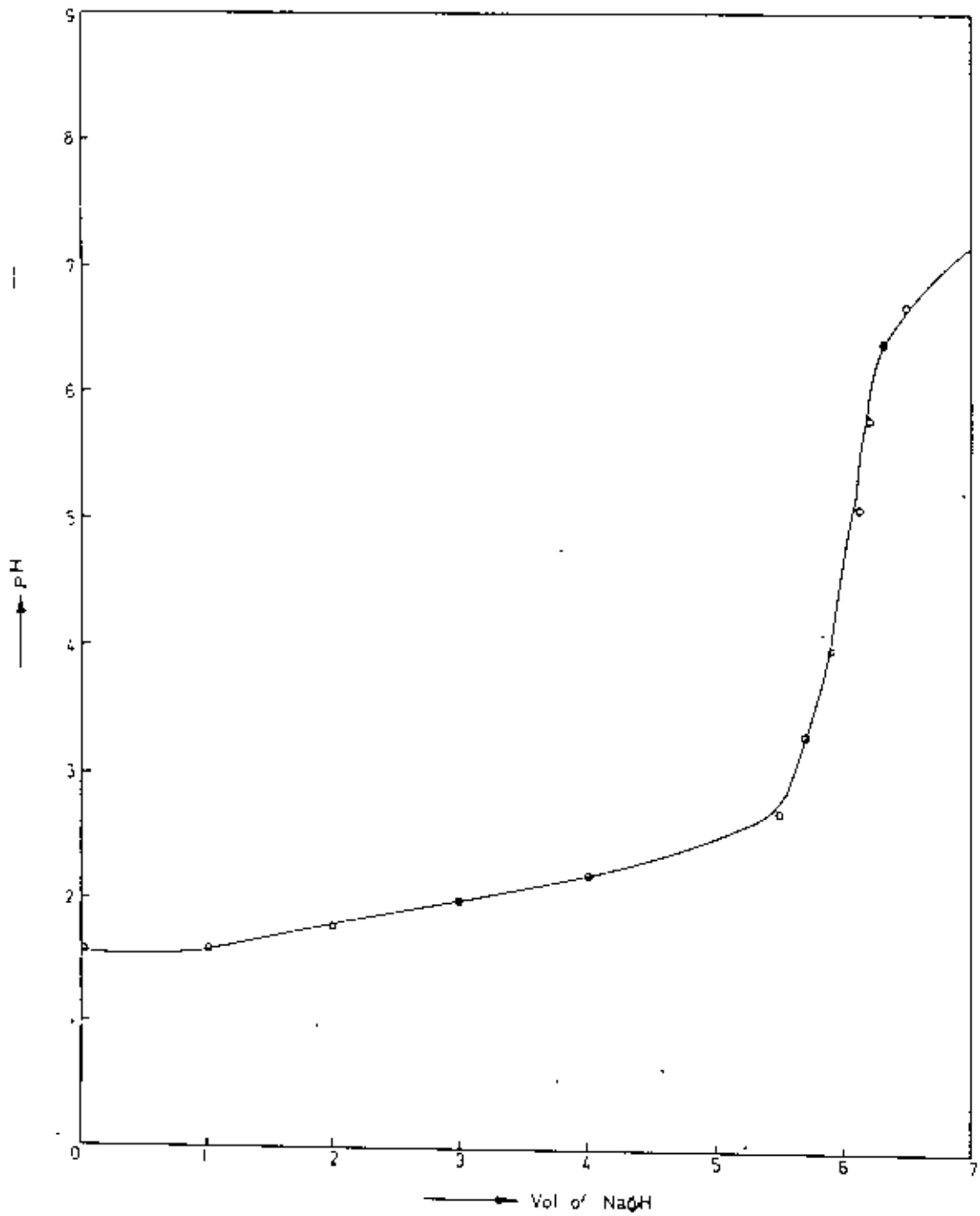
Fig. 1.5. Potentiometric titration curves of aqueous solution containing metal ion, GX and L (each 2.0 X 10^{-3}M) curve where metal ion Cu^{++} L = Tryptophan.
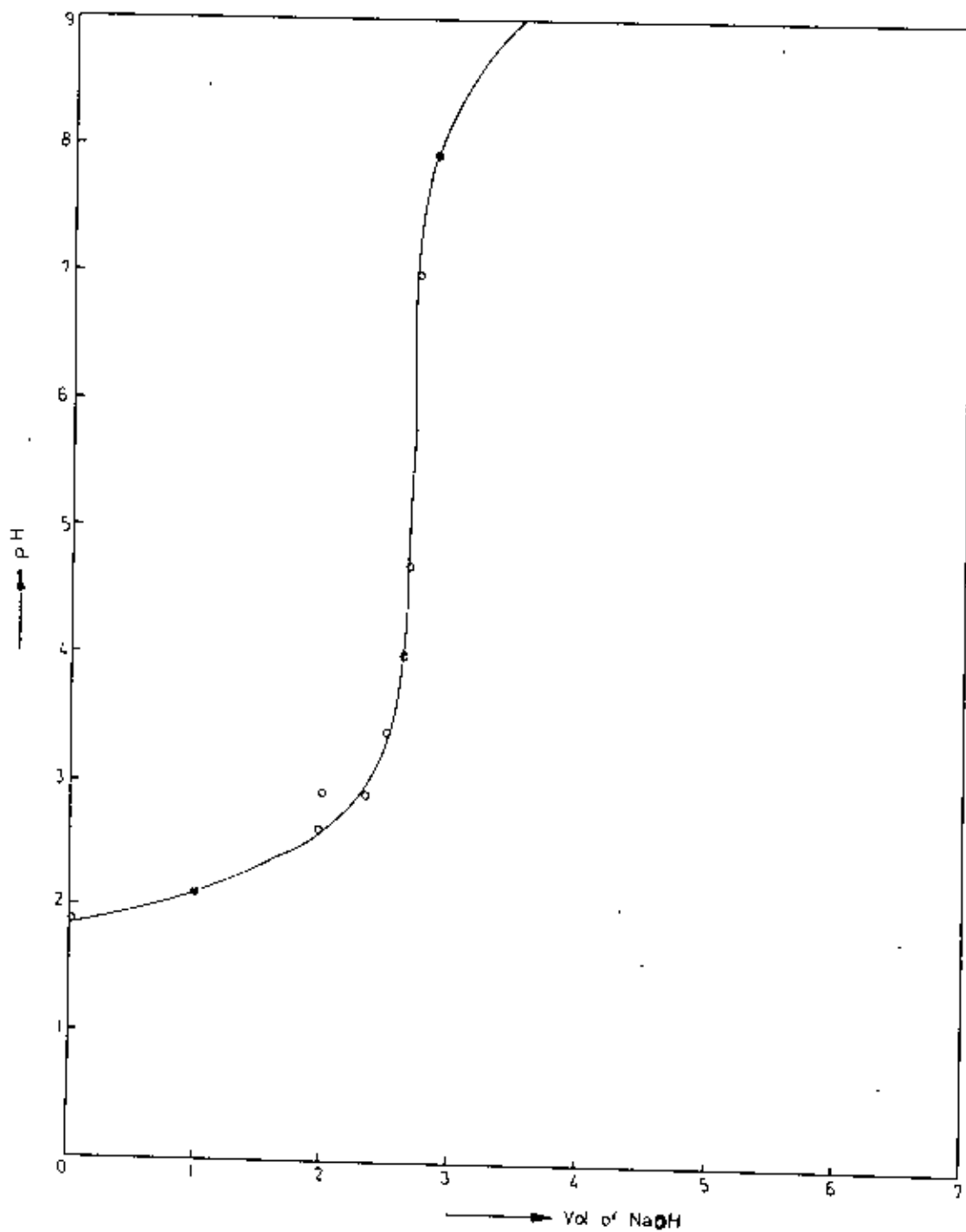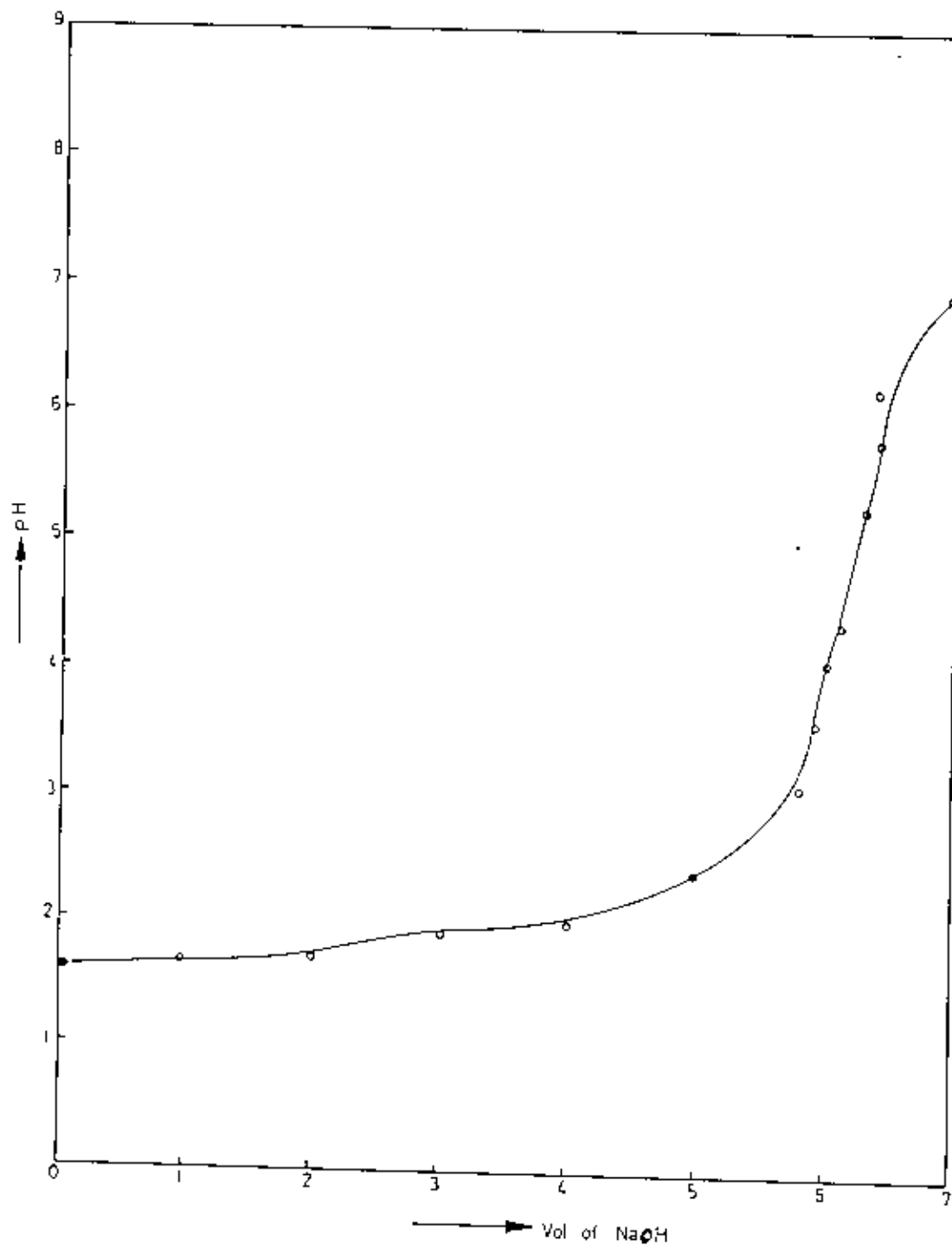
Fig 1.4. Potentiometric titration curves of aqueous solution containing metal ion, OX and L (each 2.0 X 10⁻³M) curve, where metal ion – Cu²⁺, L = α-alaline.

