CHARACTERISATION OF SOME MIXED LIGAND COMPLEXES OF IMIDES AND AMINO ACIDS

A THESIS

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in
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By

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To

The memory of my
grand mother

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled 'CHARACTERISATION OF SOME MIXED LIGAND COMPLEXES OF IMIDES AND AMINOACIDS' in fulfilment of the requirement for the award of the Degree of DOCTOR OF PHILOSOPHY, submitted in the Department of Chemistry of the University, is an authentic record of my own work carried out during a period from January 1981 to July 1984 under the supervision of Dr. C.L. Sharma.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The work embodied in this thesis is on the interaction of transition metal ions with organic ligands containing one or more salt forming groups e.g. (I)-COOH(II)-NH(III)-OH(IV)-SH etc. The chelates of such ligands are of great importance from analytical, medicinal and industrial point of view. The studies aim at investigating the nature, structure and solubility of the complexes. A part of the thesis is devoted to their thermodynamical studies. The ligands used are imides, aminoacids, amines and phenols. A major portion of the thesis is devoted to the preparation of mixed ligand complexes and their characterisation on the basis of chemical analysis, I.R., electronic spectra, Mössbauer spectroscopy, conductance and magnetic measurement. The thesis has been divided into three sections, viz., A, B and C.

SECTION - A

This section comprises of two chapters.

Chapter - I :

This chapter deals with the characterisation of the complexes formed by the interaction of potassium hexathiocyanatochromate(III) with iminodiacetic and diethylenetriaminepentaacetic acids. The complexes $K_2[Cr(NCS)_3(C_4H_5O_4N)]$ and $K_3[Cr(NCS)_4(C_{14}H_{21}O_{10}N_3)]$ could be prepared in the solid form and characterised on the basis of various physico-chemical studies. The values of 10 Dq was found to be 17000 and 18000 cm^{-1} for the first and second complex respectively. The values of B, β_{35} and L.F.S.E. have also been calculated from the bands obtained in the electronic spectra of the complexes. I.R. spectra of the complexes indicated the coordination of thiocyanate through N and of iminodiacetic acid through NH and carboxyl groups. While diethylenetriaminepentaacetic acid is coordinated through carboxyl groups and behave as a bidentate ligand.

Chapter - II :

This chapter describes the results on the studies of mixed ligand complexes of Cr(III) with nitrilotriacetic acid as primary and some phenols and phenolic acids as secondary ligands. On the basis of conductance, polarographic, I.R., electronic spectra and magnetic studies, the complexes of the type $K_2[Cr(NTA)(P)_2]$ and $K_2[Cr(NTA)(A-A)]$ where NTA = nitrilotriacetate, P = deprotonated phenol, 4-chlorophenol, 4-nitrophenol, o-cresol, hydroquinone and α-naphthol and A-A = pyrogallol, pyrocatechol, alizarin, salicylic acid, 4-aminosalicylic acid and 4-sulphosalicylic acid were found to have an octahedral structure. The coordinating power of these phenolic compounds was in the order : hydroquinone > 4-nitrophenol > phenol ≈ 4-aminosalicylic acid > 4-chlorophenol ≈ pyrogallol ≈ pyrocatechol ≈ o-cresol

$\approx$ salicylic acid $\approx$ 4-sulphosalicylic acid > α-naphthol > alizarin.

SECTION - B

This section comprises of two chapters.

Chapter - I :

In this chapter are incorporated the results of Mössbauer studies on the mixed ligand complexes of Fe(III) phthalimide with some amino-acids (histidine, anthranilic acid, glutamic acid, arginine, cysteine and methionine). The complexes having the formulae $NH_4[Fe(C_8H_4O_2N)_3(C_5H_{10}O_2NS)(H_2O)]$, $K[Fe(C_8H_4O_2N)_2(C_5H_7O_4N)(H_2O)_2]$, $K[Fe(C_8H_4O_2N)_3(C_3H_6O_2NS)(H_2O)]$, $[Fe(C_8H_4O_2N)_2(C_6H_{13}N_4O_2)(H_2O)_2]$, $[Fe(C_8H_4O_2N)_2(C_6H_8N_3O_2)(H_2O)_2]$ and $[Fe(C_8H_4O_2N)_2(C_7H_6O_2N)(H_2O)_2]$ could be prepared in the solid form. I.R. spectra of the complexes indicated the coordination of phthalimide through nitrogen and of amino-acid through amino and carboxyl groups, while cysteine and methionine were found to coordinate through sulphyhydril and carboxyl groups. Two bands at around 810 and 640 cm^{-1} due to wagging and rocking modes of coordinated water were observed in the spectra of all the complexes.

The values of magnetic moments lies in between 5.50 - 6.00 B.M. The electronic spectra of all the complexes in butanol gave three bands at 29500, 34000 and 39000 cm^{-1} corresponding to the transitions

$^6A_{1g} \rightarrow {}^4T_{1g}(P)$, $^6A_{1g} \rightarrow {}^4T_{1g}(F)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(F)$ respectively. The values of isomer shift around 0.38 mm sec^{-1} indicated a greater electron density at the nucleus. The values of quadrupole splitting in the range 0.47 - 0.68 mm sec^{-1} indicated the presence of different types of ligands inside the coordination sphere.

Chapter - II :

This chapter deals with the preparation and characterisation of mixed ligand complexes of platinum(II) palladium(II), platinum(IV), iridium(III) and rhodium(III) with phthalimide as primary and dipyridyl and o-phenanthroline as secondary ligands. Complexes of the type $[M(II)Ph_2A]$, $[M(IV)Ph_4A]$ and $[M(III)Ph_3(H_2O)A]$ where Ph = phthalimide (deprotonated) and A = dipyridyl or o-phenanthroline, could be isolated in solid form and characterised. Pt(II) and Pd(II) complexes were of square planar structure. The values of Δ_1, Δ_2 and Δ_3 have been calculated for these complexes. The absorption spectra of diamagnetic octahedrally coordinated d^6 metal ions i.e. Pt(IV), Ir(III) and Rh(III), gave three d-d transitions. Two of these are spin-allowed bands involving $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transition and the third spin-prohibited band is $^1A_{1g} \rightarrow {}^3T_{1g}$. The values of ligand field stabilisation energy and Racah parameters B and C and nephelauxetic ratio β have also been calculated. The values of ligand field splitting energy and hence the stability of the complexes decrease in the order : Pt(IV) > Ir(III) > Rh(III). I.R. spectra of the complexes indicated the coordination of phthalimide through nitrogen and the presence of dipyridyl and o-phenanthroline inside the coordination sphere. In the case of Rh(III) and Ir(III) complexes, the coordinated water molecule gave the bands at 650 and 860 cm^{-1}.

SECTION - C

This section also comprises of two chapters.

Chapter - I :

This chapter has been devoted to the thermodynamical studies of cysteinate complexes of rhodium(III) and osmium(VIII). The thermodynamical stability constants of the metal complexes have been determined by Bjerrum' -Calvin titration technique as adopted by Irving and Rossotti. The values of ΔF, ΔH and ΔS were calculated from the temperature coefficient of the equilibrium constants. A comparative study of the complexes of these metal ions with 2-mercaptopropanoic acid and α-alanine have also been carried out. Analysis of thermodynamical data indicated the coordination of cysteine through sulphydril and carboxyl groups. The complexes of cysteine could also be isolated in the solid form and their I.R. studies also confirmed the coordination through sulphydril and carboxyl groups.

The electronic spectrum of Rh(III) complex gave two spin-allowed bands at 19100 and 25500 cm^{-1} and a spin-forbidden band at 14410 cm^{-1}. The values of 10 Dq, B, β, C and L.F.S.E., (K cals.$mole^{-1}$) were found to be 21445, 400, 0.55, 2345 and 24.50 respectively. Osmium (VIII) complex also gave three bands at 26000, 28850 and 36000 cm^{-1} which seems to have arisen due to charge transfer.

Chapter - II :

This chapter has been devoted to the analytical use of cysteine in the spectrophotometric determination of osmium(VIII). The yellowish brown complex exhibits a maximum absorbance at 370 nm in the pH range 4.0-5.2. Beer's law is obeyed from 1.0-60.0 ppm, the opt. range for accurate determinations being from 5.0-55.0 ppm. The Sandell's sensitivity of the reaction is 0.132 $\mu g/cm^2$ and the molar absorptivity of the complex is 1429 ℓ $mole^{-1}$ cm^{-1}. The apparent stability constant of 1:1 complex was found to be 1.2589×10^9 at 25 ± 1°C. A large number of ions do not interfere in the determination of Os(VIII) by this method.

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Shahid Suhail Narvi

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CONTENTS

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INTRODUCTION

Imides and aminoacids offer the sites simultaneously for salt formation and coordination and hence their reactions with metal ions are very important from analytical point of view because of their insoluble character in water and highly soluble nature in non-polar solvents. Derivatives of imides have also proved to be important medicinal agents and have been suggested for use in the treatment of arthritis, tuberculosis [1], convalsions and epilepsy [2]. They have also been used as fungicides [3] and to stimulate the growth of wheat and radish seedling [4].

Apart from their importance in biological systems and industrial fields, the reactions of imides are interesting from theoretical stand point and a few of them have yet to be investigated to add to the present state of knowledge. Scanty details on the studies of simple metal imide complexes are available in the literature but a very little has been done on their mixed ligand complexes.

In the beginning the salts of imides with various metal ions were prepared under anhydrous conditions [5-7] because of their hydrolysable nature. The complexes of copper having the formulae $(C_4H_4O_2N)_4$ Cu.M.nH_2O where M = Li, Na, K, Rb or Cs ions and n = 1,2,4 or 6 were then prepared by the action of caustic alkalies on the solution of succinimide and copper acetate or chloride [8]. Succinimide gave a golden yellow compound $(C_4N_4O_2N)_3$Hg K with pot. hydroxide and mercuric acetate and reacts with gold salts or fulminating gold to give its complex [10]. Succinimide also formed addition compounds with phenols, hydrogen peroxide and titanium chloride [11]. Mary M. Rising [8] prepared Ba-Cu succinimide complex [BaCu$(C_4H_4O_2N)_4$], brownish red in colour. Livo Cambi reported the magnetic properties of potassium salts of Ni(II) and Pd(II) complexes of succinimide. A number of other metal complexes of succinimide have also been studied in relation to their preparation, chemical analysis, magnetic and infrared studies [12-18]. Malik and Sharma studied the composition, stability and analytical aspects of Co(II) succinimide complex [19,20].

Similarly the metal complexes of phthalimide have been studied in relation to their preparation, chemical analysis, magnetic properties and infrared studies [10,21-27]. The mixed ligand complexes using succinimide or phthalimide as primary and amines [28-40], polyamines [41,42] and thiocarbamides [43] as secondary ligands have also been prepared and characterised on the same lines. The vibrational, electronic, CD and Mössbauer studies [44] and recently thermal, E.S.R. and X-ray studies of some imide complexes of bivalent transition metal ions [45-47] have also been reported in the literature.

The mixed ligand complexes of nitrilotriacetic acid (NTA) also form a part of our studies. Survey of the existing literature reveals that the complexes of NTA have a great importance in analytical, biochemical and industrial fields. It is used as an analytical reagent for the determination [48] and separation of various metal ions [49,50] and is also used as a sequestering and masking reagent. Fe-NTA chelate is used to reduce iron deficiency anemia during pregnancy and has the capacity for enhancement of oral iron absorption. NTA with $CdCl_2$ reduces the deposition of Cd in liver, kidney and muscle. NTA helps in carrying out the electrodeposition of metal on a metal surface. Fe(III) chelate is used as a catalyst in the oxidation of ascorbic acid and in the polymerisation of diamines. Cobalt complexes catalyses hydroformylation of olefins and styrene. Ammonium salts of NTA containing Fe, Mg, Cu, Mn, Zn and B in addition to the main nutrient elements N, P and K are used as a foliar fertilizer. NTA chelates of bivalent metals also improve light resistant properties of polyamide fibres.

A large number of simple metal-NTA complexes [51-64] are reported in the literature. In the near past, studies have also been made on the mixed ligand complexes using NTA as primary and dipyridyl, o-phenanthroline, thiocyanate, carboxylic acids, aminoacids, imidazole and acetylaeetone as secondary ligands [65-74].

More recently, the mixed ligand complexes using NTA as primary and heterocyclic bases and some aminoacids as secondary ligands have been prepared and characterised on the basis of various physico-chemical techniques [75,76]. Different kinetic parameters for various substitution reactions are also reported in the literature e.g. substitution reaction of erichrome black-T in nitrilotriacetatonickelate(II) chelate [77], substitution reaction of Co(II)- nitrilotriacetate with CDTA [78], substitution reaction of Ni(NTA) complexes with resorcinol derivatives [79] etc.

Amino-acids have been used as secondary ligands in our studies also as their importance in biological fields is well known. They are the building units of all proteins and enzymes and are intimately associated with metal ions in biological systems. Among all amino-acids cysteine is some what peculiar as it has three coordinating sites i.e., α-amino, carboxyl and mercapto groups but only two of these coordinate simultaneously with the metal ion due to steric reasons. Cysteine (2-amino-3-mercapto propanoic acid or α-amino β-thiol propionic acid) has been used for preventing iron sulfide blackening in canned protein foods [80,81] and also in dechlorination of tap water [82], 0.2 M solution of cysteineeasily removes arsenic and mercury from the hair because of complex formation with these metal ions [83]. Complexing with cysteine increases the catalytic activity of Cu^{++} ions in oxidation of arsenictrioxide solution to arsenate [84]. Cysteine-Fe chelate acts as a catalyst in the reduction of picric acid to picramic acid [85]. The molybdenum-cysteine complexes have been found useful in the reduction of ferricytochromic C and acetylene [86,87]. Cysteine and its magnesium salt were found effective in the prevention of acrylonitrile, ethylene chloride and monochloroacetic acid poisonings [88,89]. Its complexes with $ZnSO_4$ are recommended for therapy, detoxification and urinary excretion of zinc, lead, cadmium and mercury intoxications [88-94]. Chemotherapy of malignant tumor by several metal chelates is also reported in the literature [95]. Chromium(III) complex of cysteine exhibited glucose tolerance factor properties [96]. The mixed ligand complex, bis (acetaldehydo) bis (cysteinato) iron(II), is a remedy for anemia [97].

The metal complexes of cysteine have been studied generally in relation to their preparation, analysis, magnetic measurements, electronic spectra, thermodynamical parameters and stability determinations [98-149]. Scanty details are also available on its mixed ligand complexes $[Mo_2O(C_2O_4)\ cysteine]\cdot 6H_2O$ and $[VO(C_2O_4)(AA)]$ [150-153], where AA = cysteine, $[Co(en)_2AA]^{n+}$ and $K_2[Co(CN)_4AA]nH_2O$ [154,155], [Bis(cysteinato) dicarbonyl iron(II)] dihydrate [156], $[Pd(cys)(NH_3)_2]Cl_2$, and $[Pd(cysH)_2(NH_3)_2]PdCl_4$ [157] and [Er(III)-EDTA-cysteine] [161] have been prepared, analysed chemically and characterised on the basis of i.r., electronic spectra, C.D. spectra, magnetic and conductance measurements. The determinations of composition and stability constants of [Ni-dye-cysteine] where dye = solochrome violet R and [M(NTA or cysteine)AA] where M = bivalent transition metal ions including Cd, Ca, Hg and Zn ions have also been carried out by several groups of workers [158-161].

The following conclusions were derived from this thorough survey of the existing literature.

1. The interactions of potassium hexathiocyanatochromate(III) with some of the aminoacids still remains uninvestigated.

2. The complexes of chromium(III) nitrilotriacetate with phenols and phenolic acids have not been studied so far.

3. Nothing has been done on the complexes of platinum metal phthalimides.

4. The cysteine complexes of platinum metals, viz., Rh(III), Ru(III) and Os(VIII) have also not been studied.

Investigations in this direction were, therefore, undertaken employing various physico-chemical techniques. These studies were planned merely to look into the structure and thermodynamic properties of some of these complexes. The studies on the applications of these complexes in different biochemical and industril fields could not be carried out due to the lack of facilities. The following aspects were considered worth-investigating :

1. Characterisation of the complexes of chromium(III) with (i) thiocyanate as primary and some aminoacids as secondary ligands and (ii) nitrilotriacetic acid as primary and phenolic compounds as secondary ligands.

2. Characterisation of the complexes of Fe(III), Pt(II), Pd(II), Ir(III) and Rh(III) with phthalimide as primary and amines or amino-acids as secondary ligands.

3. Thermodynamical studies of the cysteinate complexes of Rh(III) and Os(VIII).

4. Use of cysteine as an analytical reagent.

SECTION A

CHAPTER—I : Characterisation of the complexes formed by the Interaction of Potassium Hexathiocyanatochromate (III) with Iminodiacetic and Diethylenetriaminepentaacetic Acids.

Survey of the existing literature reveals that the complexes formed as a result of the interaction of potassium hexathiocyanato chromate(III) tetrahydrate with various types of organic ligands have been studied in relation to their preparation, chemical analysis, I.R., conductance and magnetic measurements [162-170]. There was either a replacement of potassium ions with organic bases [171-174] or of thiocyanate ions [175-177] forming the complexes of the type $Cr(SCN)_nL_{6-n}$ where L = aniline, acetamide, thiosemicarbazide, glycinate, alaninate, urea, thiourea, salicylate, ethylexanthate, amines and other aminoacids. The studies on the isomerization of the sulphur bonded monothiocyanato complex of Cr(III) [175-178], photosolvolysis of trans $-[Cr(NCS)_4(NH_3)_2]^-$ and trans-$[Cr(en)_2(NCS)_2]^+$ [179], solid state reactions [180], kinetics and mechanism of substitution reactions, e.g. aquation rates of Cis-$[Cr(en)_2(NCS)_2]^+$ at different temperatures [181], quenching of phosphorescence of trans-$[Cr(en)_2(NCS)_2]^+$ by $(Cr(CN)_6]^{3-}$ etc. [182] and the solvent effect on the photoaquation quantum yields of trans$[Cr(en)_2(NCS)_2]^+$ and $[Cr(NCS)_6]$ [183] are also reported in the literature, G. Contreras and R. Schmidt [176] also studied the electronic structures and determined the ligand field parameters for the complexes of the type $Cr(NCS)_nL_{6-n}$.

This chapter deals with the interactions of potassium hexathiocyanato chromate(III) tetrahydrate and iminodiacetic and diethylenetriaminepentaacetic acids. The complexes formed as a result of these interactions could be isolated in the pure form, analysed chemically and characterised on the basis of their I.R., electronic spectra, magnetic and conductance measurements. The ligand field parameters are calculated in order to know the places of these two ligands in spectro-chemical or nephelauxetic series.

EXPERIMENTAL

Reagents :

Chrome alum, potassium thiocyanate,absolute alcohol, iminodiacetic acid and diethylenetriaminepentaacetic acid, all were of AR(BDH) grade.

Physical Measurements :

I.R. spectra in the region 4000-250 cm^{-1} were run on a Beckman IR-20 spectrophotometer in KBr using thin film technique. The electronic spectra were run on a Carl Zeiss 'SPECORD' UV-VIS. Reflectance spectra were obtained with a Carl Zeiss 'SPEKOL' spectrophotometer fitted with a reflectance attachment of the Rd/O. Electrical conductances were measured with a Systronics conductivity bridge type 302. Magnetic moments were measured by using a Princeton Applied Research Model 155 Vibrating Sample Magnetometer at room temperature.

Preparation of the Complexes :

Potassium hexathiocynato chromate(III) tetrahydrate was prepared in the laboratory by a method of Roesler [184].

A moderately concentrated aqueous solution of six parts of chrome alum was heated for two hours on a steam bath and was then concentrated in dish until the cooled residual liquid solidified to a mass of red crystals. This solid was extracted with absolute alcohol in which $K_3[Cr(SCN)_6]$ dissolved very readily while K_2SO_4 remained as a residue. After evaporation of the filtered alcohol extract the salt was recrystallised once more from alcohol. The crystals of $K_3[Cr(SCN)_6]$ were of dark red violet in colour and was soluble in water and alcohol.

not clear ?

Then the solutions of acids (iminodiacetic acid or diethylenetriaminepentaacetic acid) in one equivalent potassium hydroxide and $K_3[Cr(SCN)_6]$ were mixed in the ratio of 1:1 and the mixture was allowed to stand for two hours and then acetone was added to get the red or violet crystals. They were filtered, washed several times with 50% alcohol and then dried in the oven at about 70°C.

The resulting complexes are hygroscopic and are soluble in water and dimethylsulphoxide. The results of analyses for the metal, carbon, hydrogen and nitrogen are given in Table - 1.

Table - 1 Analytical data of the complexes

S. No.	Complexes	Percentage calculated (found)				Molar conductance $ohm^{-1} cm^{2} mol^{-1}$	Colour
		Cr	C	H	N		
1.	$K_2[Cr(NCS)_3(C_4H_5O_4N)]$	11.90 (11.82)	19.35 (19.18)	1.15 (1.14)	12.90 (12.81)	250	Violet
2.	$K_3[Cr(NCS)_4(C_{14}H_{21}O_{10}N_3)]$	6.56 (6.51)	27.27 (27.06)	2.65 (2.68)	12.37 (12.28)	392	Red

Electronic Spectra of the Complexes of d^3 Ion :

In a cubic crystal field, the configuration d^3 gives rise to two quartet terms ^4F and ^4P with ^4F the ground term and ^4P being 15B higher in energy. The action of octahedral ligand field will split the ^4F into $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ states whereas ^4P goes over into a $^4T_{1g}$ state, therefore the three spin-allowed transitions expected are $^4A_{2g}(F) \longrightarrow {}^4T_{2g}(F)$ (ν_1), $^4A_{2g}(F) \longrightarrow {}^4T_{1g}(F)$ (ν_2) and $^4A_{2g}(F) \longrightarrow {}^4T_{1g}(P)$ (ν_3). The value of Racah interelectronic repulsion parameter B has been determined according to the following four different methods.

(a) Fitting in second band :

$$\nu_{2,3} = \frac{1}{2}(15B + 30Dq) \mp \frac{1}{2}[(15B - 10Dq)^2 + 12B\cdot 10Dq]^{1/2} \qquad ..(1)$$

$$\nu_1 = 10\ Dq.$$

Solving the expression of ν_2 in the above equation for B, one may base this fitting on the following expression

$$B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1) \qquad ..(2)$$

(b) Fitting the third band :

In this procedure similar to above ν_3 is used instead of ν_2. The following expression is used for the value of B

$$B = (2\nu_1^2 + \nu_3^2 - 3\nu_1\nu_3)/(15\nu_3 - 27\nu_1) \qquad ..(3)$$

$$10\ Dq = \nu_1$$

(c) Fitting the sum of second and third bands :

If all the three d-d transitions are observed, then the following simple relations may be used for B.

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15 \qquad ..(4)$$

$$10\ Dq = \nu_1$$

(d) Fitting the differences of second and third bands:

A simplification is also achieved if the differences between ν_2 and ν_3 is taken as a basis for the calculation of B. Thus the following expression where only the positive sign of B has a physical significance may be used.

$$B = \frac{1}{75}\left[3\nu_1 \pm \left\{25(\nu_3 - \nu_2)^2 - 16\ \nu_1^2\right\}^{1/2}\right] \qquad ..(5)$$

$$10\ Dq = \nu_1.$$

RESULTS AND DISCUSSION

The values of molar conductances of the complexes 1 and 2 (table-1) in water were found to be 250 and 392 $ohm^{-1}\ cm^2\ mol^{-1}$ which indicated the presence of two and three ions respectively. Table 2 contains the values of 10Dq, B, β_{35}, ligand field stabilisation energies, magnetic moments and experimental band energies with the transition energies calculated on the basis of various numerical procedures. The deviations from the experimental values $\delta\nu = \nu_{cal} - \nu_{expt}$ are also given.

Table - 2 Electronic spectral data and calculated transition energies (cm^{-1})

Complexes*	Expt. of calculation	${}^4A_{2g} \xrightarrow{(\nu_1)} {}^4T_{2g}$	${}^4A_{2g} \xrightarrow{(\nu_2)} {}^4T_{1g}(F)$	${}^4T_{2g} \xrightarrow{(\nu_3)} {}^4T_{1g}(P)$	B	β_{35}	$\lvert\delta\nu\rvert$	$\lvert\delta\nu\rvert$	LFSE Kcals/mole	μ_{eff} BM
1	Exp.	17000	23600	36720	-	-	-	-	48.75	4.10
	(a)	10 Dq	Fitted	37208	654	0.712	+508	+1.365		
	(b)	10 Dq	22617	Fitted	535	0.636	-983	-4.346		
	(c)	10 Dq	23343	36972	621	0.677	+257	±0.891		
2	Exp.	18000	25000	38880	-	-	-	-	51.43	3.65 La
	(a)	10 Dq	Fitted	39400	693	0.755	+520	+1.310		
	(b)	10 Dq	24403	Fitted	619	0.674	-597	-2.446		
	(c)	10 Dq	24723	39158	659	0.717	±277	±0.553		

* See Table 1.

The reflectance spectra of the solid complexes and the solution spectra in dimethyl sulfoxide gave the bads at approximately same wavenumbers with a deviation of ± 20 indicating no structural changes in solution.