Fig. 1.5 Potentiometric titration curves of aqueous solution containing metal ion, DPA and L (each 2.0 X 10^{-3}M) curve where metal ion = Cd^{+}, L = Phenyl-alanine.
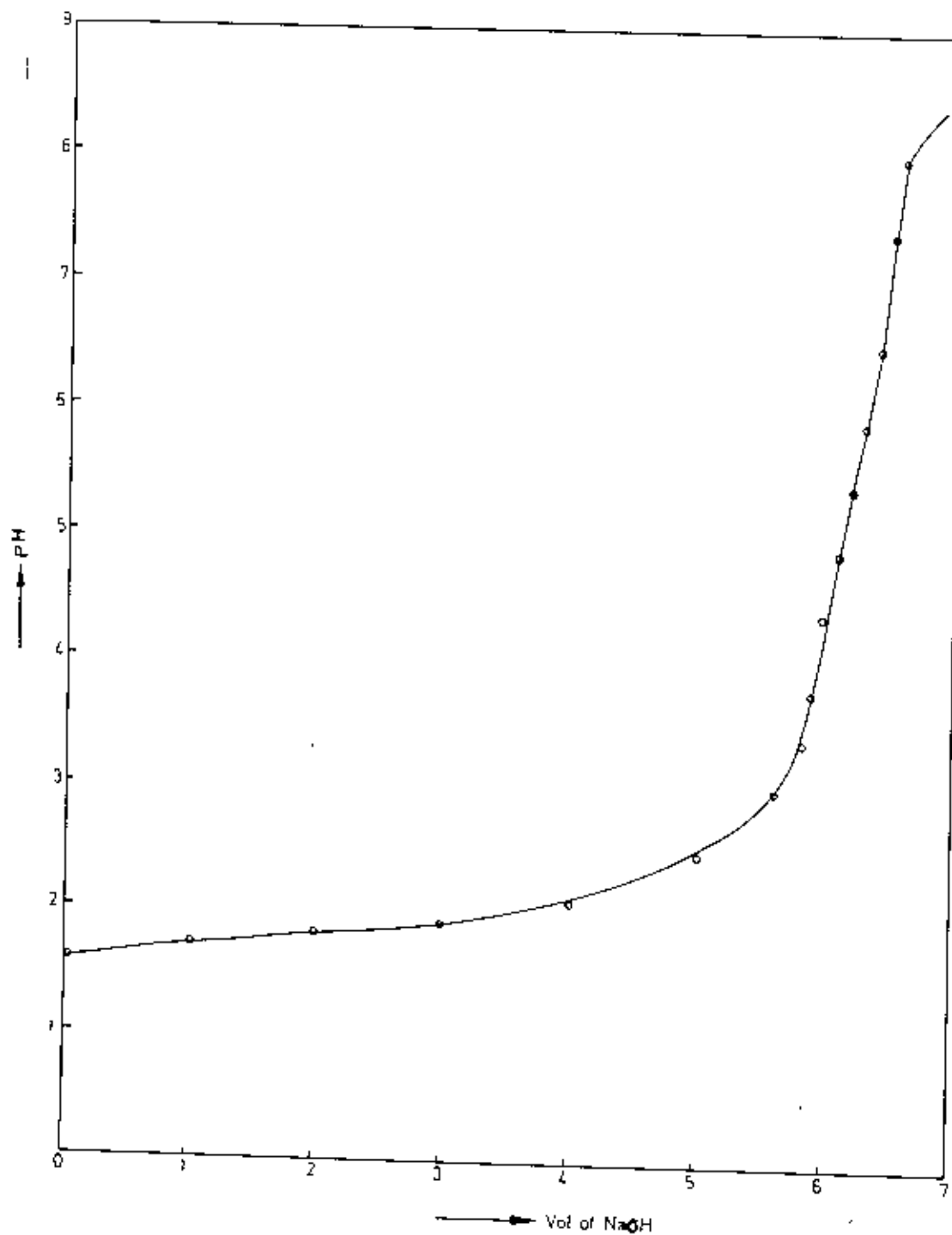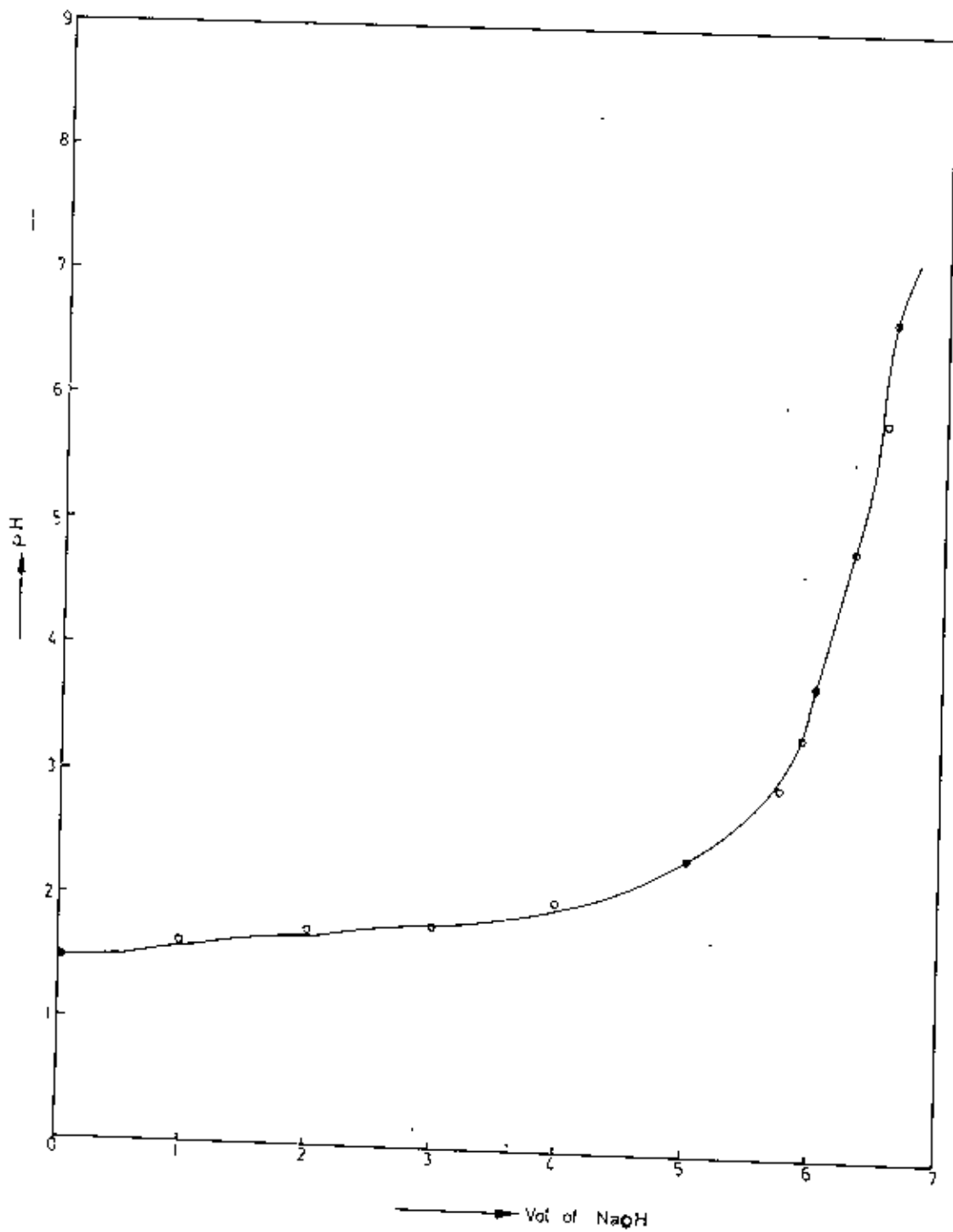
Fig. 1.6   Potentiometric titration curves of aquaous solution containing metal ion, DPA and L, (each 2.0 X 10⁻³M) curve where metal ion = Cu⁺⁺ L = Glycine.