The third band (ν_3) has not been detected in solution spectra. The failure is not unexpected as this band should be very weak, being forbidden both by the g $\not\to$ g selection rule and by the other symmetry properties of the electronic wave functions of the terms also. The charge transfer bands commence in the same region and ν_3 appears only as a shoulder on the large charge transfer band and hence not clearly visible. The reported values of ν_3 in the first line of each complex (table-2) have been taken from Tanabe Sugano diagram [185]. The ratio of ν_2/ν_1 is 1.39 which fits with 10 Dq/B = 27.1. It gives the value of $\nu_3/\nu_1 = 2.16$.

The spectral assignments are based on the energy level splitting originally proposed by Barnum [186], 10 Dq was directly derived from first spin allowed band (ν_1). The energies of ν_2 and ν_3 have been calculated using the standard equations. The value of B calculated by three different methods have been substituted in the energy equations to evaluate the extra bands energy of ν_2 and ν_3 transitions. The values given in table-2 indicate that B and β_{35} depend significantly on the method adopted for their calculation. The best fit for the transitions ν_2 and ν_3 is achieved by using the method (c) i.e. fitting the sum of second and third band ; $[B=(\nu_2 + \nu_3 - 3\nu_1)/15]$ which is quite clear from the lowest values of deviation $|\delta\nu_2,\nu_3|$. Within the approximation of the three parameter ligand field theory, the energies of both the second and third band (ν_2 and ν_3) are reproduced equally well. In addition there does not exist a misfit of ν_3 which could be redistributed on ν_2 and ν_3 if method (c) is applied. If this were true, the value of $|\delta\nu|$ intermediate between $|\delta\nu(a)|$ and $|\delta\nu(b)|$ would be expected. However $|\delta\nu(c)|$ is always smaller than both $|\delta\nu(a)|$ and $|\delta\nu(b)|$.

The ligand field strength of iminodiacetic acid is less than diethylenetriaminepentaacetic acid. This effect is also reflected in the magnetic moments of the complexes i.e. in the case of iminodiacetic acid where the ligand field strength is very weak, the value of magnetic moment is 4.10 B.M. While in the case of diethylenetriaminepentaacetic acid the value of magnetic moments is 3.65 B.M. The values of β_{35} are also in support of the above observations.

Low?

I.R. Studies:

The important observations derived from the I.R. spectra of the aminoacids and their complexes are given in table-3. The shift in the frequencies of the three fundamental modes of vibrations in the thiocyanate ion upon complexing has been widely used to determine the bond type. These frequencies in KSCN

Table 3 - Stretching frequencies (cm^{-1}) of the important bands of coordinated amino-acids and thiocyanate, differences from KSCN and the bond type**

Complexes*	amino-acids			Thiocyanate				Bond type
	ν_{N-H}	ν_{C-N}	ν_{COO^-}	ν_{C-N}	ν_{C-S}	$\delta\nu_{C-N}$	$\delta\nu_{C-S}$	
$K_3[Cr(SCN)_6]$	-	-	-	2100(VS)	n.s.	+51	-	M-S
1.	3400(S,b)	1500(m) 1280(w)	1640(s) 1380(w)	2080(VS)	820(w)	+31	+71	M-N
2.	3450(S,b)	1480(m) 1140(w)	1640(s) 1380(w)	2080(VS)	800(w)	+31	+51	M-N

VS = very strong; b= broad, m = medium, w = weak

* = see table 1-

** = the frequencies for KSCN are $\nu_{(CN)}$ = 2049 and $\nu_{(C-S)}$ = 749 cm^{-1}

$\delta\nu$ = $\nu_{(complex)}$ - $\nu_{(KSCN)}$

are; ν(CS stretching) = 749 cm^{-1}, ν(NCS bending) = 470 cm^{-1} and ν(CN stretching) = 2049 cm^{-1}. The C-S stretching frequency has often been considered diagnostic of the metal bond since ν(CS) is at 690-720 cm^{-1} for M-SCN and at 780-860 cm^{-1} for M-NCS complexes. The CN stretching frequencies of a thiocyanate complex increase in the order = CNS^- < H-NCS < M-SCN < M-SCN-M. For M-SCN it is above 2100 cm^{-1} and for M-NCS it is below or equal to 2100 cm^{-1} [187]. In general ν(CN) absorption is strong and exhibits a broad band for isothiocyanates and a sharp band for thiocyanato complexes.

According to Tramer [188] an increase in the frequency of ν(CN) of 50-70 cm^{-1} relative to free thiocyanate ions is indicative of M-SCN coordination. For M-NCS this is less than 40 cm^{-1}. A large increase of 70-120 cm^{-1} is diagnostic of strong bridged complexes. For these cases in which it is possible to assign ν(CS), the difference from the free thiocyanate ion are : an increase of 40-90 cm^{-1} for M-NCS and a decrease of 25-55 cm^{-1} for M-SCN.

In our case where the thiocyanate is N-bonded, the ν(CN) position is 2080 or 2060 cm^{-1} and ν(CS) is around 800 cm^{-1}. NH stretching vibrations appear as strong broad bands at around 3400 cm^{-1}.

The strong absorption bands observed in the region 1620-1680 cm^{-1} have been assigned to the antisymmetric stretching modes of the ionised carboxylic group. The broadness of these bands suggests that probably the ionised carboxylic group has been coupled with the NH vibration in this region.

SECTION A

CHAPTER—II : Mixed Ligand Complexes of Cr (III) with Nitrilotriacetic Acid as Primary and some Phenols and Phenolic Acids as Secondary Ligands.

Scanty details are available on the simple complexes of bivalent metal ions with nitrilotriacetic acid (NTA). Several groups of workers have also carried out the equilibrium studies on the interactions of some amino-acids, tryptophan, salicylic, sulfosalicylic and mercapto acids with bivalent metal nitrilotriacetate complex ions [189-197]. The mixed ligand complexes of bivalent transition metal ions with NTA as primary and other organic anions as secondary ligands have also been studied by several groups of workers in relation to their stability, preparation, chemical analysis, analytical importance and magnetic measurements [198-200,70,74]. Comparatively a little work has been done on the mixed ligand complexes of trivalent metal ions with NTA as primary ligand. The examples of worth mentioning are of rare earth (III)-nitrilotriacetate complexes with EDTA [202], CyDTA [201], 5-sulpho salicylic acid and tiron [202] and of Fe(III)-nitrilotriacetate complexes with sulfosalicylic and pyrocatechol-3,5-disulphonic acids [203].

The ternary complexes of chromium (III)-nitrilotriacetate with acetylacetone, phenanthroline, dipyridyl, oxalate, halide ions [72,65,66], amino-acids [76] and heterocyclic amines [75] have also been studied in relation to their stability, preparation, electronic spectra magnetic and I.R. studies. Further extension of this work has been carried out in this laboratory by preparing and characterising the complexes of chromium(III) with NTA as primary and phenolic compounds, viz., phenol, 4-cholorophenol, 4-nitrophenol, o-cresol, hydroquinone, α-naphthol, pyrogallol, pyrocatechol, alizarin, salicylic acid, 4-aminosalicylic acid and 4-sulphosalicylic acid as secondary ligands on the basis of conductance, I.R., electronic spectra and magnetic measurements.

EXPERIMENTAL

Reagents and Solutions :

Chrome alum, potassium hydroxide, ammonium carbonate, nitrilotriacetic acid and all phenolic compounds used in these studies were of A.R. (BDH) grad . All the solutions were prepared in doubly distilled water.

Physical Measurements :

As reported in Chapter I of this section. Further, the polarograms were recorded on an Elico DC Recording polarograph, model CL-25. The capillary used had a drop time, $t = 3.24$ sec and an outflow velocity of $m = 2.68$ mg/sec and at $h = 30$ cms in 1 M KCl solution.

Preparation of the Complexes :

Ammonium hydroxonitrilotriacetatoaquo chromate(III) dihydrate, $NH_4[Cr(OH)NTA(H_2O)]\ 2H_2O(I')$ derived by the method of Uehara et al.[65] was used as a starting material for the preparation of all the complexes.

(i) Potassium nitrilotriacetato bis (phenolato) chromate(III) :

$K_2[Cr(NTA)(P)_2]$: P=deprotonated phenol, 4-chlorophenol, 4-nitrophenol, O-cresol, hydroquinone and α-naphthol. The solution of I' and phenol in water and alcohol respectively were mixed in the ratio of 1 mole : 3 mole and the pH of the mixture was raised to 9.0 by the addition of KOH, refluxed on water bath for about 2 hrs. and then cooled in ice. The excess of alcohol was then added till the purple or violet crystals separated out which were filtered, recystallised from small portion of water and then dried in a vacuum desiccator over silica gel. The complexes were soluble in water and fairly stable.

(ii) Potassium nitrilotriacetato (phenolato or phenolic acido) chromate(III) :

$K_2[Cr(NTA)A\text{-}A]$: A-A = pyrogallol, pyrocatechpl, alizarin, salicylic acid, 4-aminosalicylic acid and 4-sulphosalicylic acid (all deprotonated) : These were similarly prepared by mixing one mole of I' and one mole of A-A.

Table-1 Analytical data of the complexes

S. No.	Complexes	Percentage calculated (found)			μ_{eff} B.M.	Molar* conductance $ohm^{-1} cm^2 mol.^{-1}$
		M	C	H		
1.	$K_2[Cr(NTA)(C_6H_5O_2)_2]$	9.74(9.69)	40.45(40.49)	2.99(2.96)	3.69	230
2.	$K_2[Cr(NTA)(C_6H_4O_3N)_2]$	8.75(8.70)	36.36(36.21)	2.36(2.34)	3.70	229
3.	$K_2[Cr(NTA)(C_6H_5O)_2]$	10.32(10.25)	42.86(42.58)	3.17(3.14)	3.70	300
4.	$K_2[Cr(NTA)(C_7H_5O_3N)]$	11.09(11.01)	33.26(33.37)	2.35(2.33)	3.71	228
5.	$K_2[Cr(NTA)(C_6H_4OCl)_2]$	9.09(9.03)	37.78(38.03)	2.45(2.42)	3.95	225
6.	$K_2[Cr(NTA)(C_6H_4O_3)]$	9.22(9.16)	25.53(25.68)	1.77(1.75)	4.01	300
7.	$K_2[Cr(NTA)(C_6H_4O_2)]$	12.15(12.07)	33.64(33.83)	2.34(2.31)	4.00	300
8.	$K_2[Cr(NTA)(C_7H_7O)_2]$	9.77(9.68)	45.11(44.89)	2.63(2.60)	3.98	240
9.	$K_2[Cr(NTA)(C_7H_4O_3)]$	11.45(11.39)	34.36(34.63)	2.20(2.28)	4.05	290
10.	$K_2[Cr(NTA)(C_7H_3O_6S)]$	9.76(9.70)	29.27(29.45)	1.69(1.68)	3.99	300
11.	$K_2[Cr(NTA)(C_{10}N_7O)_2]$	8.61(8.57)	51.65(51.24)	3.31(3.27)	4.10	250
12.	$K_2[Cr(NTA)(C_{14}H_6O_4)]$	9.35(9.29)	43.16(43.00)	2.16(2.13)	4.15	235

* 0.001 M solutions in water were prepared for conductance measurements (cell constant = 1.12)

Table - 2 Electronic spectral data and calculated transition energies (cm^{-1})

Complexes no.**	Method of calculation	$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{1g}$ (F)	$^4A_{2g} \rightarrow {}^4T_{1g}$ (P)	B	β_{35}	$\delta\nu$ (cm^{-1})	$\delta\nu$ (%)	L.F.S.E. K Cal/mole	$E_{1/2}$ (± 0.02)
1	2	3	4	5	6	7	8	9	10	11
1	expt	17500	24500	38000					60.00	1.61
	(a)	10 Dq	fitted	38500	700	0.76	+500	1.30		
	(b)	10 Dq	23955	fitted	630	0.68	-545	2.25		
	(c)	10 Dq	24240	38250	666	0.72	±255	0.85		
2	expt	17363	26000	38500					59.53	1.58
	(a)	10 Dq	fitted	40430	956	1.04	+1930	4.77		
	(b)	10 Dq	24591	fitted	733	0.79	-1409	5.56		
	(c)	10 Dq	15231	39263	827	0.90	± 766	2.49		
3	expt	17000	24000	37000					58.28	1.45
	(a)	10 Dq	fitted	37605	707	0.77	+ 605	1.61		
	(b)	10 Dq	23375	fitted	625	0.68	- 625	2.63		
	(c)	10 Dq	23694	37295	666	0.72	± 300	1.03		
4	expt	17000	24500	37200					58.28	1.43
	(a)	10 Dq	fitted	38175	778	0.85	+ 974	2.55		
	(b)	10 Dq	23595	fitted	653	0.71	- 906	3.76		
	(c)	10 Dq	24045	37655	713	0.78	± 454	1.54		

Table - 2 (contd.)

1	2	3	4	5	6	7	8	9	10	11
5	expt	16500	23500	35450					56.57	0.70
	(a)	10 Dq	fitted	36725	715	0.77	+1275	3.53		
	(b)	10 Dq	22120	fitted	538	0.58	-1378	5.86		
	(c)	10 Dq	22870	36080	630	0.68	± 629	2.24		
6	expt	16500	24000	37000					56.57	0.69
	(a)	10 Dq	fitted	37340	789	0.85	+ 338	0.90		
	(b)	10 Dq	23725	fitted	748	0.81	- 273	1.15		
	(c)	10 Dq	23850	37145	766	0.83	± 148	0.50		
7	expt	16500	24000	36400					56.57	0.69
	(a)	10 Dq	fitted	37355	789	0.85	+ 938	2.51		
	(b)	10 Dq	23195	fitted	673	0.73	- 804	3.40		
	(c)	10 Dq	23585	36815	726	0.79	± 417	1.44		
8	expt	16500	23500	36350					56.57	0.68
	(a)	10 Dq	fitted	36725	715	0.77	+ 375	1.02		
	(b)	10 Dq	23145	fitted	666	0.72	- 355	1.52		
	(c)	10 Dq	23320	36530	690	0.75	± 179	0.62		
9	expt	16500	23500	36100					56.57	0.68
	(a)	10 Dq	fitted	36725	715	0.77	+ 625	1.70		
	(b)	10 Dq	22895	fitted	633	0.63	- 606	2.60		
	(c)	10 Dq	23195	36395	673	0.73	± 301	1.05		

Table - 2 (Contd.)

1	2	3	4	5	6	7	8	9	10	11
10	expt	16500	23800	36800					56.57	0.68
	(a)	10 Dq	fitted	37085	759	0.82	+ 284	0.76		
	(b)	10 Dq	23565	fitted	724	0.78	- 273	0.99		
	(c)	10 Dq	23675	36925	740	0.80	± 127	0.43		
11	expt	16200	23800	34900					55.54	0.65
	(a)	10 Dq	fitted	36995	813	0.88	+2094	5.66		
	(b)	10 Dq	21837	fitted	542	0.59	-1963	8.50		
	(c)	10 Dq	22865	35830	673	0.73	± 932	3.33		
12	expt	16000	23700	35400					54.85	0.63
	(a)	10 Dq	fitted	36830	835	0.91	+1428	3.87		
	(b)	10 Dq	22590	fitted	666	0.72	-1108	4.90		
	(c)	10 Dq	23110	35995	740	0.80	± 593	2.10		

* See Table No. 1.

Chemical analysis, magnetic moments and molar conductances in water, are given in Table-1.

RESULTS AND DISCUSSION

The three spin allowed transitions were obtained in the electronic spectra of the complexes in solid state and also in aqueous solutions with the same wave numbers in both the cases, indicating no structural changes in solution. The assignments of these transitions and the methods of calculation for finding out the values of 10Dq, B and β_{35} were the same as reported by Sharma et al. [76].

Table-2 shows that the deviation $|\delta\nu_{2,\nu_3}|$ of the calculated transition energies according to procedures (a), (b) and (c) is of the order of a few percent and decreases according to $|\delta\nu(b)| > |\delta\nu(a)| > |\delta\nu(c)|$. Therefore, it is concluded that out of all the numerical procedures applicable in the spectra of the octahedral chromium(III) complexes, the best fit for the transitions ν_2 and ν_3 can be achieved by using the method (c). In the present compounds, the deviation $|\delta\nu(b)|$ resulting from method (b) is very large, thus reflecting the uncertainity in the energy of the third band ν_3. Evidently if ν_2 is employed in the fit, $|\delta\nu_3|$ (in percent) is smaller than $|\delta\nu_2|$ which results if ν_3 is used. Finally in the method (c) $|\delta\nu_2| = |\delta\nu_3|$. Therefore, within the approximation of the three parameter ligand field theory, the energies of both the second and third bands (ν_2 and ν_3) are reproduced equally well. In addition, there does not exist a misfit of ν_3 which could be redistributed on ν_2 and ν_3, if method (c) is applied. If this were true, the value of $|\delta\nu|$ intermediate between $|\delta\nu(a)|$ and $|\delta\nu(b)|$ would be expected. However, $|\delta\nu(c)|$ is always smaller than both $|\delta\nu(a)|$ and $|\delta\nu(b)|$ (Table - 2).

The observed values of 10Dq reveal that the ligand field strength of secondary ligands are in the order : hydroquinone > 4-nitrophenol > phenol $\approx$ 4-aminosalicylic acid > 4-chlorophenol $\approx$ pyrogallol $\approx$ pyrocatechol $\approx$ O-cresol $\approx$ salicylic acid $\approx$ 4-sulphosalicylic acid > α-naphthol > alizarin. This order of coordinating power is also reflected from the $E_{1/2}$ values, taken from the polarograms of 0.001 M solutions of the complexes (pH = 6.5). The effect of varying ligand field strength seems to be reflected also in the magnetic moments of the complexes e.g. chlorophenol, pyrogallol, pyrocatechol etc. in which the average ligand field strength is weak have values (3.95 - 4.15) whereas hydroquinone, 4-nitrophenol, phenol and 4-aminosalicylic acid having a greater ligand field have a moment of only 3.70 B.M. These values of magnetic moments are close to the spin only values for octahedral complexes of chromium(III). The molar conductance values indicate the presence of three ions in the complexes.

The same information regarding the coordinating capacity of phenols and phenolic acids arranged in the above order is also derived from the values of β_{35}, for their respective complexes.

IR Spectra :

The bands obtained in the IR spectra of the ligands and their complexes are given in Table-3. The uncoordinated COO^- stretching bands obtained at 1669 and 1233 cm^{-1} shift towards lower and higher side respectively in the spectra of complexes hence the bands appeared in the range 1600-1640 cm^{-1} and 1400-1490 cm^{-1} are due to coordinated carboxyl groups. Tomito and Ueno [204] also observed the tetradenate nature of NTA in the transition metal complexes.

The comparison of the spectra of free ligand and their respective complexes reveals the disappearance of the band observed at 3400 cm^{-1} (free ligand) indicating the loss of phenolic proton on complexation forming metal oxygen link. The extra bands at 3400 cm^{-1} in the spectra of complex no. 1, 4 and 6 due to uncoordinated OH, NH_2 and OH respectively, 1530 and 1350 cm^{-1} in the spectrum of 2nd complex due to $C-NO_2$, 700 cm^{-1} in the spectrum of 5th complex due to C-Cl and at 1150 and

Table - 3 IR data (cm^{-1}) and their assignments

Complex no.**	-COOH	-COO-Cr	$-COO^-$	M-N and M-O	ν_{C-H}**	δ C-H**	Complements**
$NTAH_3$	1669(VS) 1233(m)						
$NTA(NH_4)_3$			1623(VS)				
1		1620(s),1470(s)		520(m),400(w)	1300(m),1200(m) 1050(w)	950(m),800(m) 600(w)	3350(m)
2		1600(s),1380(s)		520(s),400(w)	1080(m),1040(m) 1000(w)	900(s),740(s) 600(m)	1530(m) 1350(m)
3		1600(s),1400(s)		520(s),400(w)	1100(m),1000(m)	940(m),920(m) 740(w)	-
4		1620(s),1450(s)		520(m),360(b)	1300(m),1250(m) 1150(w)	950(s),900(m) 700(w)	3400(m)
5		1600(s),1380(s)		500(m),400(w)	1200(m),1140(s) 1000(s)	900(s),740(m) 600(m)	700(s)
6		1620(s),1490(s)		540(s),380(w)	1100(w),1040(m)	950(s),750(s) 600(s)	3400(b)
7		1600(s),1470(s)		540(s),450(w)	1300(m),1200(m) 1150(m)	950(w),900(m) 700(w)	-
8		1600(s),1400(s)		520(s),400(w)	1120(m),1020(m)	850(w),700(m) 600(w)	-
9		1640(s),1420(s)		520(s),400(w)	1120(s),1050(w) 1000(w)	910(s),750(m) 620(s)	-
10		1640(s),1480(s)		540(w),360(w)	1260(m),1040(w)	920(m),840(m)	1155(m), 700(m)
11		1600(s),1480(s)		520(m),400(w)	1120(m),1040(m)	900(s),740(m) 620(w)	-
12		1600(s),1460(a)		520(m),400(b)	1300(m),1210(m) 1100(m)	950(m),900(m) 700(w)	-

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*See Table No.1; **The absorption arising from secondary L,s=strong; m=medium; b=broad and w=weak.

700 cm^{-1} in the spectrum of 10th complex due to $C\text{-}SO_3$ were obtained. The bands observed at about 520 and 400 cm^{-1} may be attributed either to M-N or M-O bond.

SECTION B

CHAPTER—I : Mössbauer Studies on the Mixed Ligand Complexes of Fe (III) Phthalimide with some Amino Acids.

Mössbauer spectroscopic studies on ferric polyamino carboxylate [205-210], ferric squarate [211,212] and the complexes of the type FeL_4X_2 [213], where L = heterocyclic amines and X = halide or SCN^- ion, have been carried out in order to establish the correlation between isomeric shifts, quadrupole splitting and molecular structure. A large number of complexes of Fe(III) phthalimide have also been reported in the literature [30,42,214-216]. In this chapter we deal with the preparation and characterisation of some new mixed ligand complexes of Fe(III) with phthalimide as primary and amino-acids (methionine, glutamic acid, cysteine, arginine, histidine and anthranilic acid) as secondary ligands.

Mössbauer spectroscopy is a recent and important technique which gives a very useful information about the electron density, the distribution of electronic charge, the magnitude of local magnetic field, chemical kinetics, surface phenomenon and the tightness of binding of the nucleus to its lattice site. All these factors are of value in examining the structure and bonding of compounds. Hence it will not be out of place if some preliminary information about Mössbauer spectroscopy is given.

Now the Mössbauer effect has been observed for a total of 38 nuclides, but ^{57}Fe is one of the most favourable and data can usually be obtained very readily using the natural abundance of this isotope. The technique is basically absorption spectroscopy using gamma-rays which are resonantly absorbed by ^{57}Fe-nuclei of the sample. In order to provide gamma-rays of appropriate energy, an active isotope which decays to the excited state of ^{57}Fe is used as a source. The most convenient being ^{57}Co (half life = 270 days). The 14.38 KeV gamma-rays emitted by such a source can, in principle, be absorbed by ground-state ^{57}Fe-nuclei in the sample. The source is mounted on a vibrator whose velocity can be controlled, and the energy, E, of the radiation incident on the sample is given by $E = E_o-(1+\frac{V}{C})$ where E_o is the source transition energy, V and C are the velocities of the source and light respectively. The energy scale of a Mossbauer spectrum is thus a velocity scale, and data are normally presented in units of mm S^{-1}; for ^{57}Fe, 1 mm S^{-1} = 48.10^{-9} eV. The spectra are characterised by two major parameters, the isomer shift (δ), and the quadrupole silliting (ΔE).

I. Isomer Shift :

The isomer shift represents the velocity of maximum absorption or in the case of two line spectrum, the mid point between the maxima. The choice of a standard for reporting of isomer shift data has varied from one investigator to another. Sodium nitroprusside, $Na_2Fe(CN)_5NO.3H_2O$ has been used extensively by chemists.

Natural iron has recently been recommended by a committee of the American Society for Testing and Materials. If the chemical environment of the source and the absorber is identical, resonant absorption will occur at zero velocity. Since the absorber has always a different environment, the resonance absorption shifts from zero velocity. The position thus obtained gives the shift in the resonance maxima and is called the isomer shift is somewhat temperature dependent, becoming more positive as the temperature is lowered. Increasing values of isomer shifts represent decreasing electron density at the nucleus. The only electrons which actually penetrate the nucleus are s-electrons, so that an increase in isomer shift means a decrease in s-electron density. Such a change might occur by decreasing the donating power of the ligands. Electrons other than s-electrons act only indirectly by screening the nucleus from s-electrons, so that this effect is much smaller than, and opposite to that of the s-electrons. The contribution of the d-electrons is by no means negligible, it accounts for the difference between the characteristic isomer-shift ranges of high-spin ferrous (d^6) and ferric(d^5) complexes, which are 0.8 - 1.5 and 0.2 - 0.6 mm S^{-1} respectively.

II. Quadrupole Splitting :

If the nucleus is not spherical (with spin 0 or $\frac{1}{2}$), there is a split in the nuclear levels. The nuclear quadrupole moment is a measure of the deviation of the nucleus from spherical symmetry. This quadrupole moment interacts with the electronic charge surrounding the nucleus and a quadrupole splitting is observed. For nuclear spin I = 3/2, the nuclear levels in iron split into I = 3/2 and I = 1/2 and a transition can be observed from each of these two levels to the ground state. The energy separation between the two transitions is the quadrupole splitting.

A ligand environment of less than cubic symmetry will give an electric field gradient, so that a complex containing more than one type of ligand will show a quadrupole splitting. For any given ligand, σ-donation gives a negative contribution to the field gradient along the metal ligand bond axis, while π-acceptance gives a positive contribution. The quadrupole splitting thus represents the difference between σ and π-bonding.

EXPERIMENTAL

Reagents and Solutions :

Amino-acids, phthalimide, sodium hydroxide and ferric chloride, all were of Analar (BDH) grade. Freshly prepared solutions in distilled water were used.

Physical Measurements :

As reported in Section-A, Chapter-I of this thesis. Mössbauer spectra of the complexes were recorded at 25 ± 1°C on a Mössbauer spectrophotometer using 256-channel analyser and a Kankeleit type constant acceleration drive [217]. The source used was 5 m Ci Co^{57} isotope in palladium matrix. The calibration of the spectrophotometer was done by the peak positions of standard natural iron which was prepared by evenly spreading the sample on cellotape.

Preparation of the Complexes :

The aqueous solutions of ferric chloride and of amino acids containing minimum amount of potassium hydroxide to make soluble were mixed in a molar ratio of 1:1 and then allowed to stand for about fifteen minutes, three moles of potassium phthalimide were then added to get the precipitates of yellow colour, which were filtered, washed several times with distilled water and then dried in a vacuum desiccator. They were soluble in n-butanol and amyl alcohol.

The results of chemical analysis, values of magnetic moments at room temperature and molar conductances in amyl alcohol are given in Table-1.

Table - 1 Analytical data and magnetic moments of the complexes

S. No.	Complexes	Percentage calculated (found)			μ_{eff} B.M.	Molar conductance (ohm^{-1} cm^2 mol^{-1})
		Fe	C	N		
1.	$NH_4[Fe(C_8H_4O_2N)_3(C_5H_{10}O_2NS)(H_2O)]$	8.21 (8.30)	51.02 (51.50)	4.10 (4.05)	5.80	85.0
2.	$K[Fe(C_8H_4O_2N)_2(C_5H_7O_4N)(H_2O)_2]$	9.90 (10.00)	44.36 (44.80)	3.34 (3.31)	5.75	80.0
3.	$K[Fe(C_8H_4O_2N)_3(C_3H_6O_2NS)(H_2O)]$	8.32 (8.40)	48.14 (48.63)	2.97 (2.94)	5.50	80.0
4.	$[Fe(C_8H_4O_2N)_2(C_6H_{13}N_4O_2)(H_2O)_2]$	10.29 (10.40)	47.40 (47.88)	4.48 (4.43)	5.64	00.0
5.	$[Fe(C_8H_4O_2N)_2(C_6H_8N_3O_2)(H_2O)_2]$	10.40 (10.50)	49.07 (49.52)	3.71 (3.68)	5.60	00.0
6.	$[Fe(C_8H_4O_2N)_2(C_7H_6O_2N)(H_2O)_2]$	10.40 (10.50)	51.30 (51.84)	3.71 (3.68)	5.70	00.0

9

RESULTS AND DISCUSSION

Infra-red Studies :

Iron(III) (phthalimide)$_3$ was prepared by mixing the aqueous solutions of ferric chloride and sodium phthalimide in the ratio of 1:4. The precipitates formed were filtered, washed several times with distilled water and finally with methanol and then dried in a desiccator over anhydrous sulphuric acid. Its infra-red spectrum was taken separately in order to compare with the infra-red spectra of complexes. The frequency of the stretching N-H vibration observed at 3300 cm^{-1} in the spectrum of free phthalimide should disappear in the spectra of complexes because of the coordination of imino group after deprotonation, but because of the presence of water molecules, a broad band at around the same wave number is observed in the spectra of all complexes. The carbonyl streching frequency of the imides in complexed form, fall within the range 1660-1680 cm^{-1} which is well removed from the 1750 cm^{-1} band in the free imide. Although the C = O group in imides does not take part in coordination, shifts to lower frequency as compared to the non-coordinated states may be due to the mass effect of heavy metal ion linked to nitrogen [41] as well as a possible weakening of the C = O linkage [41]. The stretching frequency obtained around 1470 cm^{-1} due to C-N, in the spectrum of phthalimide shifts to about 1480 cm^{-1} in the spectra of its complexes.

The spectra of mixed ligand complexes of histidine, anthranilic acid, glutamic acid and arginine showed the presence of two strong bands in the region 1600-1620 cm^{-1} and the shifting of the band due to -NH$_2$ from 3400 cm^{-1} to 3200, 3200, 3250 and 3240 cm^{-1} respectively indicating thereby the coordination of these amino-acids through carboxyl and amino-nitrogen atom. The complexes of cysteine and methionine showed 9 the shifting of S-H stretching band from 2450 cm^{-1} in the uncomplexed form to 2400 cm^{-1} while NH$_2$ band remained undisturbed. The two strong bands in the region 1600-1620 cm^{-1} were also observed in the spectra of these complexes. This indicated the coordination of cysteine and methionine through carboxyl and sulphyhydril groups. Two bands at around 870 cm^{-1} and 640 cm^{-1}, due to wagging and rocking mode of coordinated water [218] were observed in the spectra of all the complexes.

Magnetic and Electronic Spectral Studies :

All the complexes were found to be paramagnetic Low with magnetic moments 5.50 - 6.00 BM, characteristic of high spin iron(III) compounds. The electronic spectra of all the complexes in butanol gave three bands at 29500, 34000 and 39000 cm^{-1} corresponding to the transitions $^6A_{1g} \longrightarrow {}^4T_{1g}$ (P), $^6A_{1g} \longrightarrow {}^4T_{1g}$ (F) and

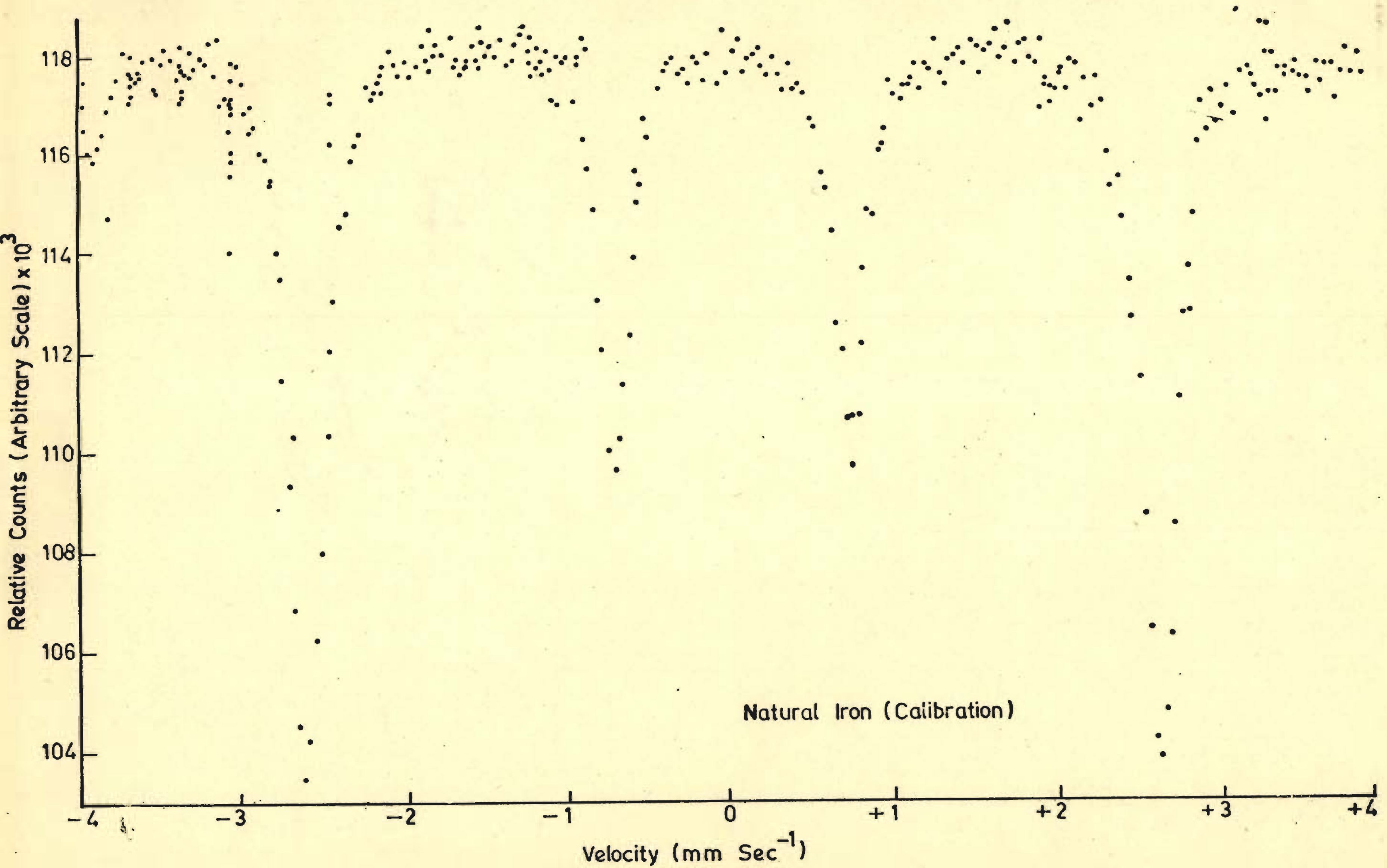
may be due charge transfer

$^6A_{1g} \longrightarrow {}^4T_{2g}$ (F) respectively.

Mössbauer Studies :

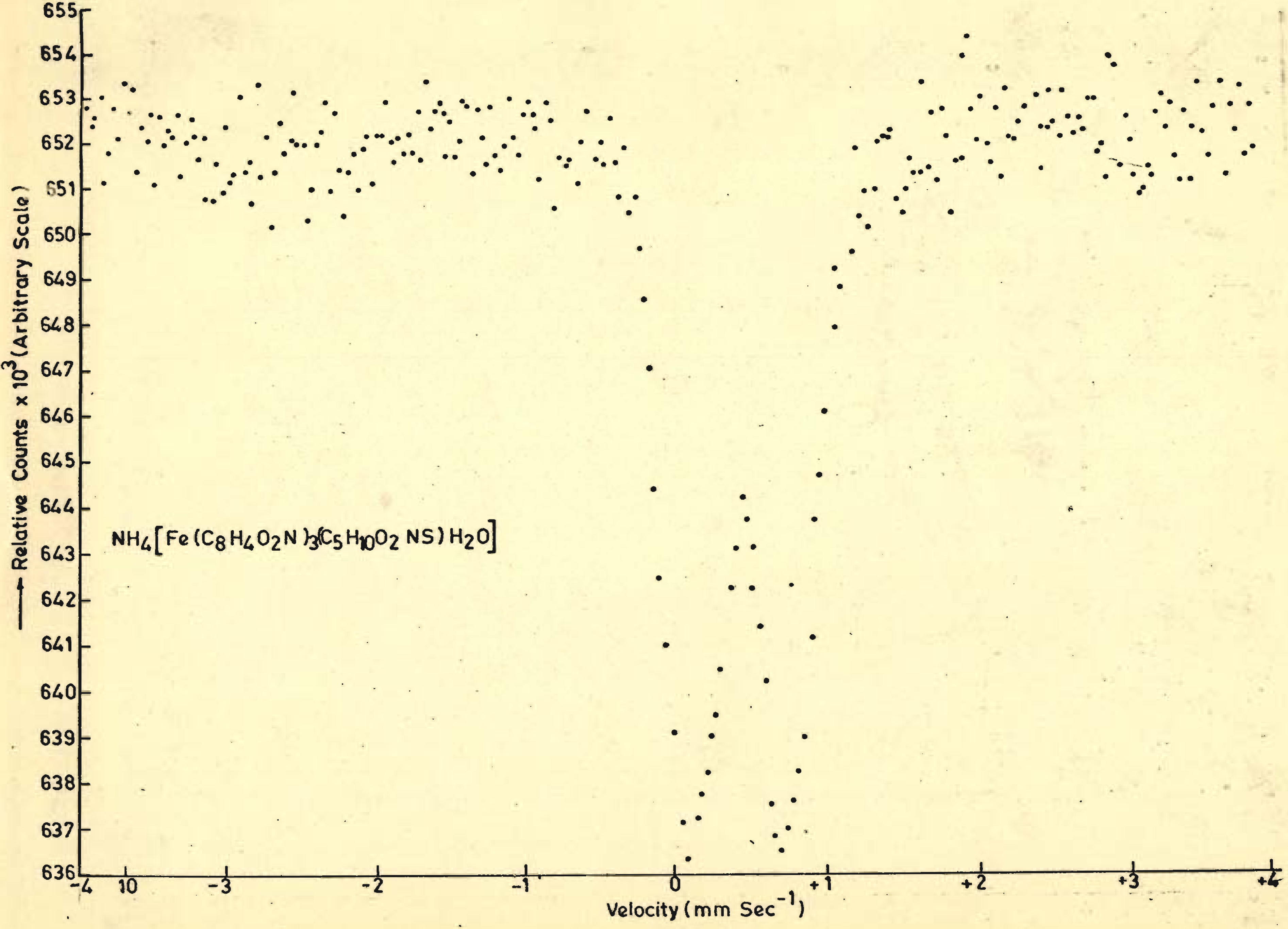
The Mössbauer spectra of natural iron and of all these complexes are given in figures (1-7) and the values of isomer shift, δ(mm/sec) and quadrupole splitting. ΔE(mm/sec) are given in Table-2 together with some of the data obtained by other workers. There is a pronounced difference in the values of isomer shift of $FeCl_3 \cdot 6H_2O$ and those of complexes under study where water molecules have been replaced by two different types of ligands i.e. phthalimide and amino-acid molecules. The values decreased to 0.38 indicating a greater electron density at the nucleus. Values of the same order were reported for $[Fe(terpy.)Cl_3]$ [219]. In the case of complexes containing histidine and anthranilate ion inside the coordination sphere, the absorption peak appeared close to zero velocity showing the strong covalent character of the bonds between Fe and donor atom.

The quadrupole splitting is caused by non-zero electric field gradient at the iron nucleus which depends on various collective factors e.g. bonding character, the crystallographic character and the electronegativity of the neighbouring atom etc. A ligand environment of less than cubic symmetry will



Velocity/ Channel = 0·03088 mm Sec^{-1}
Zero Velocity Channel = 129·5

Fig. 1



→ Relative Counts x 10^3 (Arbitrary Scale)
655
654
653
652
651
650
649
648
647
646
645
644
643
642
641
640
639
638
637
636
$NH_4[Fe(C_8H_4O_2N)_3(C_5H_{10}O_2NS)H_2O]$
-4
10
-3
-2
-1
0
+1
+2
+3
+4
Velocity (mm Sec^{-1})

FIG.-2

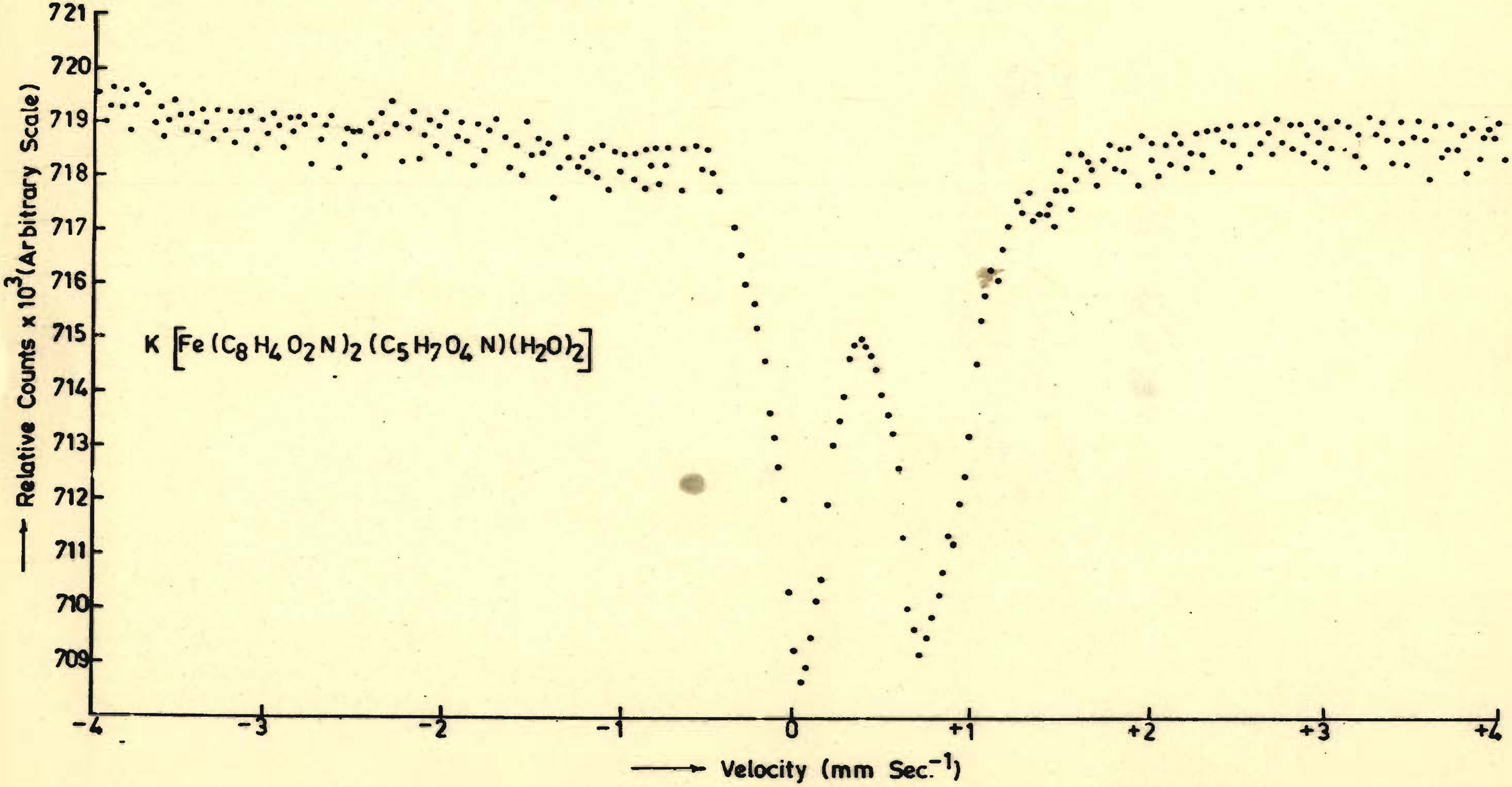

721
720
719
718
717
716
715
714
713
712
711
710
709
Relative Counts x 10^3 (Arbitrary Scale)
$K[Fe(C_8H_4O_2N)_2(C_5H_7O_4N)(H_2O)_2]$
-4
-3
-2
-1
0
+1
+2
+3
+4
Velocity (mm Sec^{-1})

Fig. 3

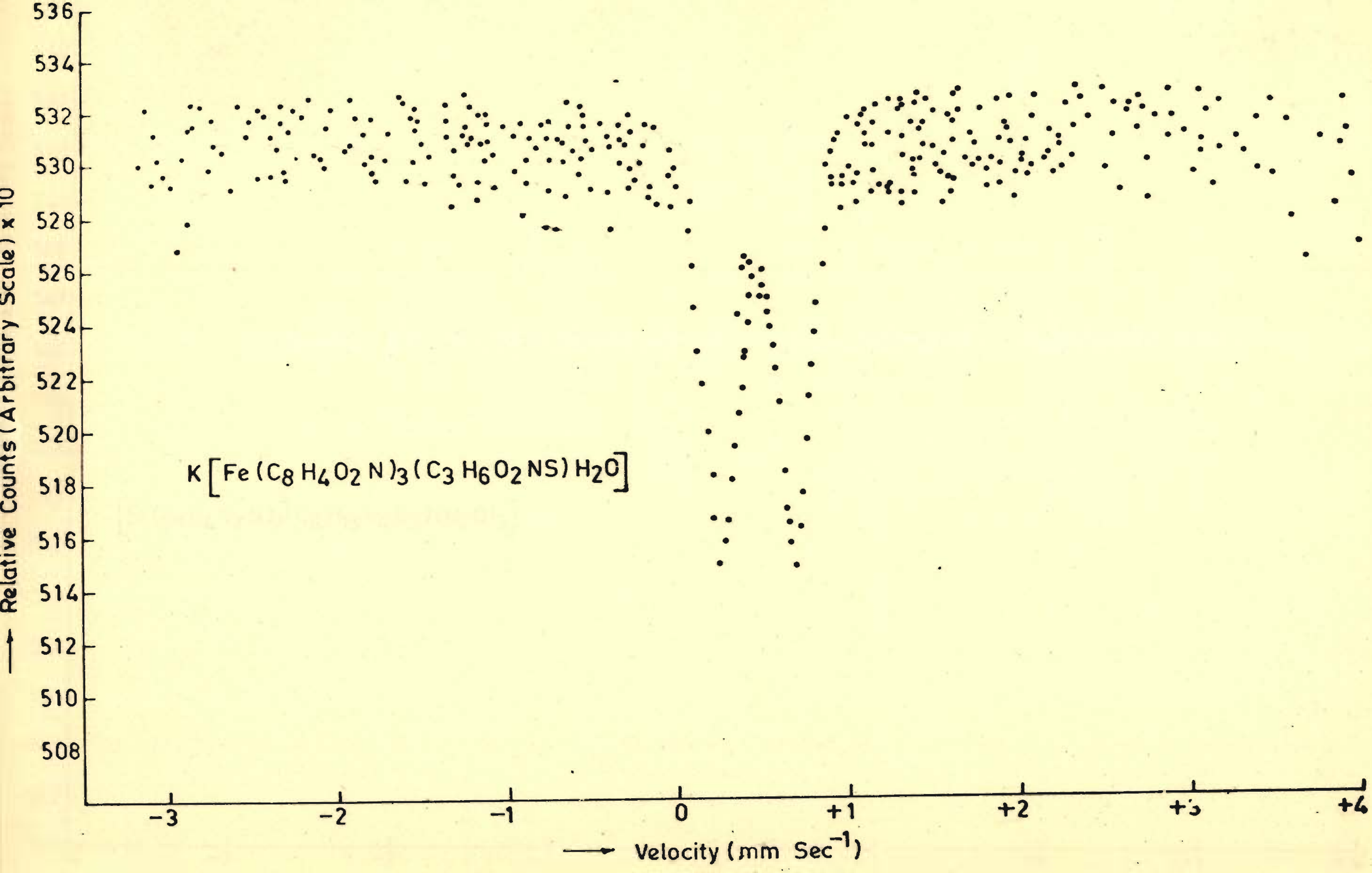

536
534
532
530
528
526
524
522
520
518
516
514
512
510
508
Relative Counts (Arbitrary Scale) x 10
$K[Fe(C_8H_4O_2N)_3(C_3H_6O_2NS)H_2O]$
−3
−2
−1
0
+1
+2
+3
+4
Velocity (mm Sec^{-1})

Fig. 4

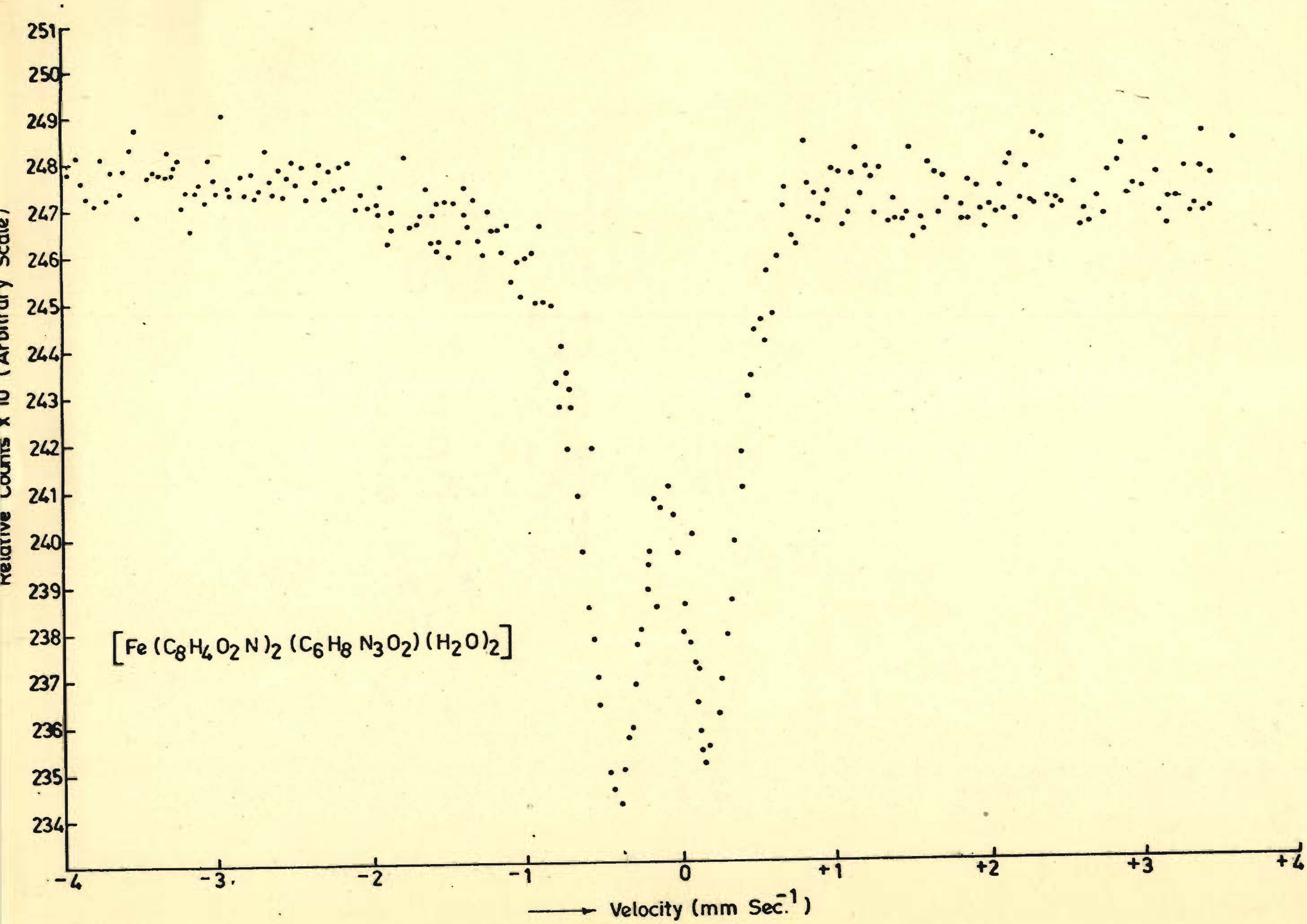

Relative Counts x 10 (Arbitrary Scale)
251
250
249
248
247
246
245
244
243
242
241
240
239
238
237
236
235
234
-4
-3
-2
-1
0
+1
+2
+3
+4
Velocity (mm Sec.$^{-1}$)
$[Fe(C_8H_4O_2N)_2(C_6H_8N_3O_2)(H_2O)_2]$