Fig.1 7   Potentiometric titration curves of aqueous solution containing
metal ion, DPA and L (each 2.0 × 10⁻³M) curve where
metal ion = Cu²⁺] = Tryptophan
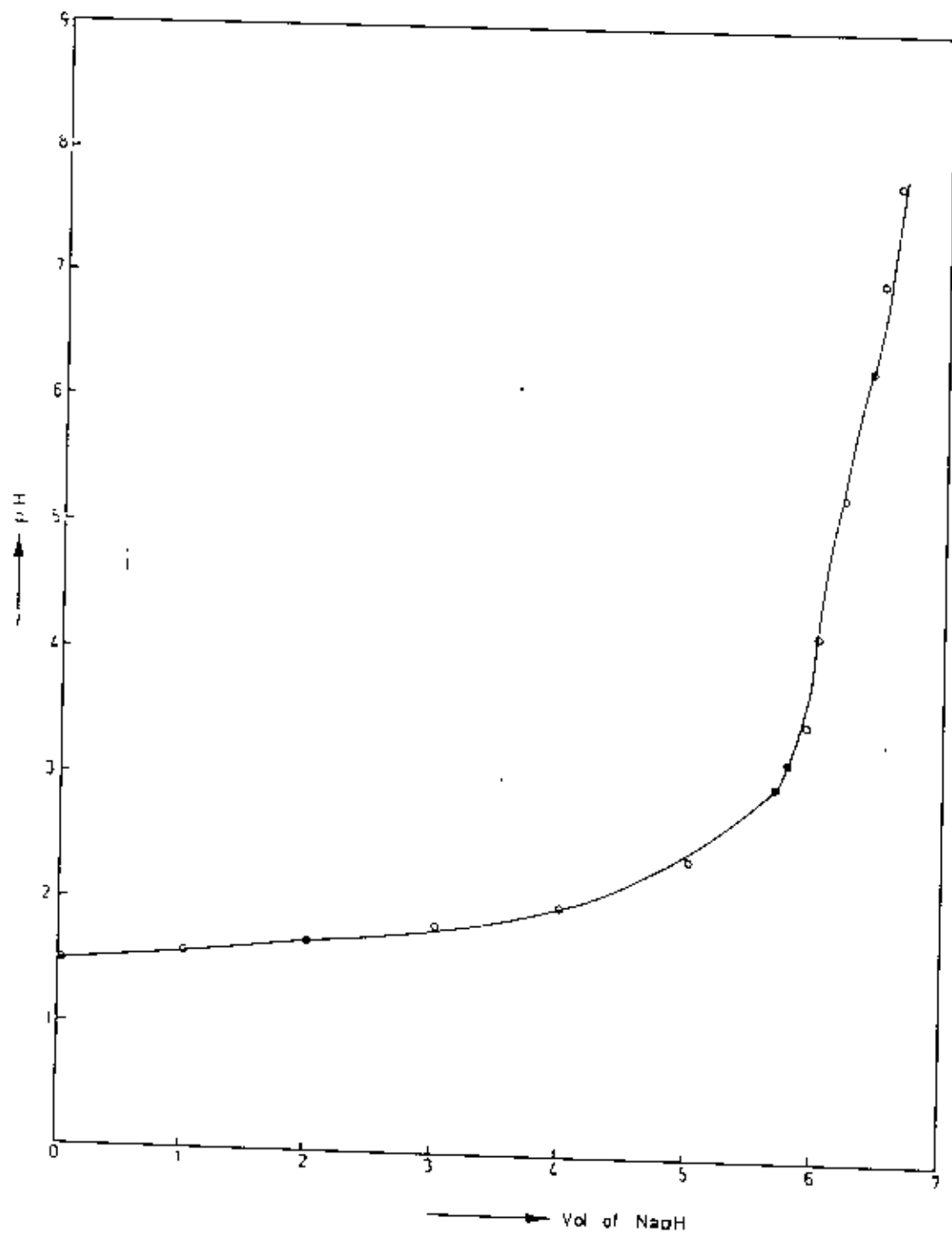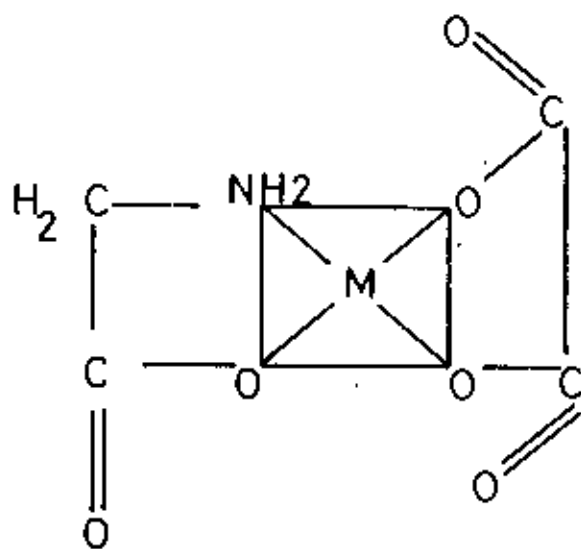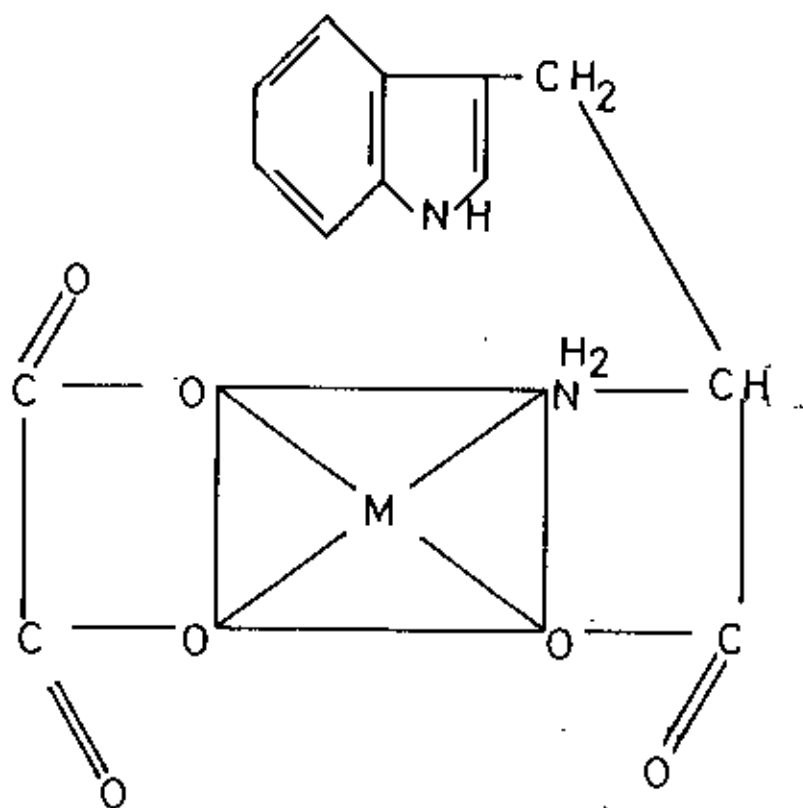
Fig. 18. Potentiometric titration curves of aqueous solution containing metal ion, DPA and L (each 2.0 X 10-3M) curve, where metal ion = Cu++ L = α-alanine.
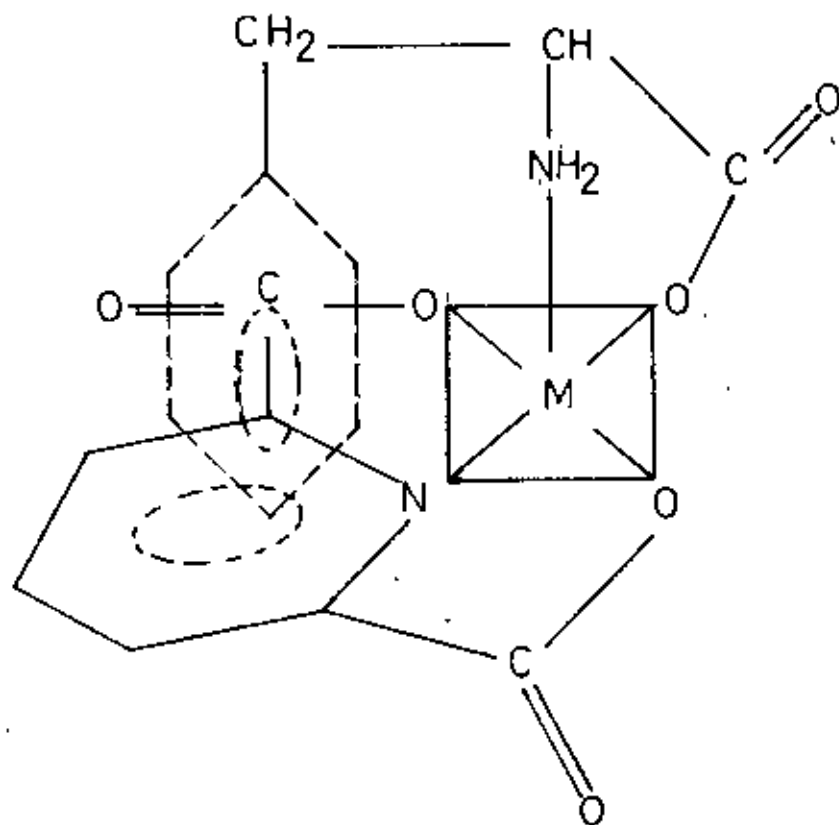
(M-OX-GLY) System·