Fig. 6

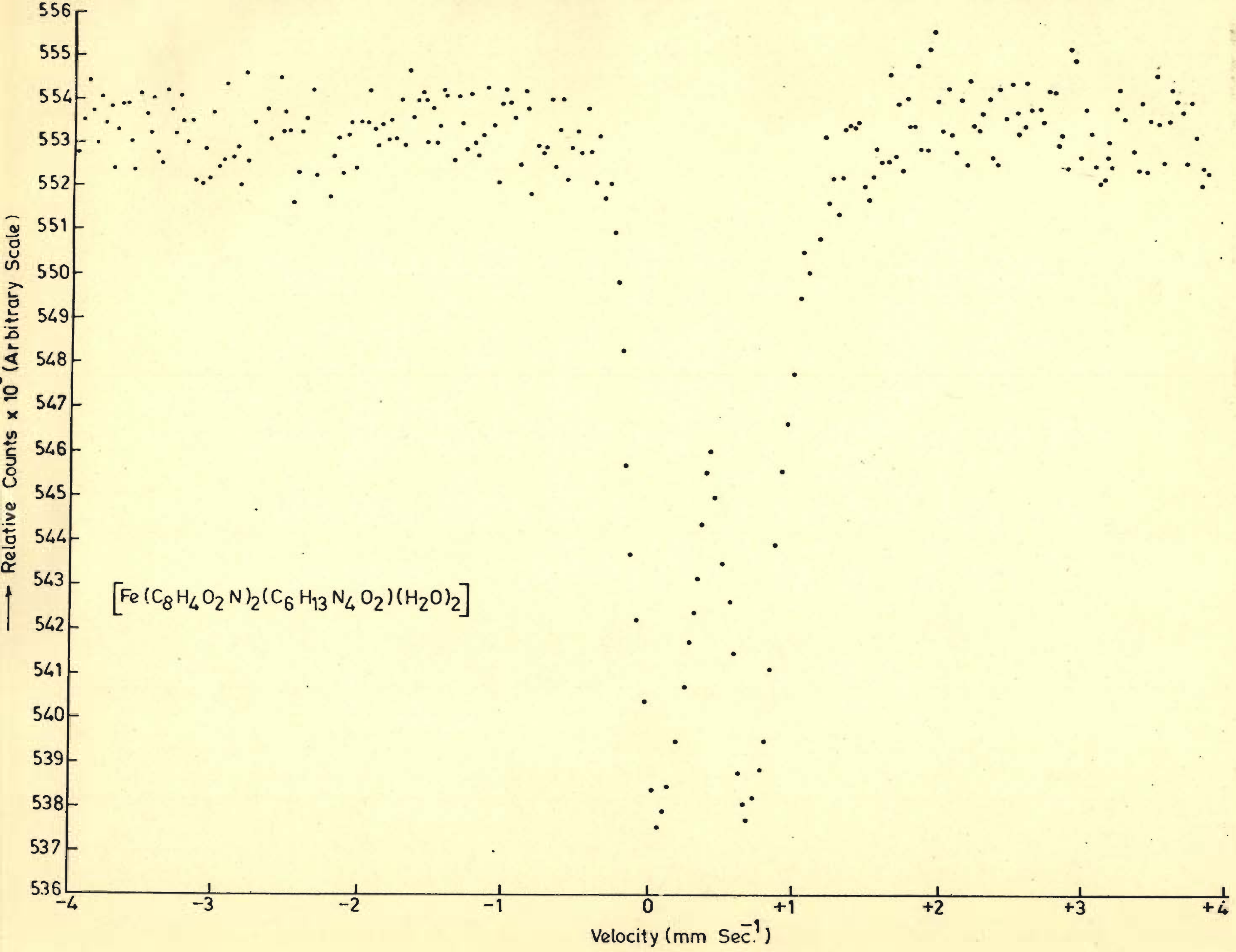

Relative Counts x 10 (Arbitrary Scale)
556
555
554
553
552
551
550
549
548
547
546
545
544
543
542
541
540
539
538
537
536
$[Fe(C_8H_4O_2N)_2(C_6H_{13}N_4O_2)(H_2O)_2]$
−4
−3
−2
−1
0
+1
+2
+3
+4
Velocity (mm $Sec.^{-1}$)

Fig. 5

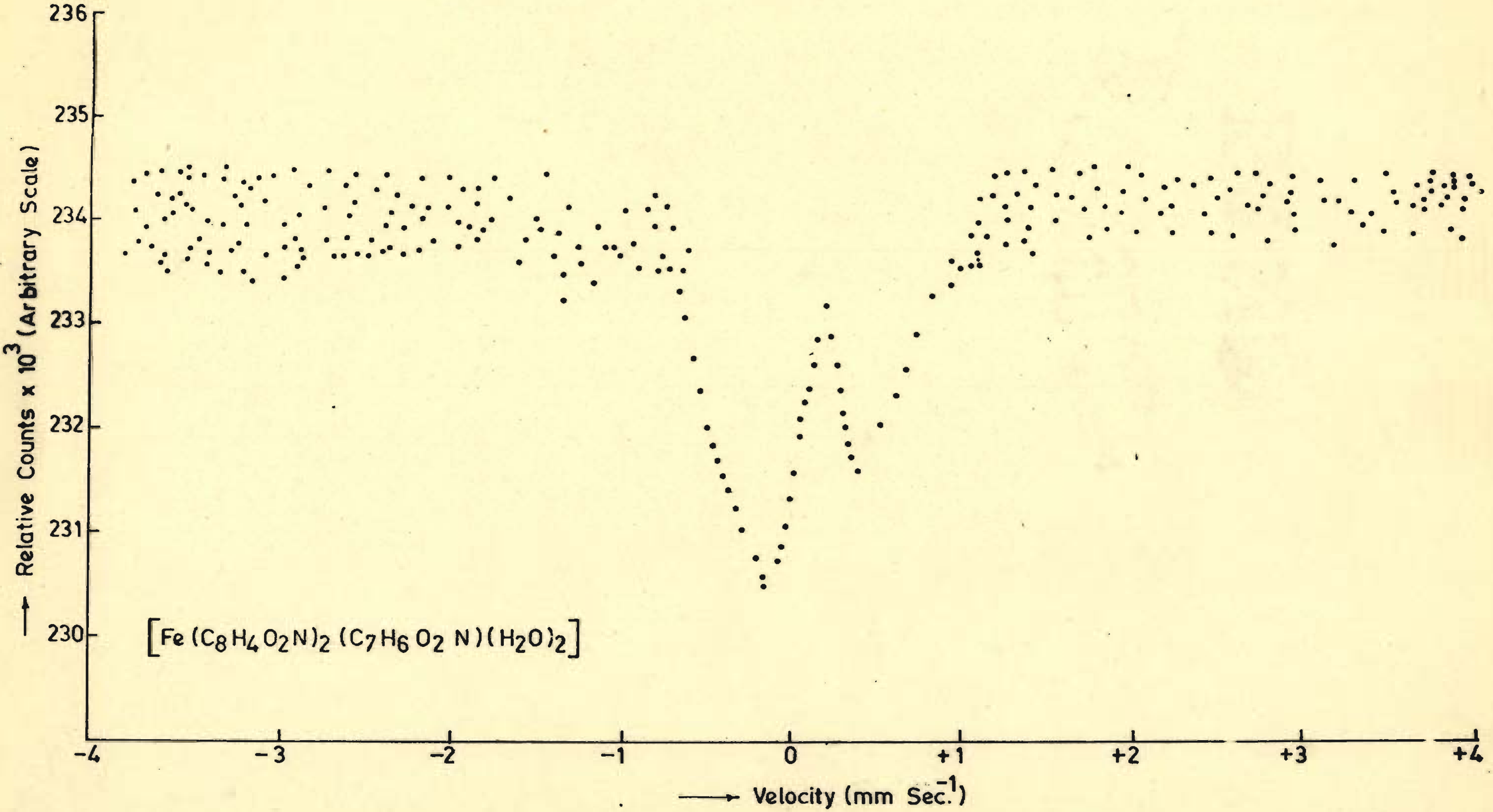

236
235
234
233
232
231
230
Relative Counts x 10^3 (Arbitrary Scale)
$[Fe(C_8H_4O_2N)_2(C_7H_6O_2N)(H_2O)_2]$
−4
−3
−2
−1
0
+1
+2
+3
+4
Velocity (mm Sec.$^{-1}$)

Fig. 7

Table 2 - Isomer shifts (δ) and quadrupole splittings (ΔE) with respect to natural iron absorber.

Complex no.*	δ (mm/sec)	Δ E(mm/sec)
1	0.38	0.61
2	0.39	0.68
3	0.40	0.46
4	0.39	0.61
5	-0.10	0.68
6	0.10	0.54
$FeCl_3$	0.93-1.01(-130°C)	1.70-3.60(-130°C)
$FeCl_3 \cdot 6H_2O$	0.65(-196°C)	0.50(-196°C)

* See Table-1.

give an electric field gradient so that a complex containing more than one type of ligand will show a quadrupole splitting. The quadrupole splitting also represents the difference between σ and π-bonding. In our case, however it appears that the sizable quadrupole splitting is due to crystallographic distortions caused by the presence of different types of ligands inside the coordination sphere.

SECTION B

CHAPTER—II : Preparation and Characterisation of Mixed Ligand Complexes of Platinum (II), Palladium (II), Platinum (IV), Iridium (III) and rhodium (III) with Phthalimide as Primary & Dipyridyl and O-Phenanthroline as secondary Ligands.

Many complexes of the platinum metals have been shown to act as active homogeneous catalysts in reactions of industrial importance, including the hydrogenation [220,221], hydrosilation [222,223], hydroformylation [224,225] and oxidative hydrolysis [226,227] of olefins and carbonylation of methanol [228,229]. Some success in the activation of alkanes has also been achieved by complexes of these metals [230]. The ease with which an organic substrate can enter the coordination sphere of a metal ion is thought to be a key factor in determining ability of such an ion to catalyse the reactions of the substrate. The complexes of platinum metals are very important from medicinal point of view also. Certain complexes of platinum exhibit potent anti-tumor activity [231] and ehrlich ascites carcinoma and Leukemias [232]. A qualified usefulness of cis-dichlorodiammineplatinum(II) as a broad spectrum anticancer agent has been established in clinical trials [233-235]. The cis-dichloro(dipyridine) platinum(II) complex is less active but is appreciably less toxic [236].

Besides their anticancer activity, this class of compounds have shown antibacterial activity, especially where metal ions have 3,4 (low spin), 5 or 6d electrons and where complex formation involves large values of ligand field stabilization energy and can persist unchanged for hours and days under conditions favourable to their dissolution. These types of metal ions with 1,10-phenanthroline and related bases have been shown to be lethal to many bacteria and pathogenic fungi e.g. tris-(1,10-phenanthroline) ruthenium(II) are bacteriostatic to a number of Gram-negative and Gram-positive microorganism and mycobacterium tuberculosis [237]. $[RhL_4X_2]Y$, where L =substituted pyridine, X and Y = halide ions, nitrate or perchlorate have high levels of antibacterial activity [238].

This chapter deals with the preparation and characterisation of some complexes of platinum metals with phthalimide as primary and 1,10-phenanthroline or dipyridyl as secondary ligands.

EXPERIMENTAL

Reagents and Solutions :

The chlorides of iridium(III), rhodium(III) and palladium(II), potassium hexachloroplatinate(IV), phthalimide, all were of AR(BDH) grade. All the solutions were prepared in doubly distilled water. Palladium(II) chloride was dissolved in dilute hydrochloric acid.

Physical Measurements :

As reported earlier in Chapters I and II of Section A.

Preparation of the Complexes: Palladium(II) Complexes:

Palladium(II) phthalimide, $Pd(C_8H_4O_2N)_2$:

The solutions of $PdCl_2$ in dil. HCl and of potassium phthalimide (prepared by mixing the solutions of alcoholic phthalimide and alcoholic potassium hydroxide in the ratio of 1:1) in distilled water were mixed in the ratio of 1:2 and stirred with a magnetic stirrer which gave a thick precipitate of light yellow colour. They were filtered, washed several times with distilled water and finally with methanol and dried in a vacuum desiccator over silica gel.

Diphthalimidoaminopalladium(II) :

Where amine is o-phenanthroline or dipyridyl. The palladium phthalimide and amine were mixed in the ratio of 1:1 and the mixture was then refluxed in absolute alcohol for about eight hours which gave blackish precipitates. They were filtered, washed several times with alcohol and then dried in vacuum desiccator over silica gel.

Platinum(II) Complexes: Potassium tetrachloroplatinate(II) :

$K_2[PtCl_4]$ was obtained by carrying out reduction of $K_2[PtCl_6]$ with sulphur dioxide [239].

Potassium diphthalimidodichloroplatinate(II) :

$K_2[Pt(C_8H_4O_2N)_2Cl_2]$ was prepared by mixing the aqueous solutions of $K_2[PtCl_4]$ and potassium phthalimide in the ratio of 1:3. The pH of the solution was adjusted to near about 7 by the addition of aqueous KOH. The volume of the mixture was then reduced to one tenth of the original volume by carrying out the slow evaporation on water bath. The complex was then dissolved on adding a mixture of acetone and alcohol (1:1). The solvent was evaporated and the solid compound so obtained was chemically analysed which corresponded to the formula $K_2[Pt(C_8H_4O_2N_2)Cl_2]$.

Diphthalimido-aminoplatinum(II) :

$[Pt(C_8H_4O_2N)_2(amine)]$ was obtained on mixing the alcoholic solution of $K_2[Pt(C_8H_4O_2N)_2Cl_2]$ and amine in the ratio of 1:1. The mixture was refluxed on water bath for about ten hours which gave brown coloured precipitates. They were filtered, washed several times with water and alcohol and then dried in a desiccator over silica gel.

Platinum(IV) Complexes : Platinum(IV) phthalimide :

$Pt(C_8H_4O_2N)_4$ was prepared on mixing the aqueous solutions of $PtCl_4$(obtained from K_2PtCl_6) [240] and potassium phthalimide in the ratio of 1:6. The pH of the mixture was raised to $\approx$ 8.0 by the addition of KOH and then refluxing of the mixture was carried out on a water bath for more than 10 hours to get the yellow precipitates which were filtered, washed several times with water and then in alcohol and dried in a vacuum desiccator over silica gel.

Tetraphthalimidoaminoplatinum(IV) :

[Pt($C_8H_4O_2N$)$_4$(amine)] was similarly prepared following the method as given in the case of [Pt($C_8H_4O_2N$)$_2$(amine)], using Pt($C_8H_4O_2N$)$_4$ and amine as reactants.

Rhodium(III) and Iridium(III) Complexes :

Metal(III) phthalimide :

M($C_8H_4O_2N$)$_3$ where M = Rh(III) and Ir(III), were prepared by mixing the aqueous solutions of MCl_3 and potassium phthalimide. The mixture was heated on water bath for about half an hour to get the yellow precipitates which were filtered, washed with distilled water and then dried in a vacuum desiccator over silica gel.

Triphthalimidoaquoaminometal(III) :

[M($C_8H_4O_2N$)$_3$(amine)H_2O] was similarly prepared following the method as given for the preparations of other mixed ligand complexes, using metal phthalimide and amine as reactants.

All the complexes were soluble in dimethyl sulfoxide (DMSO). The results of chemical analysis, Table - 1 Analytical data of complexes

S. No.	Complexes	Colour	M% Calc. (Found)	C% Calc. (Found)	H% Calc. (Found)	N% Calc. (Found)	μ_{eff} in B.M.	Conductance in DMSO $(ohm^{-1} cm^2 mol^{-1})$
1.	$[Pt(C_8H_4O_2N)_2(C_{10}H_8N_2)]$	Brown	30.326 (29.90)	48.52 (48.46)	2.48 (2.40)	8.70 (8.62)	0.00	10.20
2.	$[Pt(C_8H_4O_2N)_2(C_{12}H_8N_2)]$	Brown	28.46 (27.95)	49.05 (48.96)	2.33 (2.25)	8.39 (8.22)	0.00	10.34
3.	$[Pd(C_8H_4O_2N)_2(C_{10}H_8N_2)]$	Bluish Black	19.13 (18.85)	56.31 (56.25)	2.88 (2.78)	10.10 (10.82)	0.00	10.26
4.	$[Pd(C_8H_4O_2N)_2(C_{12}H_8N_2)]$	Bluish Black	17.78 (17.50)	56.37 (56.30)	2.68 (2.52)	9.68 (9.60)	+0.12	11.20
5.	$[Pt(C_8H_4O_2N)_4(C_{10}H_8N_2)]$	Green	20.86 (20.40)	53.90 (53.75)	2.56 (2.40)	8.98 (8.84)	+0.46	10.00
6.	$[Pt(C_8H_4O_2N)_4(C_{12}H_8N_2)]$	Yellowish green	19.95 (19.70)	54.04 (53.92)	2.45 (2.30)	8.76 (8.60)	+0.32	10.21
7.	$[Rh(C_8H_4O_2N)_3(C_{10}H_8N_2)H_2O]$	Black	14.40 (14.29)	57.06 (56.90)	3.07 (3.10)	9.79 (9.68)	0.00	10.80
8.	$[Rh(C_8H_4O_2N)_3(H_2O)(C_{12}H_8N_2)]$	Black	13.94 (13.48)	58.45 (58.20)	2.97 (2.80)	9.47 (9.33)	-0.14	10.68
9.	$[Ir(C_8H_4O_2N)_3(H_2O)(C_{10}H_8N_2)]$	Pale yellow	23.90 (23.72)	50.75 (50.70)	2.74 (2.66)	8.70 (8.66)	-0.18	11.24
10.	$[Ir(C_8H_4O_2N)_3(H_2O)(C_{12}H_8N_2)]$	White	23.21 (23.00)	52.17 (52.08)	2.66 (2.56)	8.45 (8.38)	-0.22	11.18

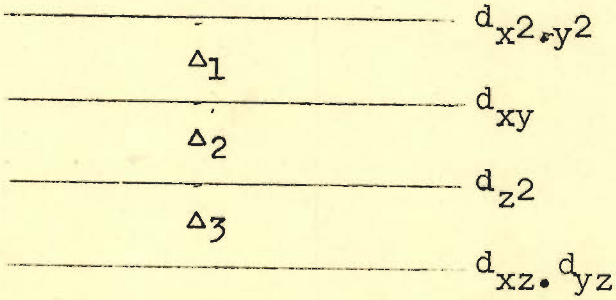
conductance and magnetic measurements are given in Table - 1.

RESULTS AND DISCUSSION

The values of molar conductances of all the complexes in dimethylsulfoxide were found near about 10.0 Ohm^{-1} cm^{2} mol^{-1} indicating their non-electrolytic nature. The magnetic measurements showed a diamagnetic behaviour for these palladium(II) and Platinum(II) complexes.

Electronic Spectra of Palladium(II) and Platinum(II) Complexes :

The electronic structure of square planar complexes of D_{4h} have been much discussed and debated in recent past [241-248]. The five degenerate d-orbitals of the uncomplexed metal ion split into four different levels of symmetric $b_{1g}(d_{x^2-y^2})$, $b_{2g}(d_{xy})$, $a_{1g}(d_{z^2})$and $eg(d_{xy},d_{yz})$, as shown in the figure :



Metal d-orbital energies for selected square planar complexes.

Therefore, the three orbital parameters, Δ_1, Δ_2 and Δ_3 are needed to describe the ligand field splitting. Almost all square planar complexes with simple ligands are diamagnetic and contain a metal ion with d^8 electronic configuration. Thus the ground state is $^1A_{1g}$. Three spin-allowed d-d transitions are anticipated corresponding to transitions from the three lower lying d-levels to the empty $d_{x^2-y^2}$ orbital, $^1A_{1g} \longrightarrow {}^1A_{2g}$; $^1A_{1g} \longrightarrow {}^1B_{1g}$ and $^1A_{1g} \longrightarrow {}^1Eg$. The charge transfer bands of lowest energy are expected to involve transitions from the highest filled metal orbitals to the most stable empty ligand molecular orbital, the $a_{2u}(\pi^*)$. The first charge transfer transition is orbitally forbidden and should have relatively little intensity. The second charge transfer band corresponds to the transition $a_{1g}(\sigma^*) \longrightarrow a_{2g}(\pi^*)$($^1A_{1g} \longrightarrow {}^1A_{2u}$). The energy of this transition is calculated to be $\Delta E(^1A_{1g} \longrightarrow {}^1B_{1u}) + \Delta_2$, corrected for difference in inter electronic repulsion energies in the $^1A_{2u}$ and $^1B_{1u}$ excited states. The third charge transfer transition is $eg(\pi^*) \longrightarrow a_{2u}(\pi^*)$ ($^1A_{1g} \longrightarrow {}^1E_u$) and is calculated to be $\Delta E(^1A_{1g} \longrightarrow {}^1B_{1u}) + \Delta_2 + \Delta_3$, again corrected for repulsion differences in the ^1E_u and $^1B_{1u}$ excited states. Similarly two allowed charge transfer transitions may be anticipated corresponding to $^1A_{1g} \longrightarrow {}^1A_{2u}$ and $^1A_{1g} \longrightarrow {}^1E_u$. These are the transitions from molecular orbitals localized on the metal atom and it has been reported that the $^1A_{1g} \longrightarrow {}^1E_u$ transition will be more intense than $^1A_{1g} \longrightarrow {}^1A_{2u}$ transition.

These complexes are square planar and diamagnetic. The spectra of the solutions of Palladium(II) complexes in DMSO gave three spin allowed d-d transitions and two charge transfer transitions and of platinum(II) complexes in same solvent gave the expected three charge transfer bands. The d-d bands for the most part were obscured by these charge transfer bands. In this case the transitions from molecular orbitals localized on the metal to molecular orbitals localized on the ligands were found. The assignment of the electronic spectra of these complexes are given in Table - 2.

Calculations were made using the orbital and inter-electronic repulsion energies of excited states for d^8 square planar complexes given in Table - 3.

The values of Δ_1, Δ_2 and Δ_3 are given in Table - 4, for comparison purposes.

The separation Δ_1 for these complexes was the largest of the three orbital parameters which indicated that the $d_{x^2-y^2}$ was much more strongly antibonding than any of the other d-orbitals. The separation Δ_3 for platinum(II) complexes is less than that of the Pd(II) complexes. In case of platinum(II) (Table-4), the d_{z^2} was more stable than d_{xy}, d_{yz}. This was

Table - 2 Spectral properties of the d^8 complexes

Complexes	λ_{max} (cm^{-1})	ε_{max}	Assignment
$[Pd(Phth)_2(dipy)]$	40000	28500	$^1A_{1g} \rightarrow {}^1E_u$
	34500	8500	$^1A_{1g} \rightarrow {}^1A_{2u}$
	31000		$^1A_{1g} \rightarrow {}^1E_g$
	28400		$^1A_{1g} \rightarrow {}^1B_{1g}$
	23100		$^1A_{1g} \rightarrow {}^1A_{2g}$
$[Pd(Phth)_2(O\text{-}Phen)]$	40000	28500	$^1A_{1g} \rightarrow {}^1E_u$
	34500	8500	$^1A_{1g} \rightarrow {}^1A_{2u}$
	31000		$^1A_{1g} \rightarrow {}^1E_g$
	28400		$^1A_{1g} \rightarrow {}^1B_{1g}$
	23100		$^1A_{1g} \rightarrow {}^1A_{2g}$
$[Pt(Phth)_2(dipy)]$	41000	1850	$^1A_{1g} \rightarrow {}^1A_{2u}$
	39500	29000	$^1A_{1g} \rightarrow {}^1E_u$
	36000	2000	$^1A_{1g} \rightarrow {}^1B_{1u}$
$[Pt(Phth)_2(O\text{-}Phen)]$	41000	1850	$^1A_{1g} \rightarrow {}^1A_{2u}$
	39500	29000	$^1A_{1g} \rightarrow {}^1E_u$
	36000	2000	$^1A_{1g} \rightarrow {}^1A_{2u}$

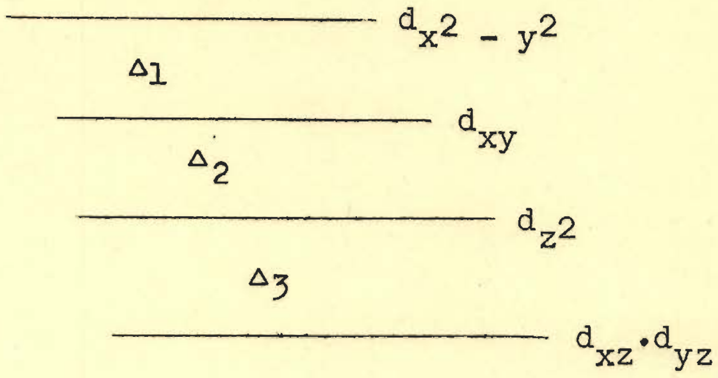
Table - 3 Orbital and Inter-electronic repulsion energies of some excited states of interest for an nd^8 square planar complex

Term Designation		Orbital Energy	Slater-Condon energy[a,b]
Singlet terms	$^1A_{1g}$	(ground state)	-
	$^1A_{2g}$	Δ_1	$-35F_4$
d-d transitions	$^1B_{1g}$	$\Delta_1 + \Delta_2$	$-4F_2 - 15F_4$
	^1E_g	$\Delta_1 + \Delta_2 + \Delta_3$	$-3F_2 - 20F_4$
Charge transfer transitions	$^1B_{1u}$	$E(^1B_{1u})$	-
	$^1A_{2u}$	$E(^1B_{1u}) + \Delta_2$	$-20F_2 + 100F_4$
	^1E_u	$E(^1B_{1u}) + \Delta_2 + \Delta_3$,	$-15F_2 + 75F_4$

a Referred to the ground state as zero

b For the approximation used to estimate the Slater-Condon energy for the charge transfer transition (see ref. 249).