(M-OX-Tryp) System·

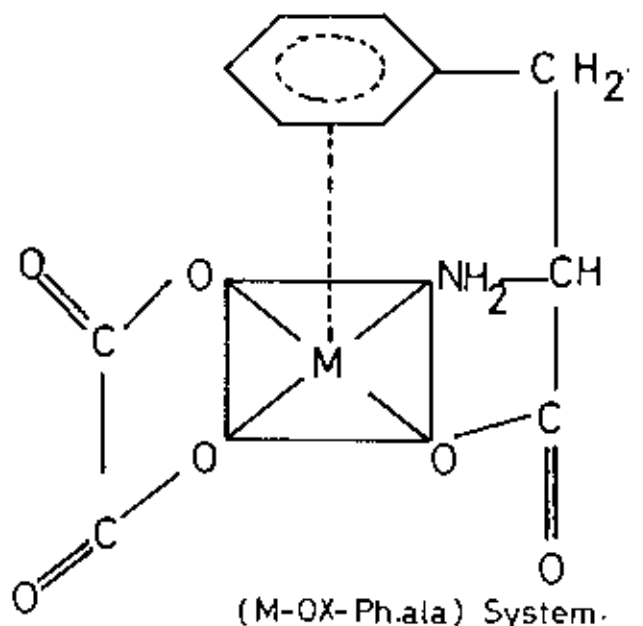Fig 1.9 : (MAL-System) where M=Metal , A=Oxalic Acid and
L=glycine or Tryptophan·

(M-DPA-Ph.ala.) System.

(M-OX-Ph.ala) System.

Fig.1.10:(MAL System) where M=Metal,
A=2,6-Pyridinedicarboxlic acid
or Oxalic acid and L=Phenylalanine.

Fig. 1.11: Species distribution diagram for the [Cu-OX-Tryp] Ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

Fig.1.12: Species distribution diagram for the [Cu-OX-∝-ala] Ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