Table - 4 Metal d-orbital energies for square planar complexes



Orbital energy differences (cm^{-1}) for $F_2=10F_4$ = 700 cm^{-1}

Complexes	Δ_1	Δ_2	Δ_3
$[Pd(Phth)_2(dipy)]$	25550	6700	2250
$[Pd(Phth)_2(Phen)]$	25550	6700	2250
$[Pt(Phth)_2(dipy)]$	-	12000	-3250
$[Pt(Phth)_2(Phen)]$	-	12000	-3250

Phth = deprotonated phthalimide

dipy = dipyridyl

Phen = O-phenanthroline

compatible with the idea that the axial interaction of the solvent molecules in the case of palladium(II) is greater than platinum(II).

Electronic Spectra of Platinum(IV), Iridium(III) and Rhodium(III) Complexes :

The values of molar conductances and of magnetic moments as given in Table-1 indicated their non-electrolytic nature and diamagnetic character. The survey of the existing literature also reveals that the complexes of $4d^6$ and $5d^6$ metal ions are generally diamagnetic in nature [250-252].

The absorption spectra of diamagnetic octahedrally coordinated d^6 metal ion complexes give rise to two spin-allowed ${}^1T_{1g}$ and ${}^1T_{2g}$ and two spin-forbidden ${}^3T_{1g}$ and ${}^3T_{2g}$ excited states. Three d-d transitions have been observed in the spectra of each Pt(IV), Ir(III) and Rh(III) complexes. Two of these are spin-allowed bands involving transitions ${}^1A_{1g} \longrightarrow {}^1T_{1g}$ and ${}^1A_{1g} \longrightarrow {}^1T_{2g}$ and the third one (a very broad spin-prohibited band) is due to ${}^1A_{1g} \longrightarrow {}^3T_{1g}$. These three bands obtained in the case of our complexes are given in Table-5. By using the descent-in-symmetry method, the following three equations may be given corresponding to these three transitions.

Table - 5 Electronic spectral data (cm^{-1}) of platinum(IV), iridium(III) and rhodium(III) complexes

S. No.	Complexes	$^1A_{1g} \rightarrow {}^3T_{1g}$ (cm^{-1})	$^1A_{1g} \rightarrow {}^1T_{1g}$ (cm^{-1})	$^1A_{1g} \rightarrow {}^1T_{2g}$ (cm^{-1})	10Dq (cm^{-1})	B (cm^{-1})	β	C (cm^{-1})	C/B	L.F.S.E. Kcals/mole
1.	[Pt(Phth.)$_4$(dispy)]	19000	27000	35250	31000	515.6	0.72	4000	7.76	35.42
2.	[Pt(Phth)$_4$(Phen)]	19000	27000	35250	31000	515.6	0.72	4000	7.76	35.42
3.	[Ir(Phth)$_3$(dipy)H$_2$O]	18000	23500	29500	26250	375.0	0.57	2750	7.33	29.99
4.	[Ir(Phth)$_3$(Phen)H$_2$O]	18000	23500	29500	26250	375.0	0.57	2750	7.33	29.99
5.	[Rh(Phth)$_3$(dipy)H$_2$O]	15000	19500	26250	21750	421.8	0.58	2250	5.33	24.85
6.	[Rh(Phth)$_3$(Phen)H$_2$O]	15000	19500	26250	21750	421.8	0.58	2250	5.33	24.85

$$10\ Dq - C = ({}^{1}A_{1g} \longrightarrow {}^{1}T_{1g})\ \Delta E$$

$$10\ Dq + 16B - C = ({}^{1}A_{1g} \longrightarrow {}^{1}T_{2g})\ \Delta E$$

$$10\ Dq - 3C = ({}^{1}A_{1g} \longrightarrow {}^{3}T_{1g})\ \Delta E$$

The values of ligand field stabilization and Racah parameters B and C and of nephelauxetic ratio β are also listed in Table-5. In addition to the d-d transitions, the platinum(IV) and iridium(III) complexes gave two charge transfer bands. In the case of Pt(IV) complexes these bands were obtained at 39000 and 50000 cm^{-1}, while in the case of Ir(III) complexes at 37500 and 45000 cm^{-1} whereas only one charge transfer band at 45000 cm^{-1} has been observed in the spectra of Rh(III) complexes. These have been assigned as ligand to metal charge transfer bands, since empty ligand orbitals are expected to be at energies too high to participate to any extent in bonding. The value of ligand field splitting energy and hence the stability of these complexes decrease in the following order: Pt(IV) > Ir(III) > Rh(III). This stability order is in agreement with the spectrochemical series of the metal ions.

Infra-red Studies :

Phthalimide , which is a common constituent of all the complexes has two interesting (NH and CO stretching) frequency regions. The I.R. spectra can not make a sharp distinction whether coordination is through nitrogen or oxygen of the carbonyl group because any change in the imide nitrogen which is directly linked to the carbonyl group, will alter the molecules environment and hence the frequency of the later even if it is not coordinated [253]. However on the basis of lewis-acid concept it may be established that the negatively charged phthalimide nitrogen will have better possibilities of being coordinated than the oxygen [254]. Secondly, there will be steric hindrance if coordination is through nitrogen. There is a shifting of carbonyl stretching frequency from 1750 cm^{-1} to 1700 cm^{-1} in the spectra of complexes. This negative shift may be due to the mass effect [255]. Secondly the filled orbital of phthalimide nitrogen is made available by quasi-aromatic delocalization which would give a lower bond order to C=O and thus a lower frequency. The stretching at 1480 cm^{-1} due to C-N in the spectrum of complexes, indicating thereby the coordination of phthalimide to the metal ion [256].

In the spectra of dipyridyl or o-phenanthroline complexes, two bands of the free ligand at about 740 cm^{-1} and 995 cm^{-1} have been suggested of most usefully diagnostic in the coordination with the metal ion. These bands shifts to higher side in complexes [257]. In our case the former shifted to 775 cm^{-1} in the spectra of Rh(III) and Ir(III) complexes and 785 cm^{-1} in the spectra of Pd(II), Pt(II) and Pt(IV) complexes. The second band observed at 900 cm^{-1} was shifted to

920 cm^{-1} in the spectra of Rh(III) and Ir(III) complexes while this band was observed at 940 cm^{-1} in the spectra of complexes of other metal ions. All these bands gained intensity in the spectra of complexes which was also a characteristic feature of dipyridyl and phenanthroline complexes [257,258].

The two extra bands obtained at around 860 cm^{-1} and 650 cm^{-1} in the spectra of complexes of Rh(III) and Ir(III) may be assigned to the coordinated water molecule [259]. A band due to this reason was also obtained at around 3300 cm^{-1}. In the far I.R. region the bands appearing around 450 cm^{-1} are tentatively assigned to metal nitrogen vibrations [260].

SECTION C

CHAPTER—I : Thermodynamics for the Formation of Cysteinate Complexes of Rhodium (III) and Osmium (VIII)

A large number of references are available on the thermochemistry of transition metal ion complexes A number of reviews [260-263] dealing with the thermochemistry of transition metal ions complexes have also appeared in the literature. Significant work has been done on the metal chelates of aminoacids. Majority of the data available refers to the complexes of metal ions of first transition series and to a limited extent of second and third transition series. A very little has been done on the thermochemistry of amino-acid chelates of platinum metal ions despite of their catalytic and biological interest. Most of the data is confined to the halo-complexes of Rh, Pd and Pt ions. A few attempts have also been made on their complexes with organic acids.

Platinum metal ions are known to have a tendency to form π-bonded complexes with multiple bonded systems but a very little thermochemical information regarding such systems is available. Bott and Poë [264] have measured, by spectrophotometric methods, the equilibrium constant for the stepwise replacement of chloride ions by bromide ions in the complex trans-$[Rh(en)_2Cl_2]^+$. Equilibrium constants for both the steps were found to be the same at 85 and 95°C indicating a zero enthalpy-change. They concluded from the values of ΔG_1 and ΔG_2 that Rh(III) is a soft acceptor but it comes close to the border line between hard and soft acceptors.

Overall free energy change for Rh(III)-systems (-0.3 Kcals/mole) is less negative than that for the similar Pt(IV) systems [265] ($\overset{-}{\Delta}G_2$ = 2.3 Kcals/mole at 20°C), showing that the Rh(III) ions in these complexes is less 'soft, than Pt(IV) ions.

Mathur et al. [266] in their thermodynamical studies have shown that cysteine in Fe(II)-cysteinate chelate coordinates through the sulphydril and carboxyl groups while in nickel(II)-cysteine chelate, through amino and sulphydril groups [267]. Sharma and De [268] in their thermodynamical studies on the cysteinate chelates of lanthanide(III) ions indicate the coordination through amino and carboxyl groups. They have also carried out thermodynamical studies on the formation of mixed ligand complexes of bivalent transition metal ions using cysteine as a secondary ligand [269]. Nothing has been done on the cysteinate complexes of platinum metal ions and an attempt is being made to fill this gap by carrying out the thermodynamical studies on Rh(III) and Os(VIII)-cysteine systems. A comparative study with α-alanine and 2-mercaptopropanoic acid have also been carried out which help in deciding the coordinating sites of cysteine in these systems. The complexes could also be isolated in the solid form and characterised on the basis of chemical analysis, magnetic and conductance measurements, I.R., electronic and thermal studies.

EXPERIMENTAL

Reagents and Solutions :

Osmium tetraoxide and rhodium(III) chloride were purchased from Jhonson Mathey Ltd. (London) and cysteine-hydrochloride was obtained from Koch-Light company, England. All other chemicals were of A.R.(B.D.H.) grade. The solutions of Os(VIII) and Rh(III) prepared in double distilled water were standardised by gravimetry [270] as $[Os(NH_2\text{-}CS\text{-}NH_2)_2][Cr(SCN)_6]$ complex and by spectrophotometric [271] method respectively. The solution of cysteine hydrochloride was prepared in doubly distilled water without further purification. Carbondioxide free sodium hydroxide (A.R. grade) solution was used for pH-metric titrations which were carried out in a double walled glass titration vessel provided with inlet and outlet tubes circulating water at constant temperature (variations ± 0.10 °C) from a thermostate. After each addition of alkali titrant, the solution was well stirred with magnetic stirrer and allowed to stand for attainment of equilibrium before noting the pH of the solution.

Physical Measurements :

Expanded scale (solid-state) pH-823 ECIL made pH-meter was used for pH-metric titrations. All other physical instruments were the same as reported earlier (Chapter-I, Section A).

Composition and Stability Constants :

The thermodynamic stability constants of Os(VIII) and Rh(III) complexes with cysteine, α-alanine and 2-mercaptopropanoic acid were determined potentiometrically following the Bjerrum-Calvin titration techniques as adopted by Irving and Rossotti [272]. Thus the formation curves were obtained from the values of $\bar{n}$ and pL which were calculated from the following expressions.

$$pL = -\log \left[\frac{2[C_A] + [HClO_4] - [NaOH] - [H^+] + [OH^-]}{\frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1K_2}} \right]$$

$$\text{and} \quad \bar{n} = \frac{C_A - [A]\left[\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1\right]}{C_M}$$

where the terms have their usual meaning. Values of $\bar{n}$ then plotted against pL. The values of pL at $\bar{n} = 0.5$, 1.5 and 2.5 were taken as $\log K_1$, $\log K_2$ and $\log K_3$ respectively. The determinations were carried out at four different molar concentrations of $NaClO_4$ (1.0, 0.50, 0.25 and 0.10) and from these values an extrapolation to zero ionic strength was possible.

The enthalpy change ΔH, the free energy change ΔF and the entropy change ΔS for the formation of these complexes were calculated from the temperature coefficient of the equilibrium constants using the following equations.

$$\Delta F = -RT \ln K$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

and $$\Delta F = \Delta H - T\Delta S$$

pK-values of the ligands :

pK values at four different ionic strengths and three different temperatures were determined by pH-metric titrations following the method of Irving and Rossotti [272]. The values of $\bar{n}_H$ at different pH were calculated from the equation

$$\bar{n}_H = \left[Y T_{CL}^{o} + \frac{(V'-V'')(N^o+E^o)}{V^o+V'} \right] / T_{CL}^{o}$$

A graph was plotted in $\bar{n}_H$ versus pH and the values of pH corresponding to the values of $\bar{n}_H = 0.5$, 1.5 and 2.5 were taken as the pK values of the ligands. Since the separation of pK_2 and pK_3 in the case of cysteine was less than 2.9 units. Hence the values of pH were plotted against the equivalent of base (b') added [273]. The values of b 'were calculated from the formula

$$b' = \frac{b - a + H^+ - OH^-}{C}$$

where a, b, C, H^+ and OH^- are the molar concentrations of $HClO_4$, base, ligand, hydrogen ions and hydroxyl ions respectively. The pH values corresponding the values of b' 1.5 and 2.5 were taken as pK_2 and pK_3.

The following sets of titrations were performed against sodium hydroxide (0.05 M) at 25 ± 0.10, 35 ± 0.10 and 45 ± 0.10°C and at four different concentrations of $NaClO_4$ i.e. 1.0, 0.50, 0.25 and 0.10 M.

(a) 25.0 ml $HClO_4$(0.002 M)

(b) 25.0 ml $HClO_4$(0.002 M) + 5.0 ml Cysteine (0.01 M).

The total volume in each case was made upto 50 ml and the required ionic concentration was made with $NaClO_4$. The pK values thus calculated are given in Table-1.

Table - 1 pK values of cysteine at different temperatures and ionic concentrations

Temp.°C	Molar Conc.of $NaClO_4$	pK_1	pK_2	pK_3
25	1.00	1.963	8.675	10.35
	0.50	2.500	8.770	10.37
	0.25	2.535	8.840	10.40
	0.10	2.960	8.950	10.75
35	1.00	1.533	8.225	9.850
	0.50	1.980	8.250	9.855
	0.25	2.140	8.335	10.025
	0.10	2.356	8.350	10.060
45	1.00	1.530	8.100	9.725
	0.50	1.879	8.155	9.750
	0.25	1.980	8.254	9.950
	0.10	2.128	8.260	10.00

Stability Constants of the Metal Complexes :

The titrations of cysteine with and without metal ions were performed against standard NaOH. The data is given in the following tables. The accuracy of pK values is ± 0.02 units and the accuracy of logK values is ± 0.04 log units, therefore the precision of ΔH and ΔS are ± 0.56 KCal $mole^{-1}$ and ± 2.4 Cal $mole^{-1}deg^{-1}$. The calculations were made on DEC 2050 Digital Computer. Similarly the titrations were carried out at 35 and 45°C and in 1.0, 0.50, 0.25 and 0.10 M $NaClO_4$. The shapes of the titration curves were the same as given in Fig. 1. The formation curves obtained at these two other temperatures and four different ionic concentrations are given in Figs. 3 and 4 respectively. Studies were also made at 0.02 M and 0.015 M of cysteine and metal ions which gave almost the same values of $\bar{n}$ and pL as given in Table-4.

Table - 2 Titration of cysteine in absence of metal ion, with NaOH(0.05 M) at 25°C and 0.50 M $NaClO_4$.
10 ml cysteine (0.01 M) + 4.0 ml $HClO_4$(0.002 M)
Total volume was made-upto 25.0 ml with distilled water

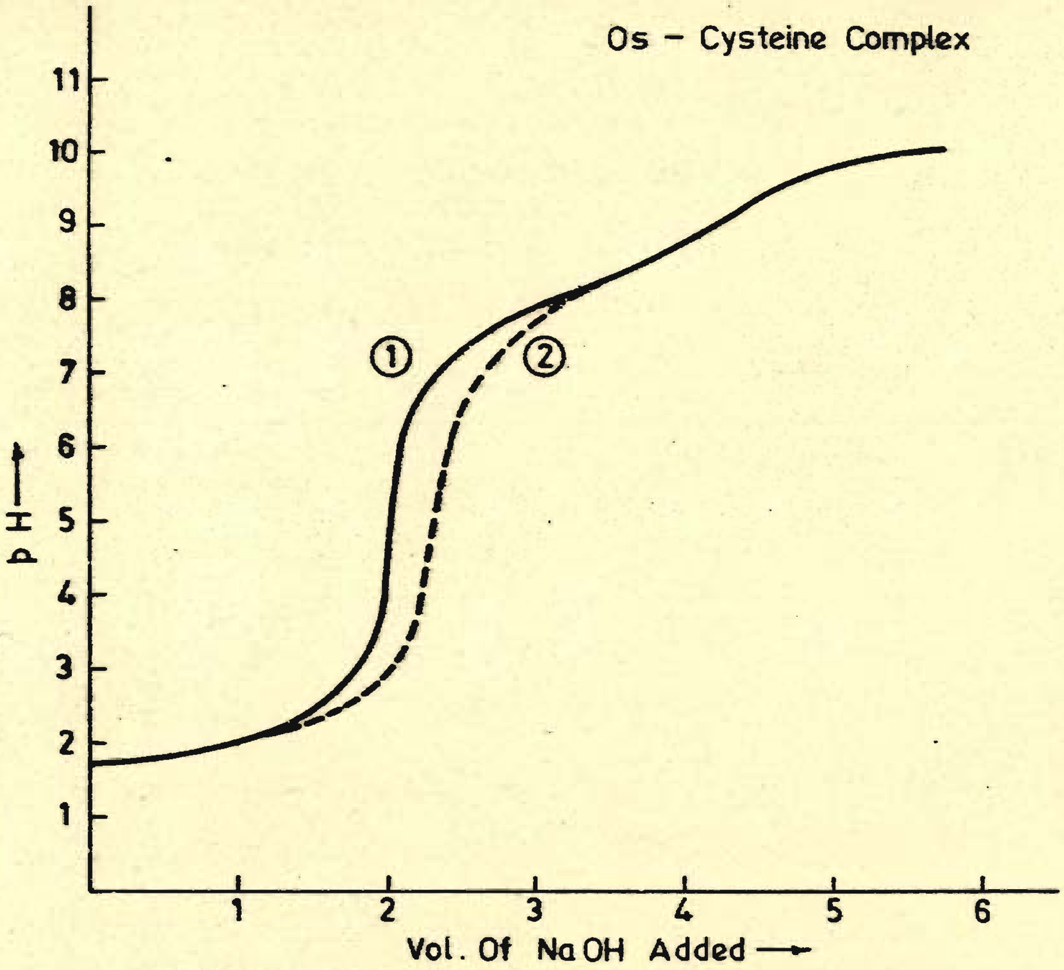
Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	1.70	3.20	7.86
0.20	1.80	3.40	8.10
0.40	1.80	3.60	8.40
0.60	1.85	3.80	8.50
0.80	1.90	4.00	8.70
1.00	2.00	4.20	9.00
1.20	2.10	4.40	9.20
1.40	2.40	4.60	9.30
1.60	2.50	4.80	9.60
1.80	2.70	5.00	9.70
2.00	3.90	5.50	9.80
2.20	6.80	6.00	10.00
2.40	7.10	6.50	10.40
2.60	7.40	7.00	10.60
2.80	7.60	8.00	10.90
3.00	7.80	9.00	11.00

(Fig. 1, Curve - 1).

Table - 3 Titration of cysteine in presence of Os(VIII) with NaOH (0.05 M) at 25°C and 0.50 M $NaClO_4$.
10 ml. cysteine(0.01 M) + 4 ml. $HClO_4$(0.002 M) + 2 ml. of Os(VIII) ions (0.01 M).
Total volume was made - upto 25.0 ml.

Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	1.66	1.70	2.40	4.00	8.70
0.10	1.68	1.80	2.50	4.20	9.00
0.20	1.70	2.00	2.90	4.40	9.20
0.30	1.70				
0.40	1.80	2.20	3.90	4.60	9.30
0.50	1.76				
0.60	1.80	2.40	5.60	4.80	9.60
0.70	1.84	2.60	7.00	5.00	9.70
0.80	1.90	2.80	9.30	5.50	9.80
0.90	1.94			6.00	10.00
1.00	2.00	3.00	7.60	6.50	10.40
1.20	2.10	3.20	7.80	7.00	10.60
1.40	2.24	3.40	8.06	8.00	10.90
1.50	2.30	3.60	8.34	9.00	11.00
1.60	2.40	3.80	8.54	10.00	11.14

(Fig. 1, Curve - 2)



Curve 1= In Absence of Metal ion (See Table-2)
2= In Presence of Metal ion (See Table-3)

Fig. 1

Table - 4 Calculation table for the formation curve of Os(VIII) - Cysteine complex at 25°C, and 0.50 M $NaClO_4$

pH	$\bar{n}$	pL
2.10	0.225	9.606
2.20	0.375	9.433
2.30	0.500	9.200
2.40	0.600	9.093
2.50	0.625	8.923

(Fig. 2)

The formation curves obtained at 25°C and 1.0, 0.25 and 0.10 M $NaClO_4$ are also given in Fig. 2.