Fig. 1.13: Species distribution diagram for the [Cu-OX-Ph-ala] Ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.
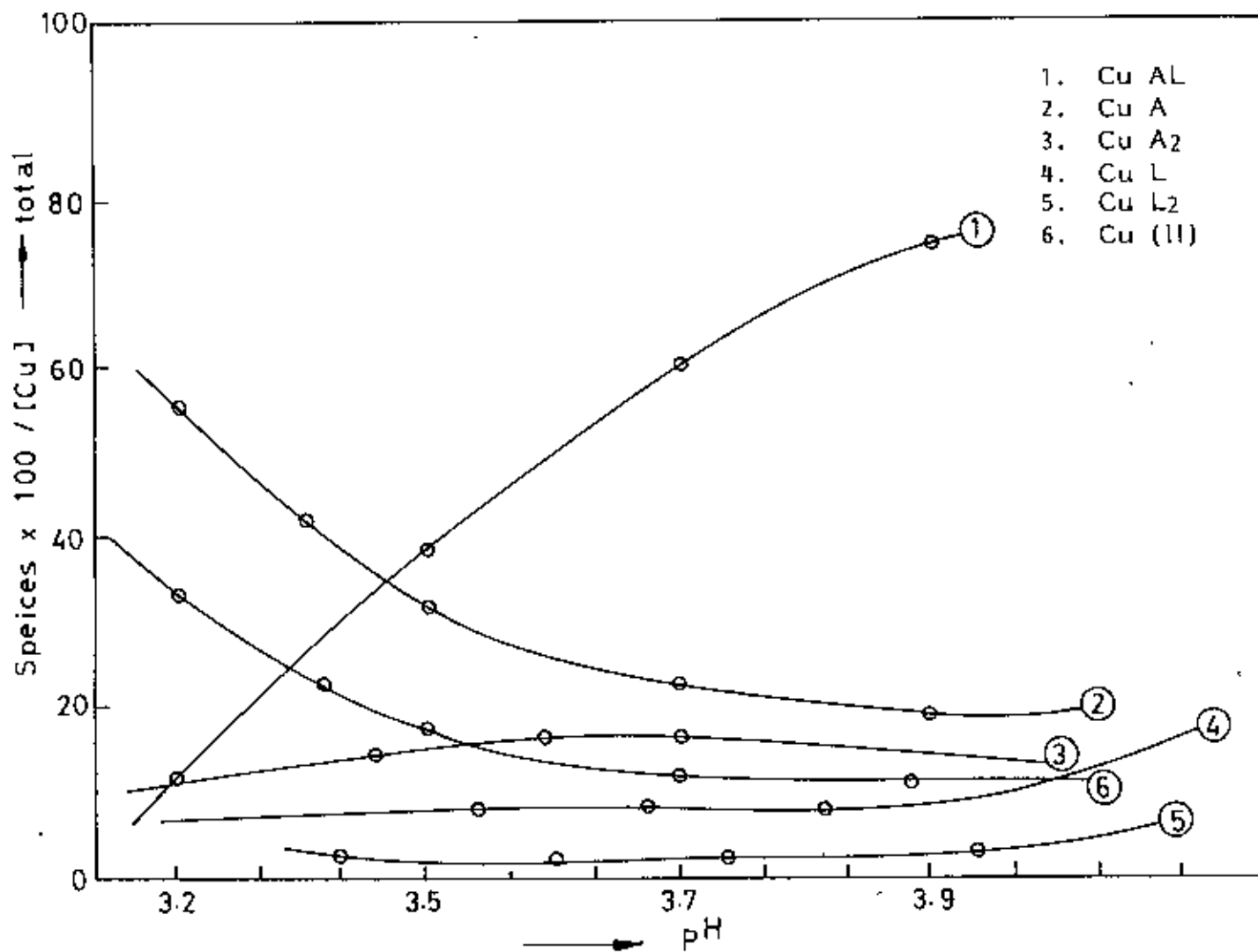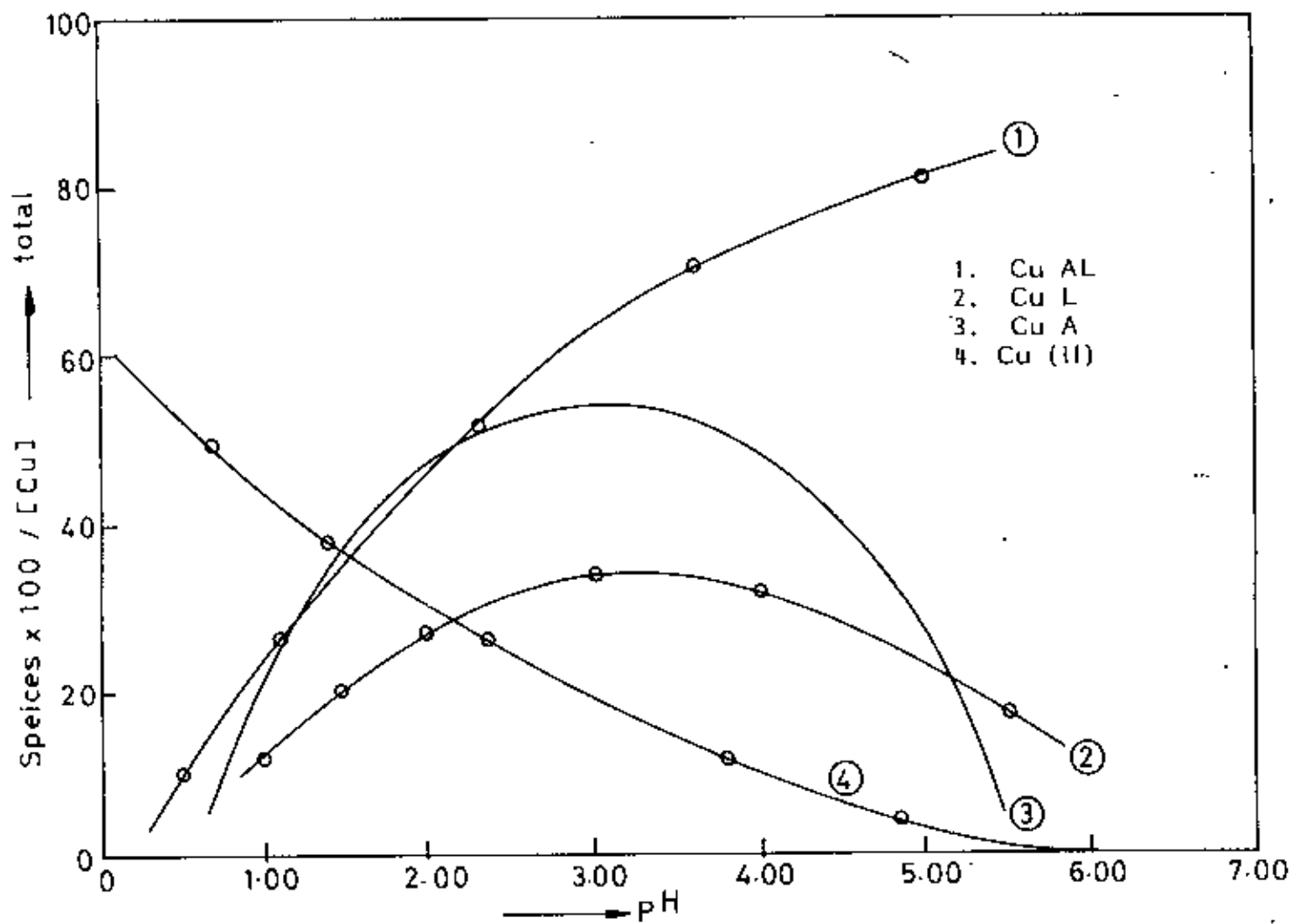
Fig.1.14:   Species distribution diagram for the [Cu-OX-Gly] Ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.
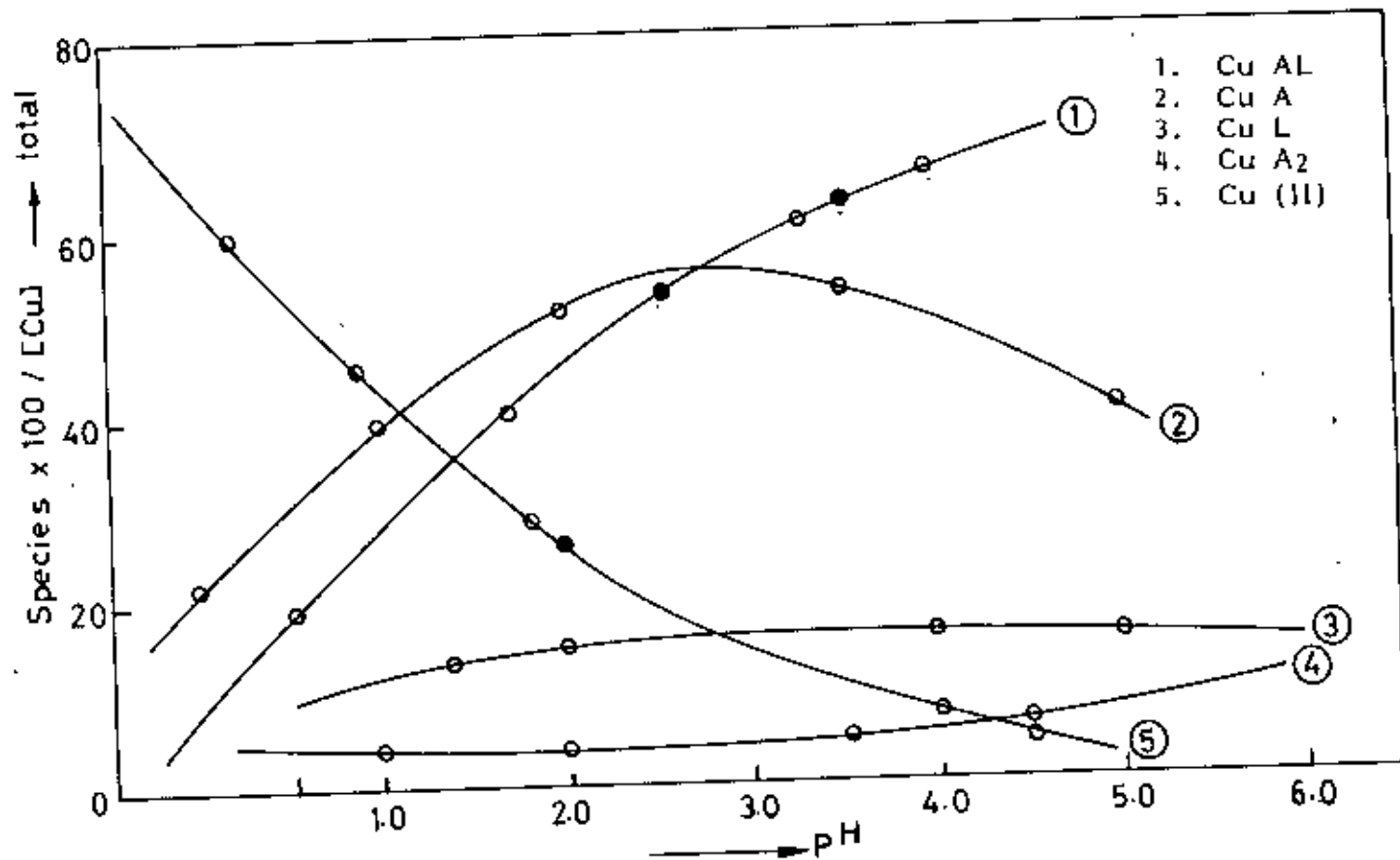
Fig.1.15: Species distribution diagram for the [Cu-DPA-x-ala] Ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

Fig.1.16: Species distribution diagram for the [Cu-DPA-Gly] Ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

Fig.1.17: Species distribution diagram for the [Cu-DPA-Tryp] Ternary system showing the formation percentage relative to total concentration of the metal as the function of pH.
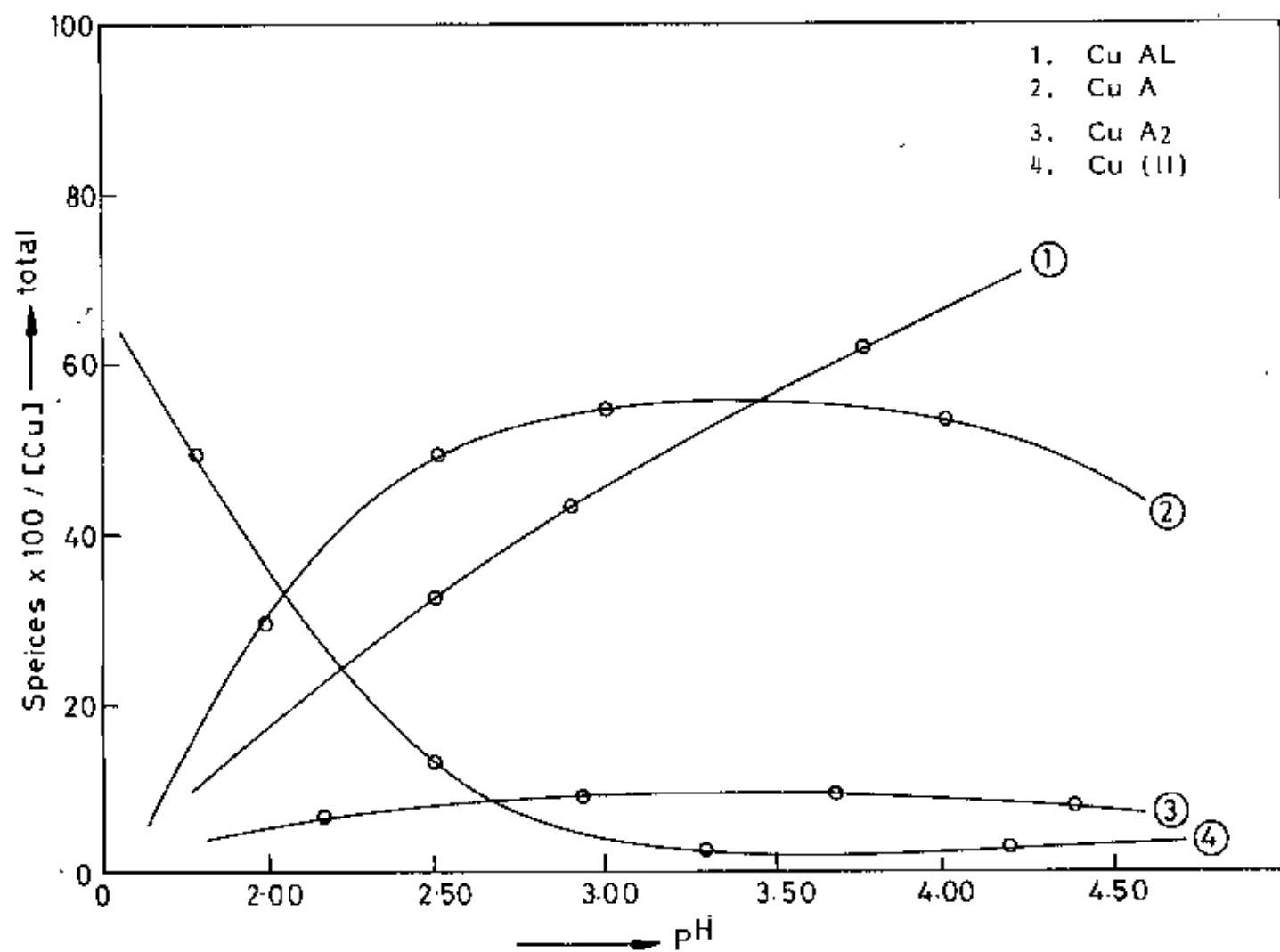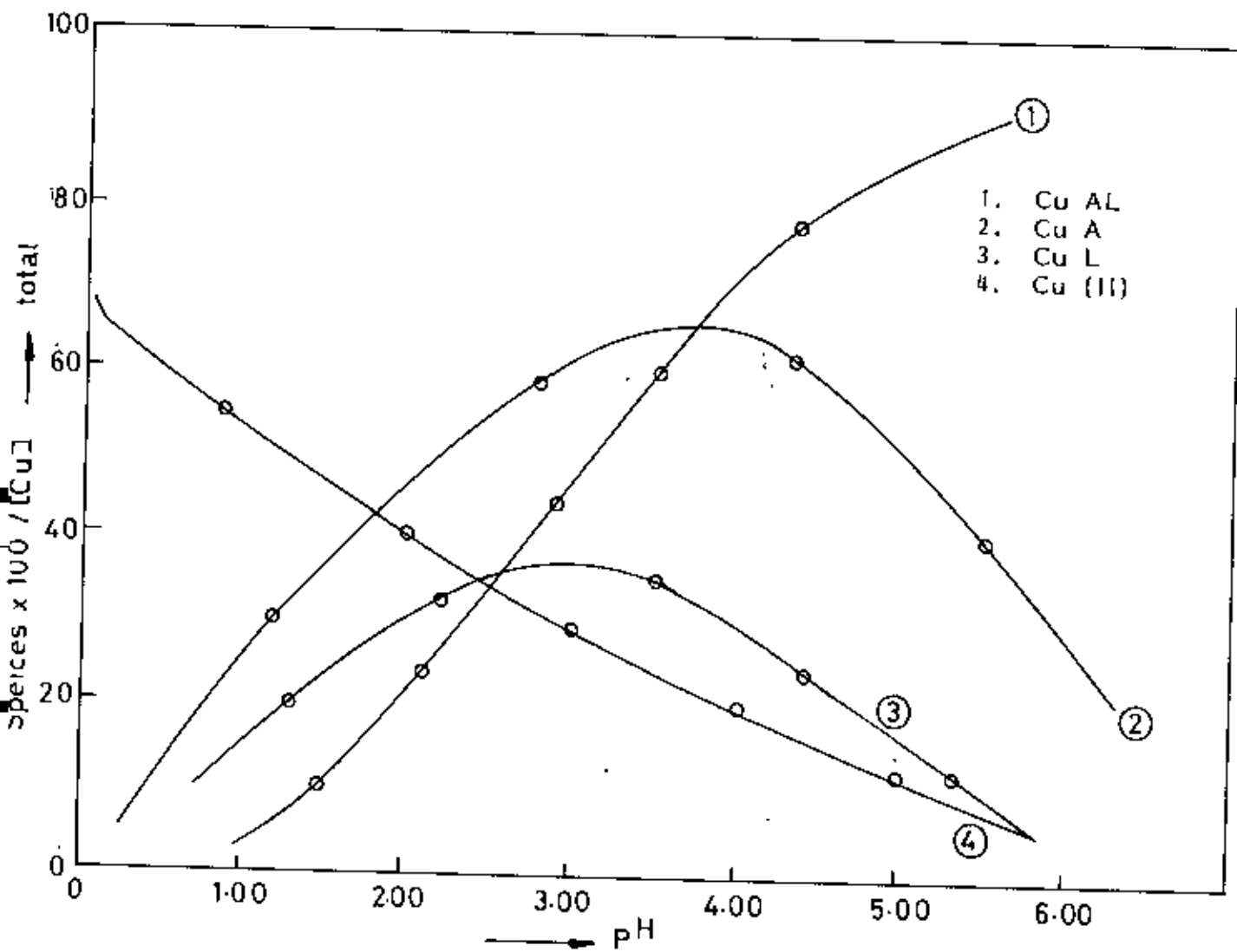