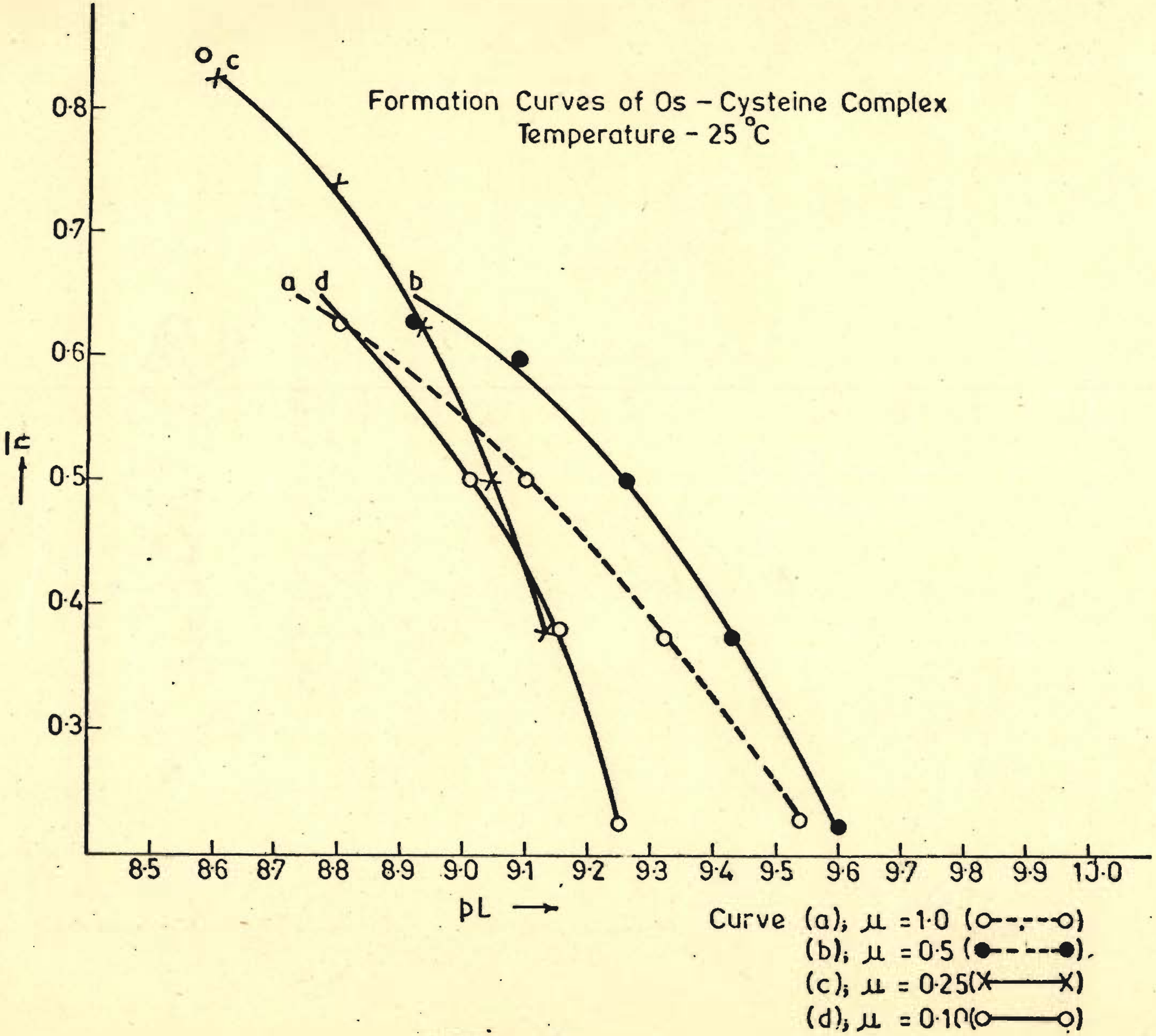

Formation Curves of Os – Cysteine Complex
Temperature – 25 °C
$\bar{n}$ →
0·8
0·7
0·6
0·5
0·4
0·3
a
d
b
c
8·5
8·6
8·7
8·8
8·9
9·0
9·1
9·2
9·3
9·4
9·5
9·6
9·7
9·8
9·9
10·0
pL →
Curve (a); μ = 1·0 (o--·--o)
(b); μ = 0·5 (●-----●)
(c); μ = 0·25 (X——X)
(d); μ = 0·10 (o——o)

Fig. 2

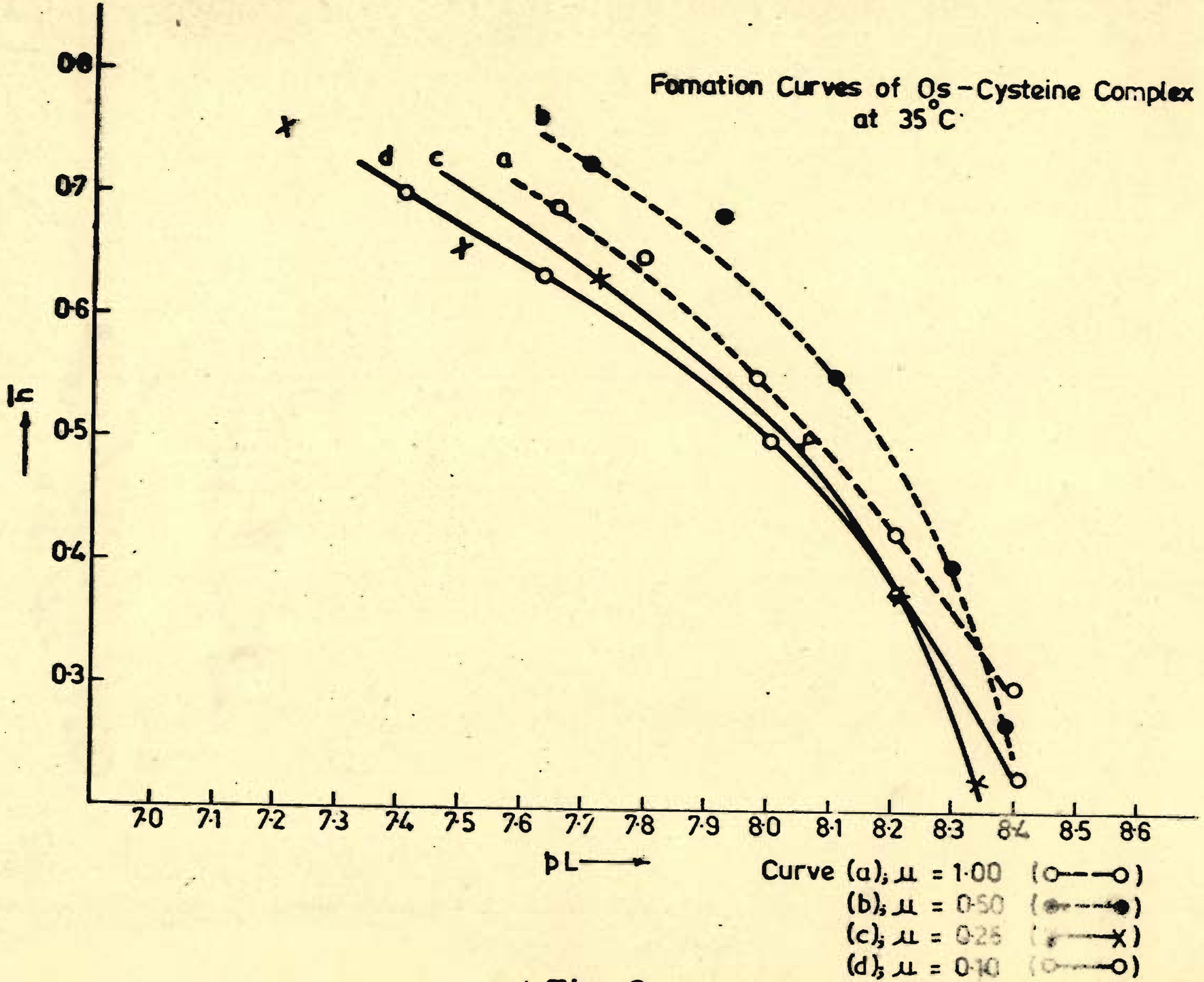

Fomation Curves of Os-Cysteine Complex
at 35°C
0·8
0·7
0·6
0·5
0·4
0·3
n̄
7·0
7·1
7·2
7·3
7·4
7·5
7·6
7·7
7·8
7·9
8·0
8·1
8·2
8·3
8·4
8·5
8·6
pL
a
b
c
d
Curve (a); μ = 1·00 (o----o)
(b); μ = 0·50 (●----●)
(c); μ = 0·25 (x——x)
(d); μ = 0·10 (o——o)

Fig. 3

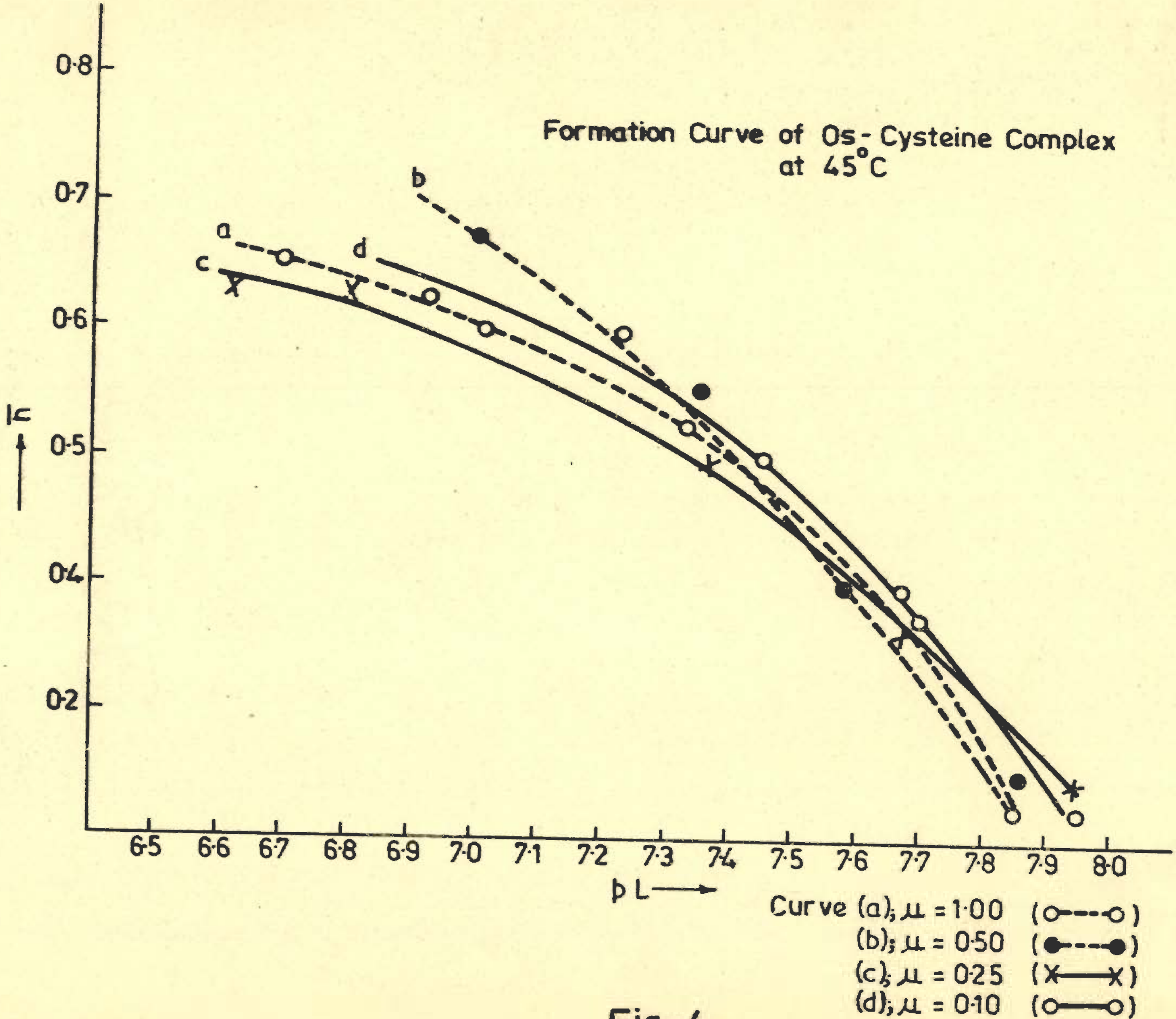

Formation Curve of Os - Cysteine Complex
at 45°C
0·8
0·7
0·6
0·5
0·4
0·2
$\bar{n}$ →
6·5
6·6
6·7
6·8
6·9
7·0
7·1
7·2
7·3
7·4
7·5
7·6
7·7
7·8
7·9
8·0
þ L →
a
b
c
d
Curve (a); μ = 1·00 (○----○)
(b); μ = 0·50 (●----●)
(c); μ = 0·25 (X——X)
(d); μ = 0·10 (○——○)

Fig. 4

Table 5 - Titration of cysteine in absence of Rh(III) ions at 35°C and 0.10 M $NaClO_4$ with NaOH (0.05 M)
10 ml. cysteine(0.01 M) + 4.0 ml. $HClO_4$(0.002 M).
Total volume was made-upto 25 ml. with distilled water.

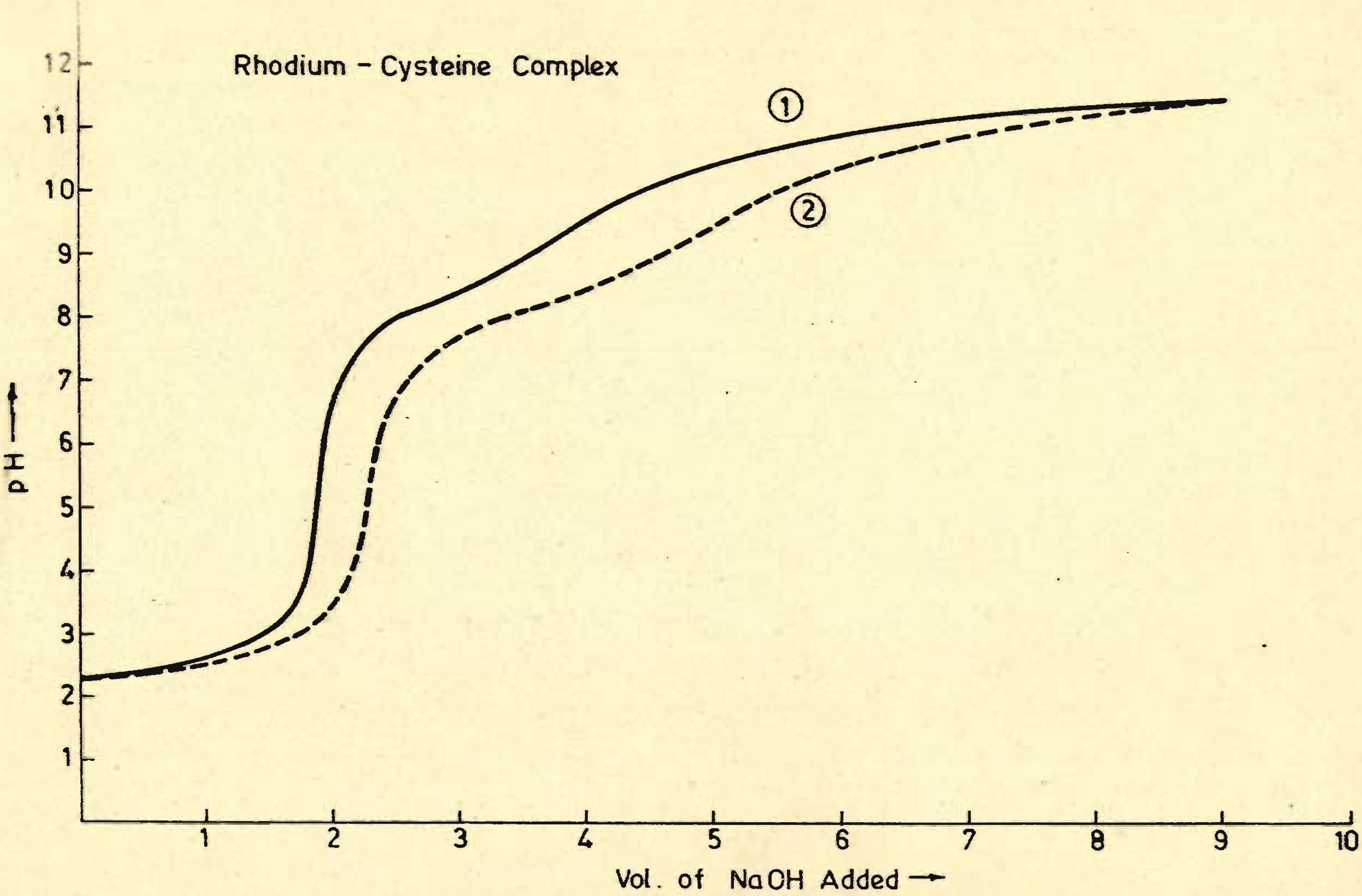
Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	2.30	3.60	9.00
0.20	2.36	3.80	9.26
0.40	2.42	4.00	9.54
0.60	2.48	4.20	9.78
0.80	2.56	4.40	10.00
1.00	2.68	4.60	10.08
1.20	2.80	4.80	10.24
1.40	2.96	5.00	10.34
1.60	3.20	5.20	10.48
1.80	3.70	5.40	10.58
2.00	6.70	5.60	10.66
2.20	7.40	5.80	10.76
2.40	7.86	6.00	10.84
2.60	8.00	6.50	11.02
2.80	8.16	7.00	11.14
3.00	8.36	7.50	11.24
3.20	8.56	8.00	11.34
3.40	8.78	9.00	11.42

(Fig. 5, Curve - 1)

Table - 6 Titration of cysteine in presence of Rh(III) ions at 35°C and 0.10 M $NaClO_4$ with NaOH(0.05 M)
10 ml. cysteine (0.01 M) + 4.0 ml $HClO_4$(0.002)+ 2.0 ml. Rh(III) ions(0.01 M).
Total volume was made-up to 25 ml.

Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	2.24	3.60	8.08
0.20	2.28	3.80	8.22
0.40	2.34	4.00	8.40
0.60	2.40	4.20	8.58
0.80	2.46	4.40	8.74
1.00	2.54	4.60	8.94
1.20	2.62	4.80	9.18
1.40	2.74	5.00	9.42
1.60	2.90	5.20	9.64
1.80	3.10	5.40	9.90
2.00	3.48	5.60	10.00
2.20	4.44	5.80	10.14
2.40	6.24	6.00	10.26
2.60	7.02	6.50	10.60
2.80	7.40	7.00	10.86
3.00	7.66	7.50	11.02
3.20	7.86	8.00	11.16
3.40	8.00	9.00	11.36

(Fig. 5, Curve - 2)



Curve 1= in Absence of Metal ion (See Table -5)
2= In Presence of Metal ion (See Table-6)

Fig. 5

Table - 7 Calculation table for the formation curve of Rh(III) - cysteine complex at 35°C and 0.10 M $NaClO_4$.

pH	$\bar{n}$	pL
2.50	0.385	8.3523
2.80	0.615	7.9107
3.00	0.750	7.6518
4.00	0.870	6.5235
5.00	1.000	5.5132
6.00	1.125	4.5196
6.50	1.250	4.0024
7.00	1.375	3.5344
7.50	1.625	3.05134
8.00	2.000	2.5780
8.50	2.490	2.1159
9.00	2.625	1.6302
9.50	2.750	1.4438

(Fig.6)

The formation curves obtained at 35°C and 1.0, 0.50 and 0.25 M $NaClO_4$ are also given in Fig. 6.

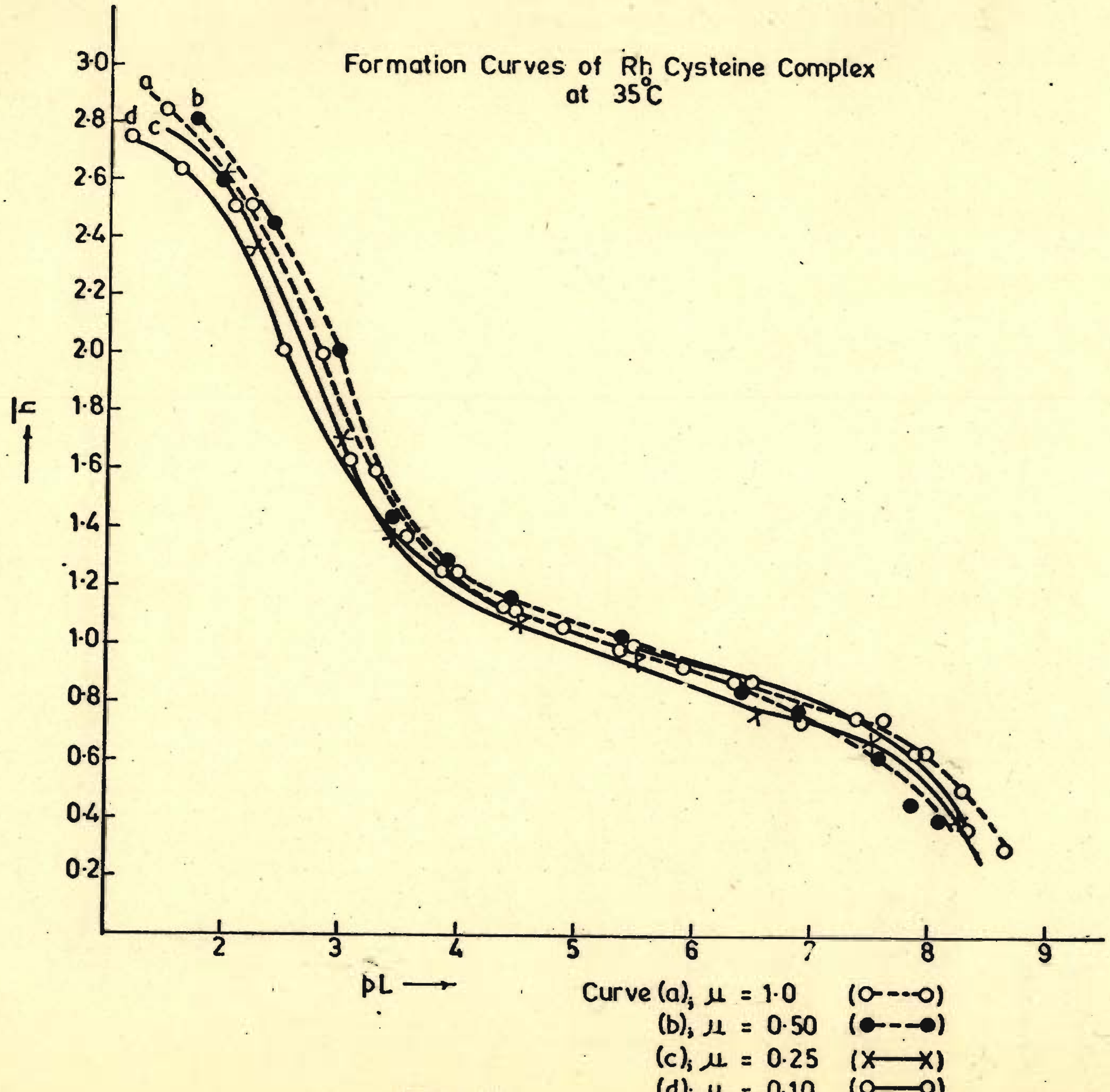

Formation Curves of Rh Cysteine Complex
at 35°C
$\bar{n}$
pL
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
2
3
4
5
6
7
8
9
a
b
c
d
Curve (a); μ = 1·0 (o---o)
(b); μ = 0·50 (●---●)
(c); μ = 0·25 (x—x)
(d); μ = 0·10 (o—o)

Fig. 6

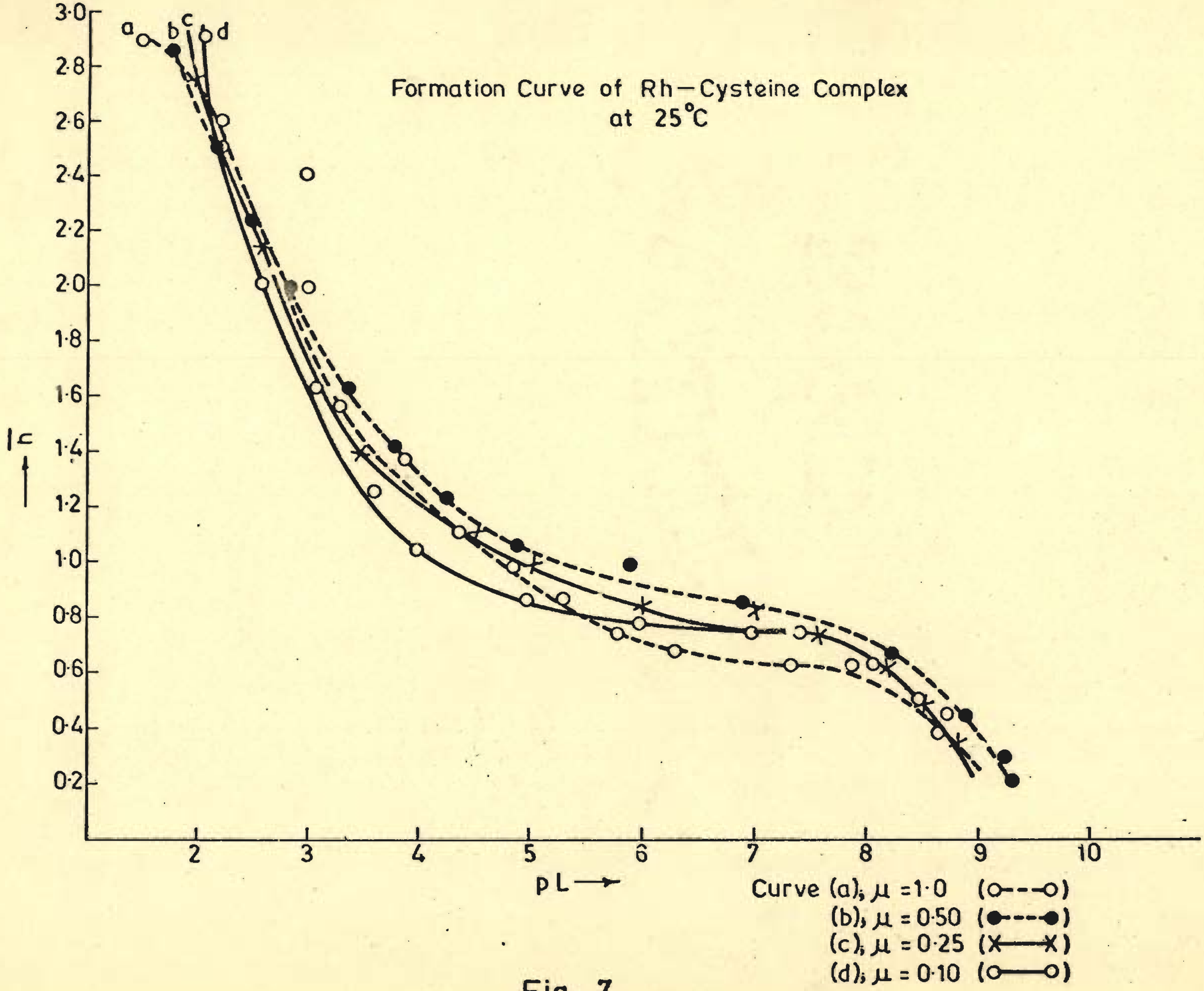

Formation Curve of Rh—Cysteine Complex
at 25°C
n̄
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
2
3
4
5
6
7
8
9
10
pL
a
b
c
d
Curve (a); μ = 1·0 (o---o)
(b); μ = 0·50 (●---●)
(c); μ = 0·25 (x—x)
(d); μ = 0·10 (o—o)