Fig. 1.18: Species distribution diagram for the [Cu-DPA-Ph-ala] Ternary System showing the formation percentages relative to total concentration of the metal as the function of pH.
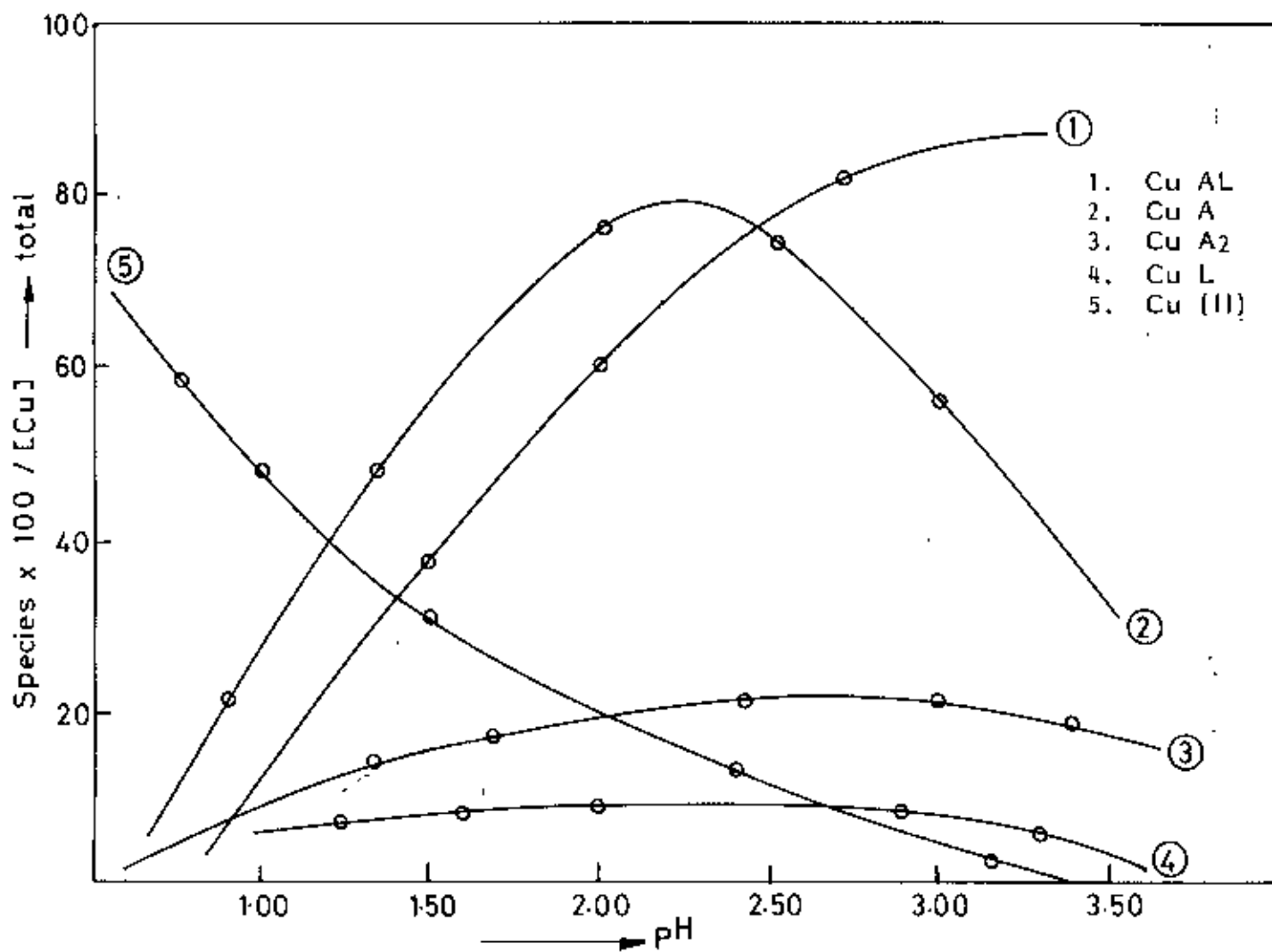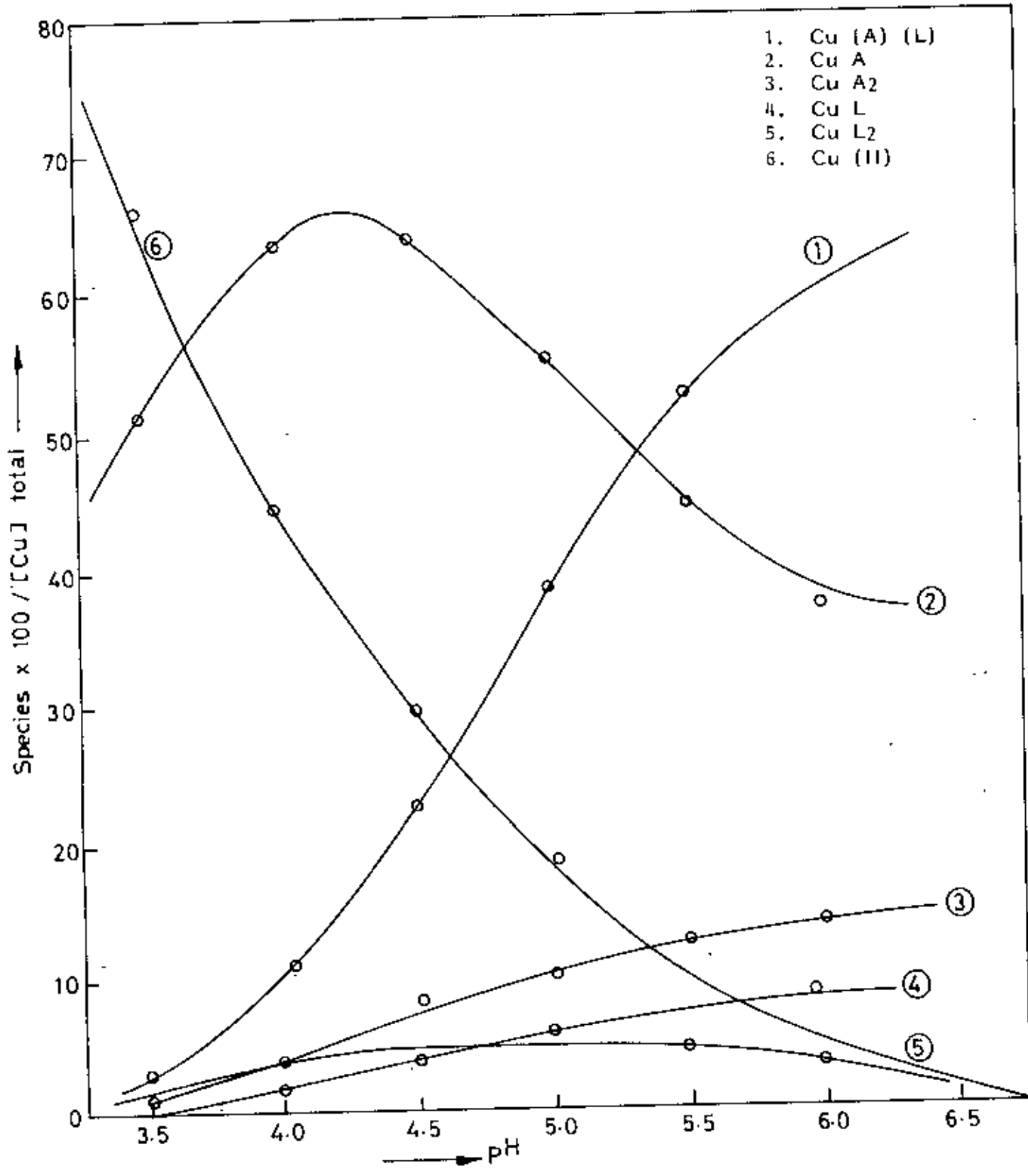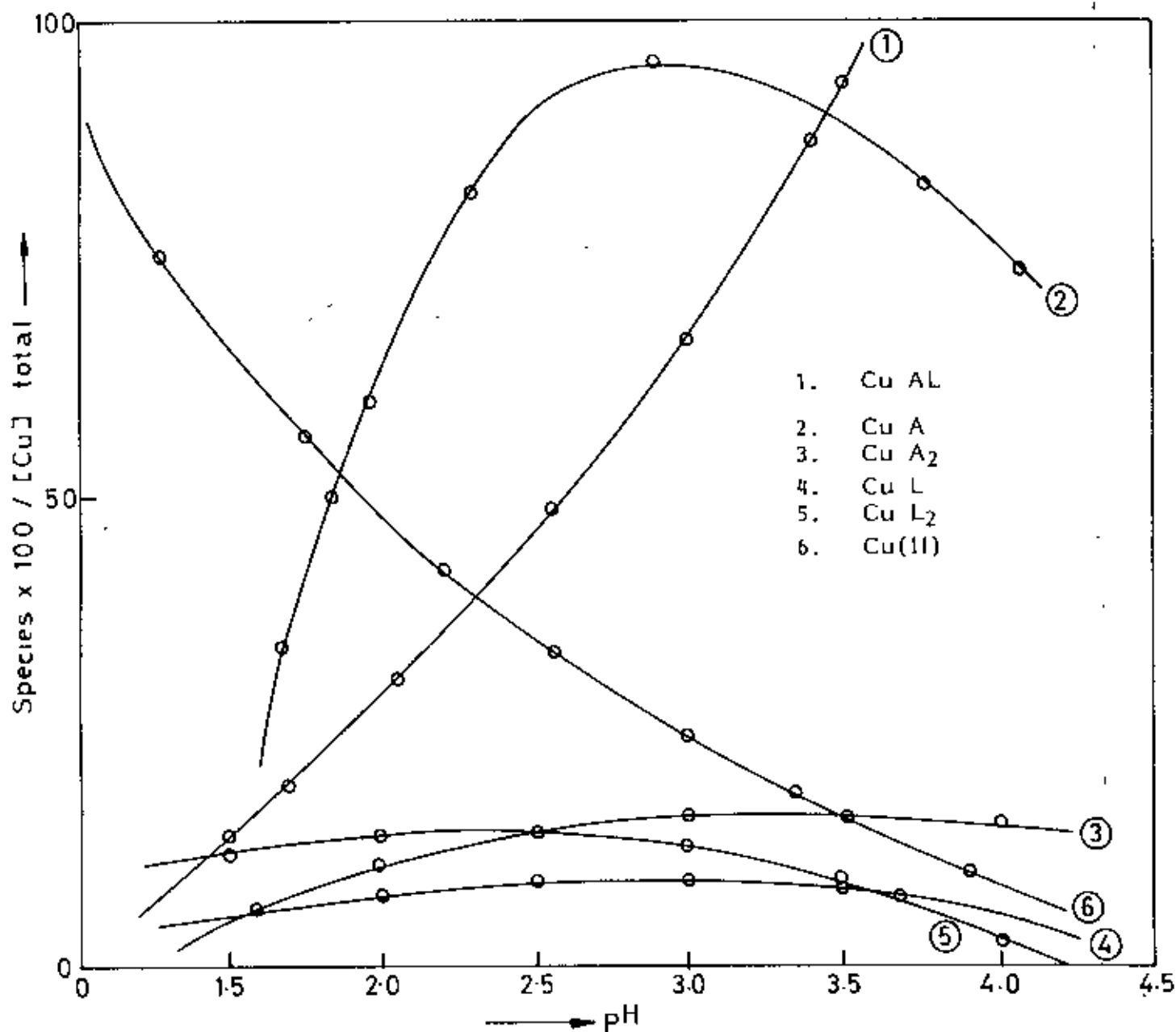
2.2   DISCUSSION

The analysis of the species distribution curves shows that in the p^H range 3.5 to 6.00, MA and MAL are the major species. The percentage of all other species is less than 1% in case of [M(DPA) (L)] system. This is because DPA forms stable binary complex M-DPA(MA) at low p^H and L combines with MA to form MAL ternary complexes.

It is observed that in general $\Delta logK$ for the MAL complex studied is negative, as expected from the statistical consideration. It is interesting to observe that $\Delta logK$ is more negative in case of [Cu(DPA)(L)] compare to [Cu(OX)(L)] complexes. This is due to the tridentate ligand DPA occupy the three equatorial position around the metal ion. Hence in the formation of ternary complex, the bidentate ligand (L) has to occupy one equatorial and the one axial position. Due to John Teller effect in case of [Cu (A) (L)] complexes the ligand is strained in occuping the axial position and hence its tendency to co-ordinate with the MA is much less than in the binary complex, where bidentate ligand occupied two equatorial position. Hence log K_{MAL}^{MA} is

much less than log K_{ML}^{M} and $\Delta logK$ is more negative. In the absence of John Teller distortion in [Cu(OX)(L)] complexes, two bidentate ligands occupy four equatorial positions. It does not feel any strain in occupying two equational positions.

It is observed that for the complexes [Cu(DPA)(L)], where L = Phenyl alanine or tryptophan, $\Delta logK$ is less negative than the complexes were L=glycine or α−alaline.

This is because of intramolecular inter ligand interaction. Phenyl alaline and tryptophan are bidentate ligand hence occupy one equatorial and one axial position as in the case of glycine and α-alaline. The non co-ordinated side group, Phenyl of phenylalanine and indol ring of tryptophan respectively come over the pyridyl ring of DPA and hence noncovalent hydrophobic interaction is possible. This intramolecular inter ligand interaction stabilized the ternary complex, leading to less negative $\Delta logK$ value. This may be because of the tridentate ligand occupying two equatorial, one axial position. The bidentate amino acid occupies two equatorial position and the nonco-ordinated side group occupies a position in the axial direction closer to the neutral Cu(DPA) which is less hydrophobic.

Table-(1.1): Proton ligand formation constant of the ligands, formation constants of Cu-binary complexes in aqueous medium with 1 = 0.2 M (NaClO$_4$) at 30°C ± 1°C.

Ligands A	$LogK_1^H$	$LogK_2^H$	$LogK_{CuA}^{Cu}$	$LogK_{CuA_2}^{Cu}$
OX	3.82	1.20	4.82	8.44
DPA	4.35	2.04	8.89	16.28

Ligand L	$LogK_1^H$	$LogK_2^H$	$LogK_{CuL}^{Cu}$	$LogK_{CuL_2}^{Cu}$
Gly	9.62	2.40	6.98	14.35
α.ala.	9.65	2.11	7.14	14.76
Ph.ala.	9.20	1.91	6 71	14.12
Tryp.	9.43	1.92	6.35	15.35

Table−(1.2): Stability constants of mixed ligand complexes, $\Delta \log K$ and $\log K_{mgml}$ in aqueous medium, $1 = 0.2$ M (NaClO$_4$) at 30°C ± 1°C.

Ligand L	[Cu−OX−L] System		[Cu−DPA−L] System	
	$Log K_{CuAL}^{Cu}$	$\Delta \log K$	$Log K_{CuAL}^{Cu}$	$\Delta \log K$
Glycine	11.35	−0.45	15.82	−0.97
α−alanine	11.64	−0.32	16.00	−0.79
ph.alanine	12 00	+0.47	16.12	−0.22
Tryptophan	12.17	+1.02	16.50	−0.14

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2.4 Template Condensation Reactions of Formaldehyde with Tetramine and Diamines: Synthesis, Structure and Properties of Co(II), Ni(II) and Cu(II) Complexes of Hexaza Macroyclic Ligands Containing Perchlorate Anion.

Some hexadentate macrocyclic ligand complexes of Co(II), Ni(II) and Cu(II) have been synthesized by the interactions of ethylenediamine and triethylenetetramine with formaldehyde in the presence of metal ion in aqueous–method as reaction medium. The products have been characterized by elemental analysis, spectral studies, thermogravimetric analysis and X–ray diffraction analysis.