Fig. 7

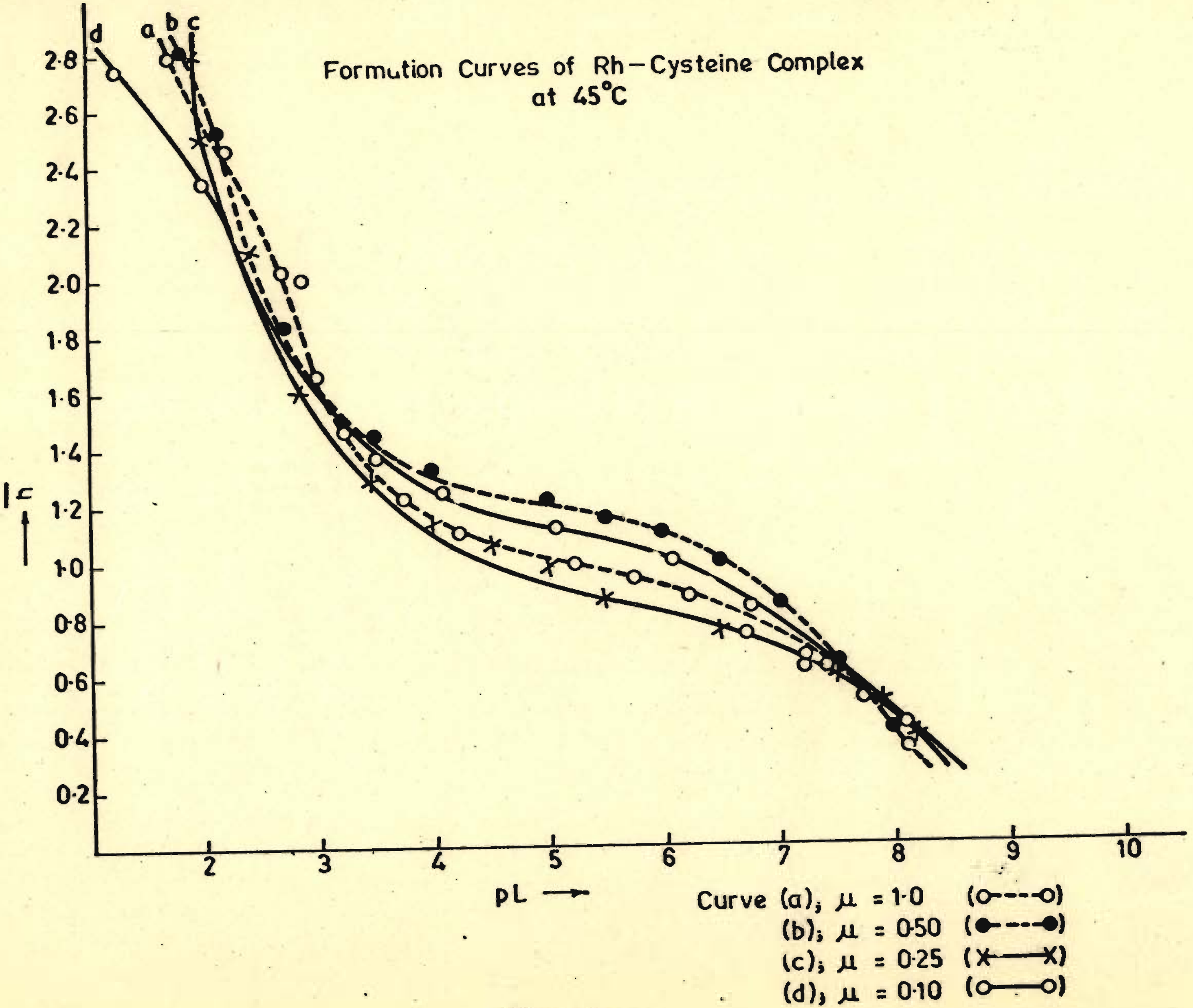

Formution Curves of Rh–Cysteine Complex
at 45°C
d
a
b
c
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
n̄ →
2
3
4
5
6
7
8
9
10
pL →
Curve (a); μ = 1·0 (o----o)
(b); μ = 0·50 (●----●)
(c); μ = 0·25 (x——x)
(d); μ = 0·10 (o——o)

Fig. 8

Similarly the titrations were carried out at 25 and 45°C and in 1.0, 0.50, 0.25 and 0.10 M $NaClO_4$. The shapes of the titration curves were the same as given in Fig. 5. The formation curves obtained at these two other temperatures and four different ionic concentrations are given in Figs. 7 and 8 respectively. Studies were also made at two other concentrations of ligand and metal ions, i.e. 0.02 and 0.15 M of cysteine and rhodium(III) ions which gave the same values of $\bar{n}$ and pL as given in Table - 7.

Such type of titrations were also carried out with α-alanine and 2-mercaptopropanoic acid. Two curves of these ligands, in absence and presence of Os(VIII) ions were found overlapping indicating thereby the absence of complex formation. However in the case of rhodium(III) ions, favourable results were obtained. In this case three sets of titrations were performed.

(I) $HClO_4$

(II) $HClO_4$ + Ligand

(III) $HClO_4$ + Ligand + Metal ions.

Rhodium(III)-α-Alanine System

Table - 8 Titration of perchloric acid with NaOH(0.05 M) at 25 °C and 1.0 M $NaClO_4$.5.0 ml $HClO_4$(0.01 M) diluted to 25 ml. with distilled water.

Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	2.56	0.80	9.76
0.10	2.58	0.90	10.00
0.20	2.64	1.00	10.20
0.30	2.76	1.10	10.28
0.40	3.00	1.20	10.34
0.50	3.50	1.30	10.46
0.60	5.48	1.40	10.60
0.70	9.28	1.50	10.80

(Fig. 9, Curve - 1)

Table - 9 Titration of α-alanine in absence of metal ion at 25°C and 1.0 M $NaClO_4$. 5.0 ml. $HClO_4$(0.01 M) + 5ml. α-alanine (0.01 M).
Total volume was made-upto 25 ml.

Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	2.56	1.20	9.22
0.10	2.58	1.30	9.40
0.20	2.66	1.40	9.50
0.30	2.78	1.50	9.58
0.40	3.00	1.60	9.60
0.50	3.48	1.80	9.76
0.60	5.20	2.00	9.92
0.70	7.88	2.20	10.06
0.80	8.44	2.40	10.18
0.90	8.76	2.60	10.36
1.00	9.00	2.80	10.42
1.10	9.14	3.00	10.52

(Fig. 9, Curve - 2)

Table - 10 Titration of α-alanine in presence of Rh(III) ions at 25°C and 1.0 M $NaClO_4$ 5.0 ml. $HClO_4$(0.01 M) + 5.0 ml. of α-alanine (0.01 M) + 1.0 ml. of Rh(III) ions (0.01 M).

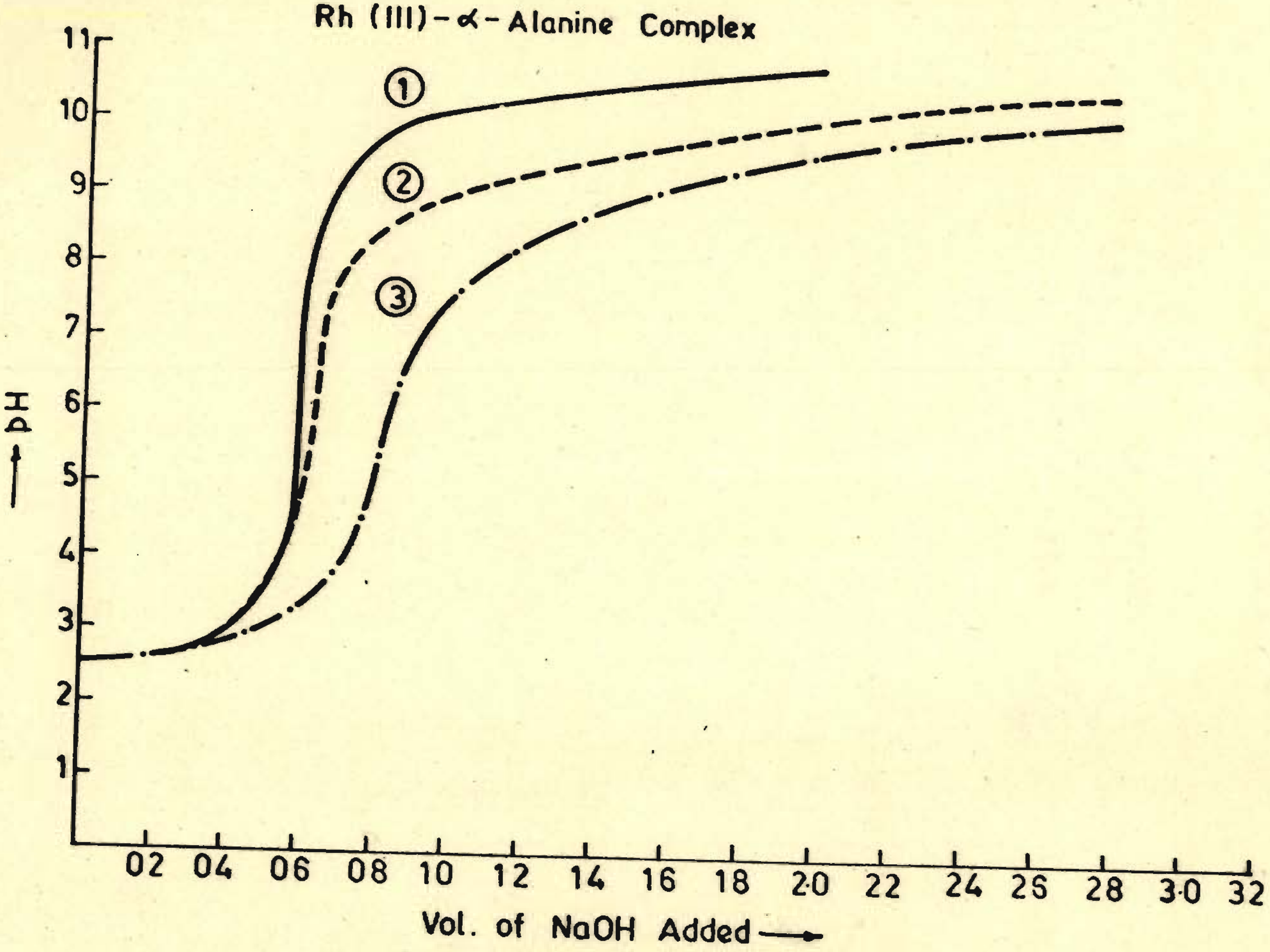
Total volume was made upto 25 ml.

Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	2.58	1.00	7.54
0.10	2.60	1.10	8.00
0.20	2.64	1.20	8.18
0.30	2.74	1.30	8.50
0.40	2.88	1.40	8.72
0.50	3.04	1.50	8.90
0.60	3.34	1.60	9.12
0.70	3.92	1.80	9.44
0.80	5.26	2.00	9.68
0.90	6.72	2.50	9.90
		2.80	10.30

(Fig. 9, Curve - 3)

Table - 11 pK-values of α-alanine at different temperatures.

Temperature °C	pK_1	pK_2
25	9.70	10.48
35	9.66	10.44
45	9.04	9.64



Curve 1 = $HClO_4$ (See Table – 8)
2 = $HClO_4$ + α – Alanine (See Table – 9)
3 = $HClO_4$ + α – Alanine + Rh (III) (See Table – 10)

Fig. 9

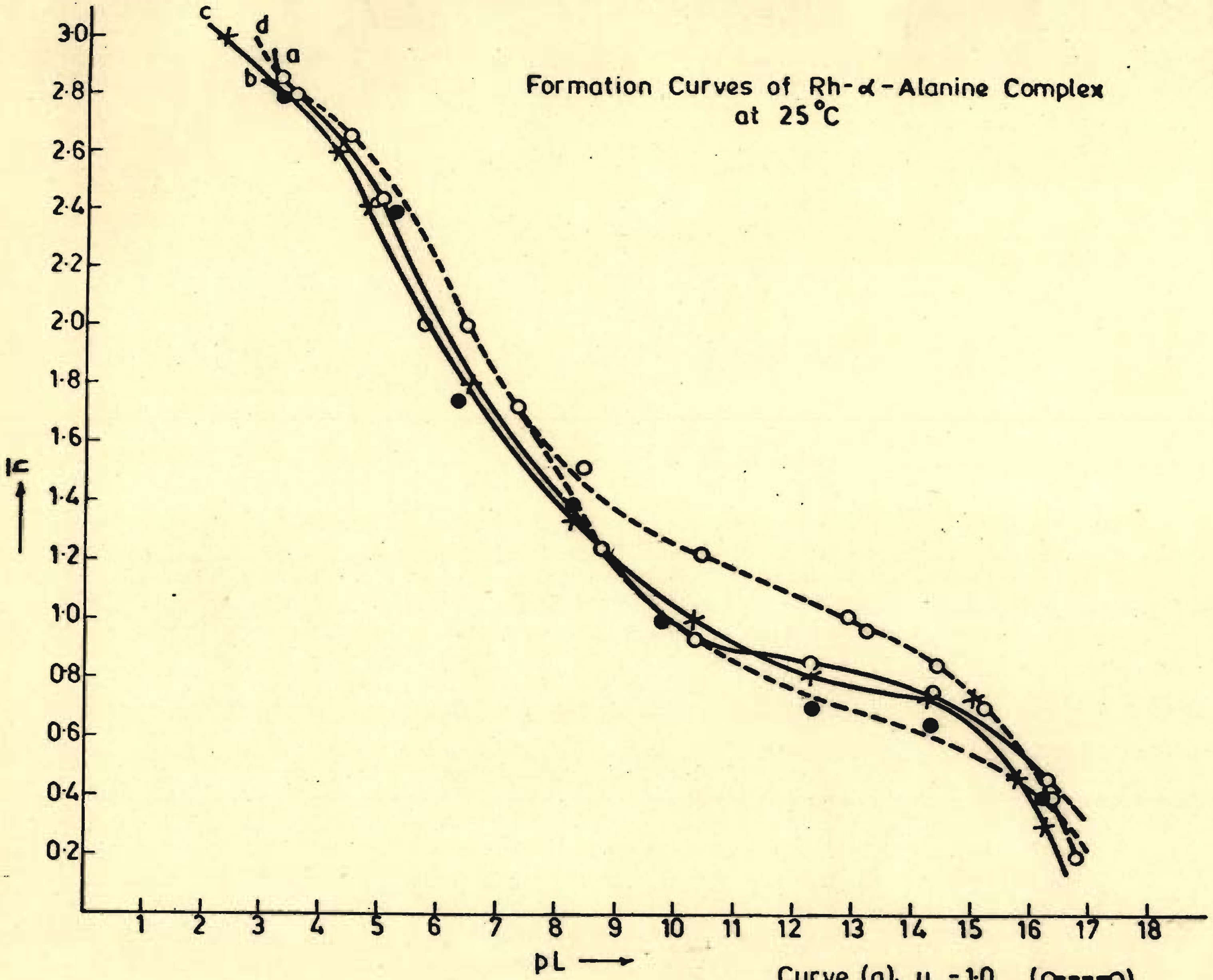
Table - 12 Calculation table for the formation curve of Rh(III) - α-alanine complex at 25°C and 1.0M $NaClO_4$.

pH	$\bar{n}$	pL
2.80	0.200	16.8132
3.00	0.400	16.4204
3.60	0.703	15.2108
4.00	0.855	14.4366
4.60	0.957	13.2400
5.00	1.058	12.9902
6.00	1.211	10.4483
7.00	1.462	8.4083
8.00	2.031	6.4763
9.00	2.652	4.5057
9.50	2.800	3.5236

(Fig. 10)

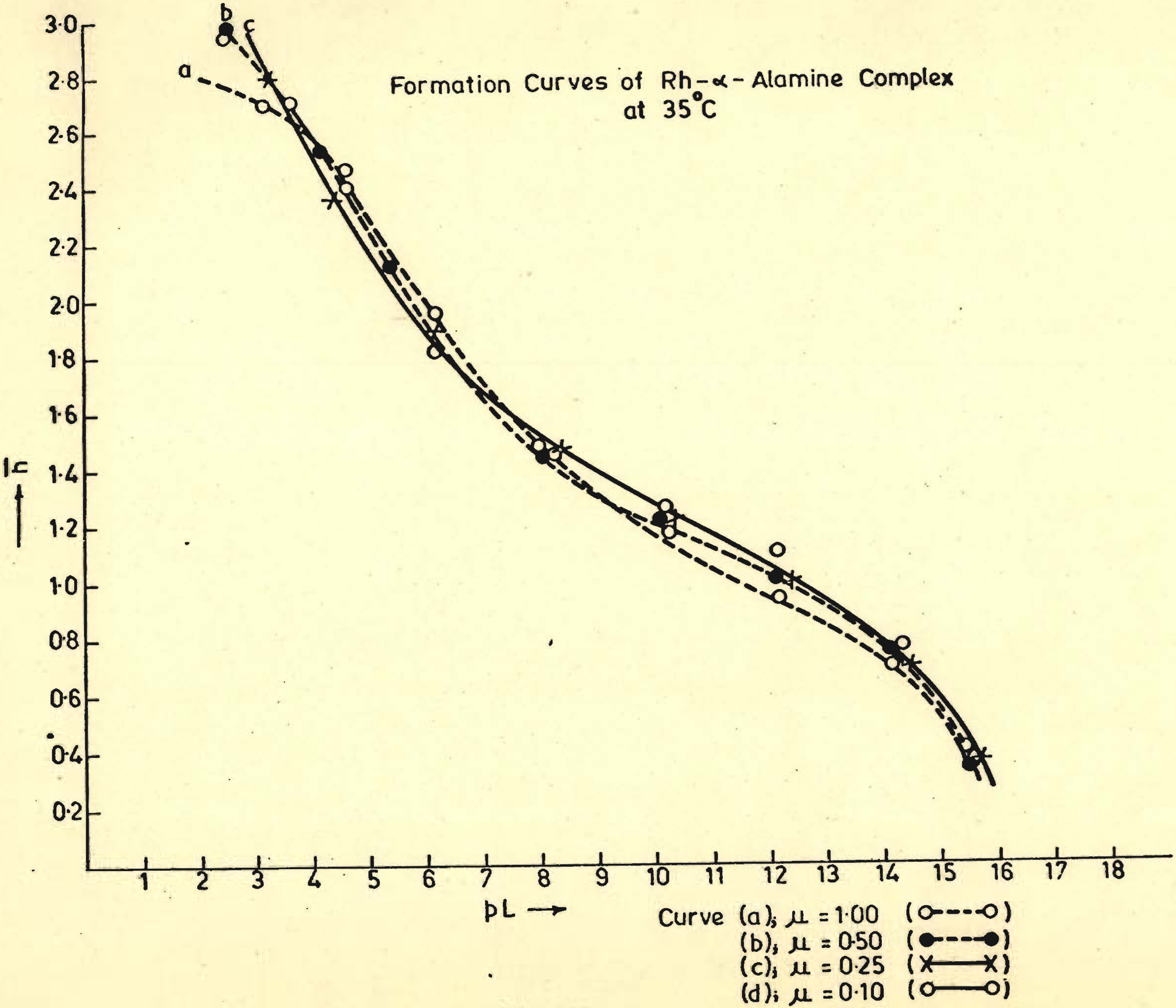
The formation curves obtained at 25°C and 0.50, 0.25 and 0.10 M $NaClO_4$ are also given in Fig. 10.

Similarly the titrations were carried out at 35 and 45°C and in 1.0, 0.50, 0.25 and 0.10 M $NaClO_4$. The shapes of the titration curves were the same as given in Fig. 9. The formation curves obtained at these two other temperatures and four different ionic concentrations are given in Figs. 11 and 12 respectively. Studies were also made at two other concentrations of ligand and metal ions, i.e. 0.02 M and 0.015 M of α-alanine and rhodium(III) ions which gave the same values of $\bar{n}$ and pL as given in Table - 12.



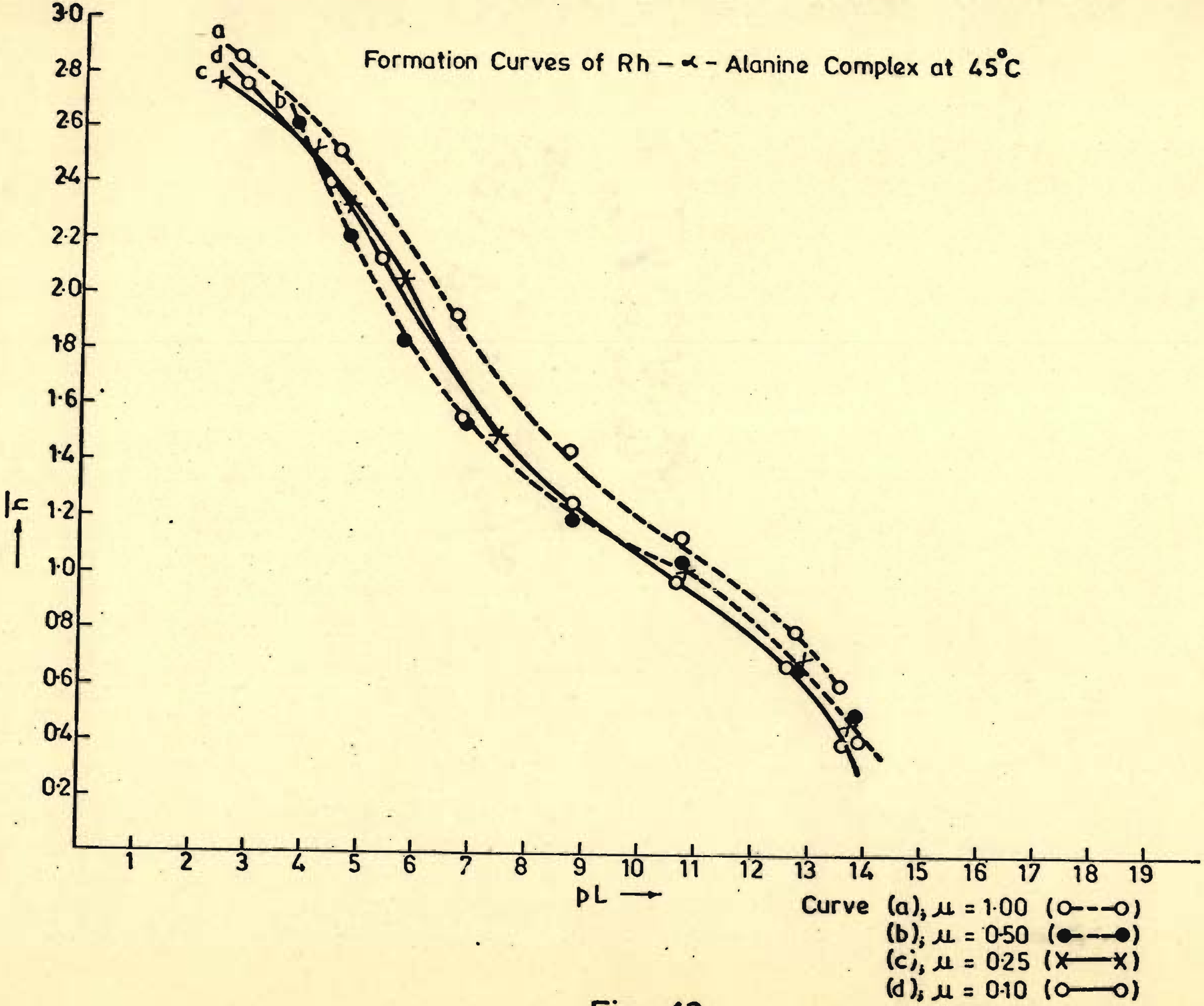
Curve (a); μ = 1·0 (○----○)
(b); μ = 0·50 (●----●)
(c); μ = 0·25 (×——×)
(d); μ = 0·10 (○——○)

Fig. 10



Formation Curves of Rh-α-Alamine Complex at 35°C

Fig. 11



Formation Curves of Rh – α – Alanine Complex at 45°C

Fig. 12

Rhodium(III)-2-Mercaptopropanoic Acid System

Table - 13 Titration of perchloric acid with NaOH(0.05 M) at 25^{o}C and 0.25 M $NaClO_4$. 10.0 ml. $HClO_4$(0.01 M). Total volume was made upto 25 ml.

Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	2.54	1.20	3.18
0.20	2.56	1.30	3.40
0.40	2.60	1.40	3.85
0.60	2.68	1.50	7.94
0.80	2.80	1.60	9.40
1.00	2.92	1.70	9.92
1.10	3.04	1.80	10.00

(Fig. 13, Curve - 1)

Table - 14 Titration of 2-mercaptopropanoic acid in absence of Rh(III) ions with NaOH (0.05 M) at 25^{o}C and 0.25 M $NaClO_4$. 10.0 ml.$HClO_4$(0.01 M) + 2.50 ml. ligand (0.01 M).
Total volume was made upto 25 ml.

Volume of NaOH added in ml	pH	Volume of NaOH added in ml.	pH
0.00	2.54	1.70	3.70
0.20	2.56	1.80	3.96
0.40	2.64	1.90	4.44
0.60	2.70	2.00	6.90
0.80	2.80	2.10	8.94
1.00	2.88	2.20	9.42
1.20	3.00	2.30	9.72
1.40	3.18	2.40	9.86
1.60	3.48	2.50	10.00

(Fig. 13, Curve - 2)

Table - 15 Titration of 2-mercaptopropanoic acid in presence of Rh(III) ions at 25°C and 0.25 M $NaClO_4$ with NaOH(0.05 M). 10.0 ml. $HClO_4$(0.01 M) + 2.50 ml. ligand (0.01 M) + 0.50 ml. Rh(III) (0.01 M).

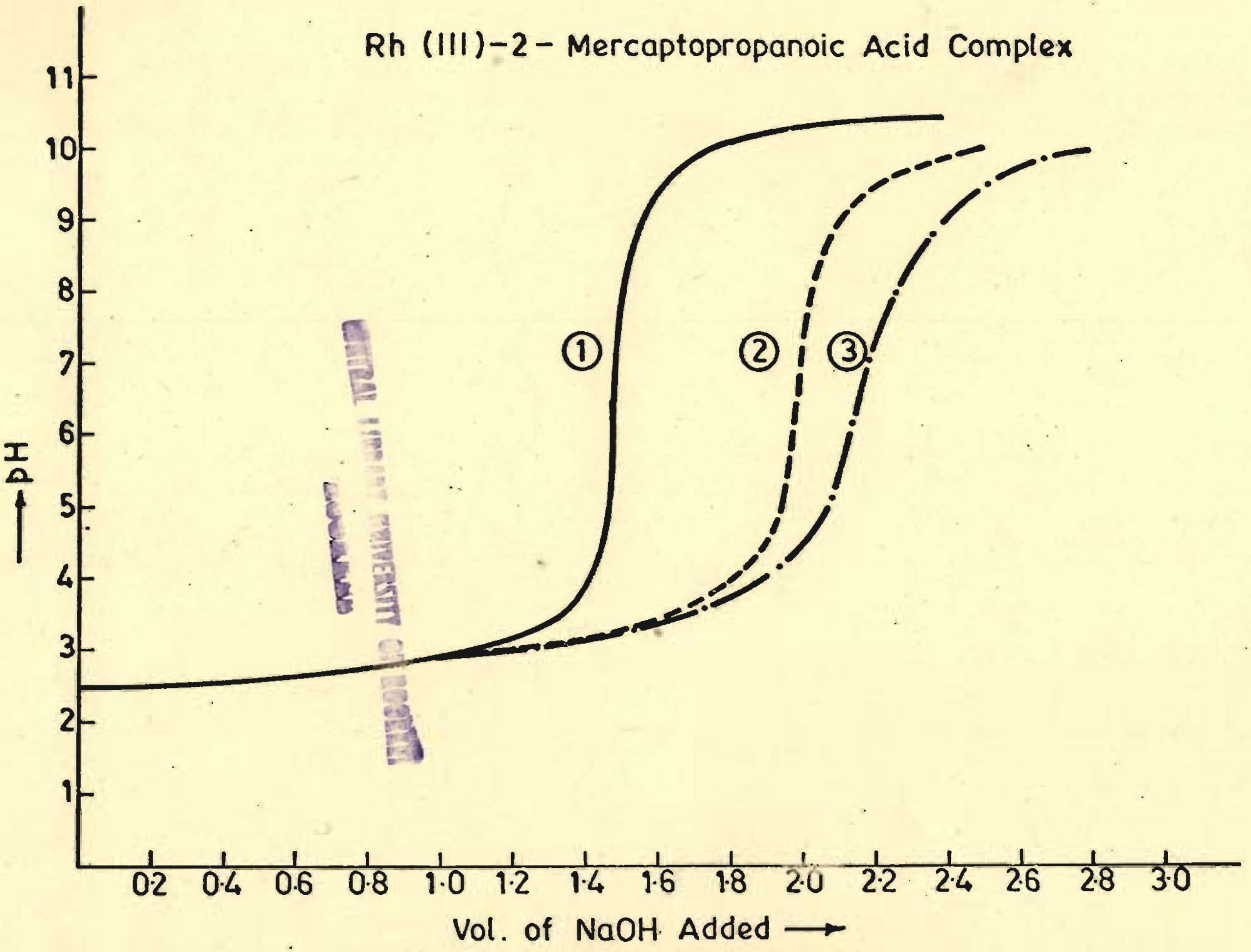
Total volume was made-upto 25 ml.

Volume of NaOH added in ml.	pH	Volume of NaOH added in ml.	pH
0.00	2.50	1.90	4.00
0.20	2.54	2.00	4.36
0.40	2.56	2.10	5.40
0.60	2.62	2.20	7.22
0.80	2.70	2.30	8.42
1.00	2.80	2.40	9.08
1.20	2.94	2.50	9.44
1.40	3.10	2.60	9.72
1.60	3.40	2.70	9.86
1.80	3.74	2.80	10.06

(Fig. 13, Curve - 3)

Table - 16 pK-values of 2-mercaptopropanoic acid at different temperatures.

Temperature °C	pK_1	pK_2
25	3.24	9.71
35	3.14	9.70
45	3.12	9.50



Curve 1 = $HClO_4$ (See Table-13)
2 = $HClO_4$ + Ligand (See Table-14)
3 = $HClO_4$ + Ligand + Metal ion (See Table-15)

Fig. 13

Table -17 Calculation table for the formation curve of Rh(III)-2 mercaptopropanoic acid complex at 25°C and 0.25 M $NaClO_4$.

pH	$\bar{n}$	pL
3.40	0.2801	9.3657
3.60	0.5340	9.3455
3.80	0.7750	9.1205
4.00	0.7914	8.8760
4.20	0.9109	8.6753
4.40	0.9629	8.4654
4.60	1.0790	8.2680
4.80	1.2745	8.0840
5.00	1.4000	7.8948
5.50	1.5295	7.4062
6.00	1.5945	6.9131
6.50	1.8057	6.4411
7.00	2.0619	5.9783
7.50	2.2771	5.5136
8.00	2.5472	5.0653
8.50	2.8266	4.6362
9.00	3.2280	4.2775

(Fig. 14)

The formation curves obtained at 25°C and 1.0, 0.5 and 0.10 M $NaClO_4$ are also given in Fig. 14.

Similarly the titrations were carried out at 35 and 45°C and in 1.0, 0.50, 0.25 and 0.10 M $NaClO_4$. The shapes of the titration curves were the same as given in Fig. 13. The formation curves obtained at these two other temperatures and four different ionic concentrations are given in Figs.15 and 16 respectively. Studies

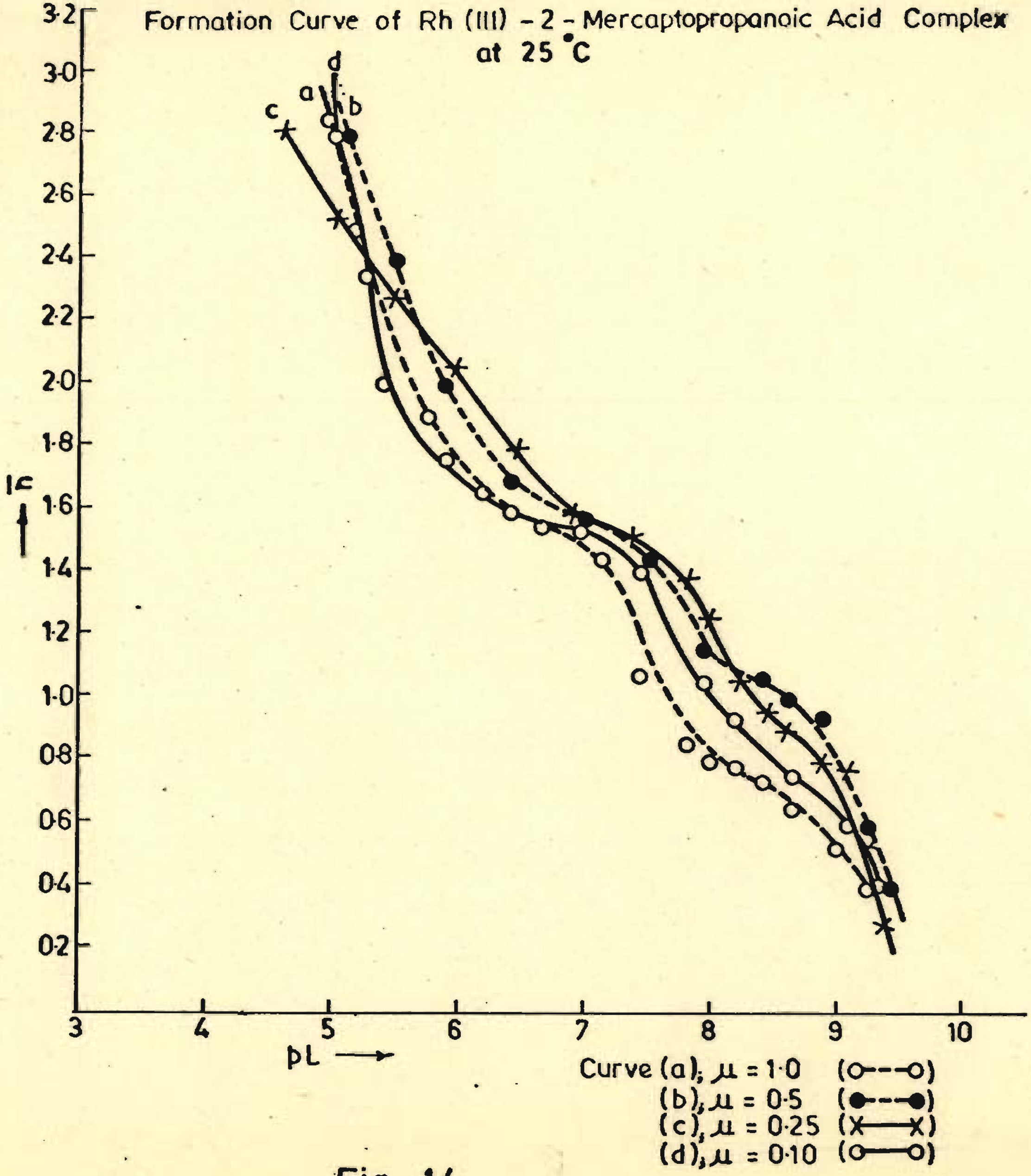

Formation Curve of Rh (III) - 2 - Mercaptopropanoic Acid Complex
at 25 °C
n̄
3·2
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
3
4
5
6
7
8
9
10
pL →
a
b
c
d
Curve (a), μ = 1·0 (o---o)
(b), μ = 0·5 (●---●)
(c), μ = 0·25 (x—x)
(d), μ = 0·10 (o—o)

Fig. 14

Formation Curves of Rh (III) – 2 – Mercaptopropanoic Acid Complex at 35°C

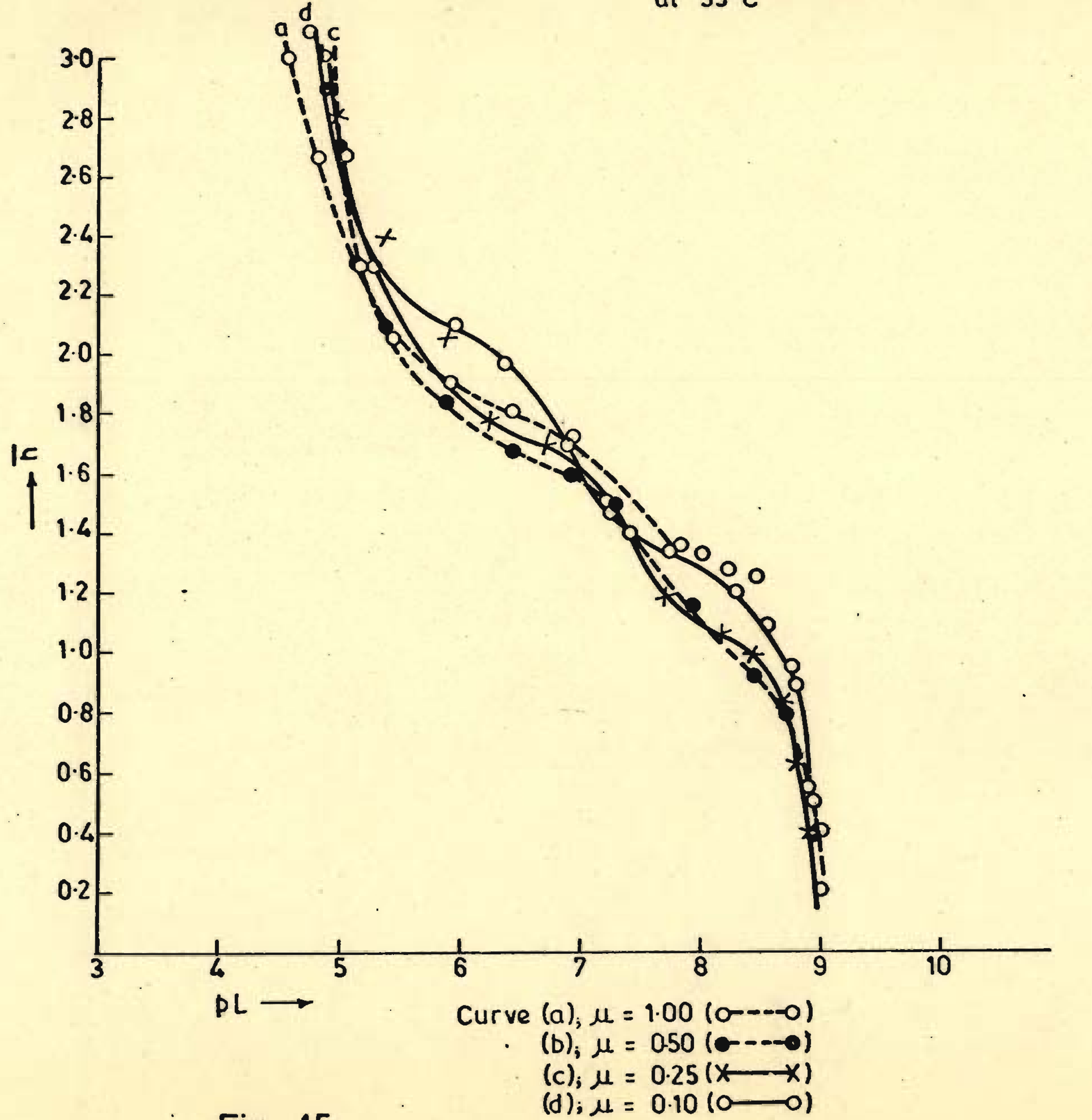


Fig. 15

Formation Curves of Rh (III) - 2 - Mercaptopropanoic Acid Complex at 45 °C

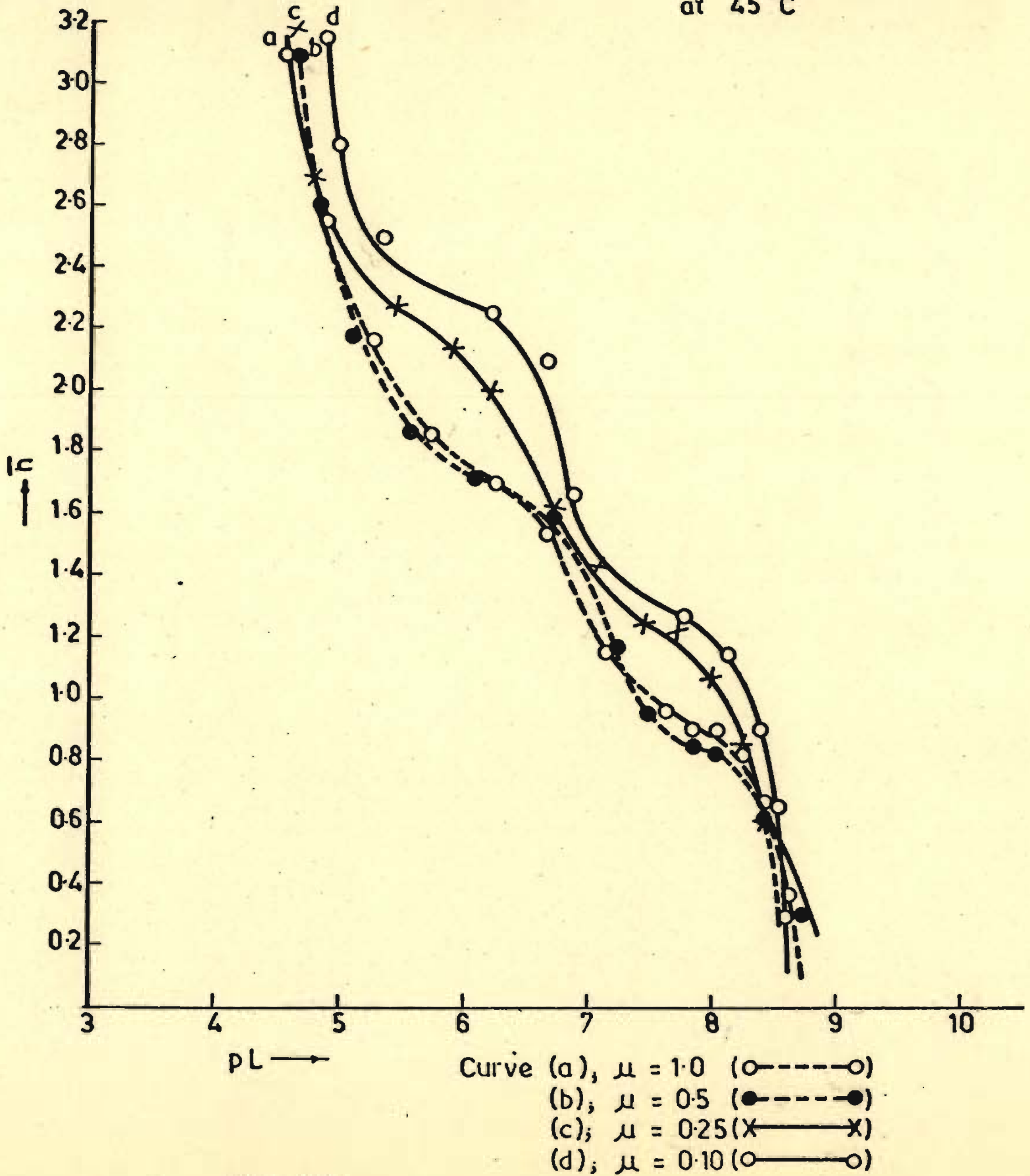


Fig. 16

were also made at two other concentrations of ligand and metal ions, i.e. 0.02 M and 0.015 M of 2-mercaptopropanoic acid and rhodium(III) ions which gave the same values of $\bar{n}$ and pL as given in Table - 17.

The values of thermodynamical stability constants and other thermodynamical parameters for all these complexes are given in the Tables 18-21.

Table - 18 Thermodynamical stability constants of cysteine complexes of Os(VIII) and Rh(III) ions at three different temperatures.

Metal ion system	Temperature ^{o}C	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta$
Os(VIII)	25	9.05	-	-	9.05
	35	8.00	-	-	8.00
	45	7.40	-	-	7.40
Rh(III)	25	8.60	3.35	2.25	14.20
	35	8.25	3.20	2.15	13.60
	45	7.90	3.10	2.05	13.05

Table - 19 Stepwise ΔF, ΔH (K cals mole^{-1}) and ΔS (K cals mole^{-1} degree^{-1}) values for Os(VIII) and Rh(III)-cysteine complexes.

Metal ion system	Temperature °C	Thermodynamical paramter	I	II	III
Os(VIII)	25	ΔF	-12.341	-	-
	35	ΔF	-11.275	-	-
	45	ΔF	-10.768	-	-
	25-35	ΔH	-44.081	-	-
	25	$-\Delta S$	0.1065	-	-
Rh(III)	25	ΔF	-11.7275	-4.4682	-3.0682
	35	ΔF	-11.6277	-4.5102	-3.0302
	45	ΔF	-11.4959	-4.5110	-2.9831
	25-35	ΔH	-14.6938	-4.2973	-4.1982
	25	ΔS	- 0.00995	-0.0058	-0.00379

Table - 20 Thermodynamical stability constants of Rh(III) complexes of α-alanine and 2-mercaptrop-opanoic acid at three different temperatures.

Ligand system	Temperature °C	log K_1	log K_2	log K_3	log β
α-Alanine	25	15.95	8.00	4.35	28.30
	35	15.00	7.70	4.25	26.95
	45	13.85	7.45	4.05	25.23
2-Mercapto-propanoic acid	25	9.125	7.30	5.35	21.54
	35	8.850	7.12	5.12	21.09
	45	8.500	6.85	4.90	20.25

Table - 21 Stepwise ΔF, ΔH (K cals mole^{-1}) and ΔS (K cals mole^{-1} degree^{-1}) values for the formation of Rh(III)-alanine and Rh(III)-2-mercaptopropanoic acid complexes.

Ligand System	Temperature °C	Thermodynamical parameter	I	II	III
α-Alanine	25	$-\Delta F$	21.67	10.8790	5.911
	35	$-\Delta F$	21.06	10.8143	5.96
	45	$-\Delta F$	20.08	10.8020	5.87
	25-35	ΔH	-39.88	-12.599	-4.198
	25	ΔS	- 0.061	- 0.0057	+0.0057
2-Mercapto-propanoic acid	25	$-\Delta F$	12.40	9.920	7.269
	35	$-\Delta F$	12.42	9.995	7.190
	45	$-\Delta F$	12.33	9.930	7.102
	25-35	ΔH	-11.5451	-7.5599	-5.2477
	25	ΔS	+ 0.00286	+0.00792	+0.0068

Preparation of the Complexes :

The solutions of Rh(III) chloride and cysteine, both of them of 0.05 M concentration, were mixed in the ratio of 1:3. The pH of the mixture was raised to $\approx$ 7.0 by adding sodium hydroxide solution. The reaction mixture was concentrated by evaporation on water bath till the yellow precipitates were formed which were filtered and washed with cold water-alcohol (50%) mixture, and dried in a vacuum desiccator.

The osmium complex was prepared by mixing the metal ion and cysteine solutions in the ratio of 1:5. The mixture was evaporated to dryness and then complex was extracted by treating the solid mass with 50 % (V/V) solvent ether-alcohol mixture. The solvent was then evaporated in an electric oven at 25°C and the complex was then dried in a vacuum desiccator over silica gel.

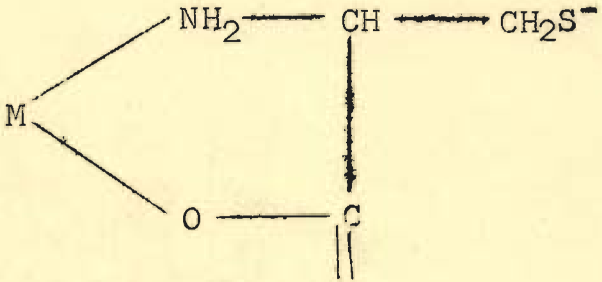
The complexes were then analysed chemically for the metal ion, carbon, hydrogen and nitrogen. The results of analysis, molar conductance and magnetic measurements are given in Table - 22.

Table - 22 Analytical data of complexes.

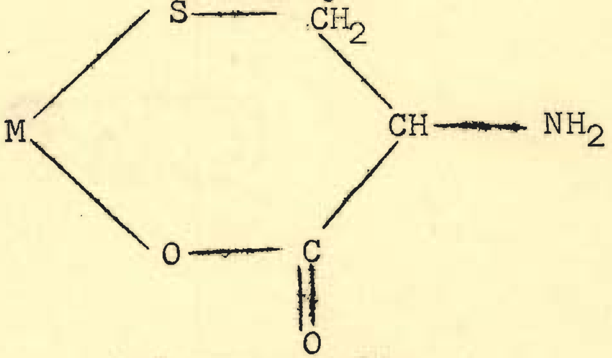
Complexes	Percentage of M calc. (Found)	Percentage of C calc. (Found)	Percentage of H calc. (Found)	Percentage of N calc. (Found)	μ_{eff} B.M.	Molar conductance ohm^{-1} cm^{2}mol^{-1}
$Na_2[OsO_4(C_3H_5O_2NS)]$	45.22 (45.30)	8.56 (8.48)	1.19 (1.00)	3.35 (3.30)	1.04	298.3
$Na_3[Rh(C_3H_5O_2NS)_3]$	19.57 (19.30)	20.50 (20.42)	2.85 (2.76)	7.94 (7.82)	0.72	340.10

RESULTS AND DISCUSSION

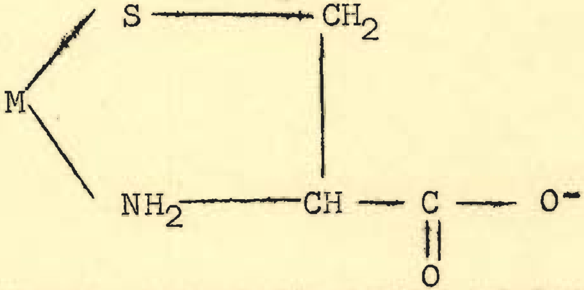
The values of dissociation constants pK_1, pK_2 and pK_3 corresponding to the deprotonation of -COOH, -SH and $-NH_3^+$ respectively, at 25, 35 and 45°C and at different ionic strengths (1.0,0.50,0.25 and 0.10 M,$NaClO_4$) are given in Table-1. They are in good agreement with the published values [274, 267]. The small differences may be due to a difference in temperature or ionic strengths. Table-18 summarizes the values of the formation constants. The values of F, H and S are given in Table-19. The difference between the successive formation constants at 25°C is much larger for bis-cysteinato complexes of Rh(III) ($\log K_1/K_2 \approx 2.56$). This indicate the formation of 1:2 (M:L) complex with greater difficulty in comparison to 1:1(M:L) complex which may be due to some steric reasons and statistical factors. It was confirmed that with the high ligand to metal ratio of 5:1 used in our studies, the presence of polynuclear species could be neglected since the formation curves determined from the ligand-metal ratios of 5:1 and 6:1 were found to be identical. Only two out of three donor groups can bind to the metal ion simultaneously due to steric reasons [275] and hence 1:1 metal-cysteine complex can have either of the following structures.



I



II



III

The fact that the value of $\log K_1$ at 25°C is almost equal to the formation constant of Rh(III)-2-mercaptopropanoic acid chelate, Table - 20 ($\log K_1 \approx 9.0$) and very much different from Rh(III)-α-alanine chelate ($\log K_1 \approx 16.0$). The value of $\log K_1$ for the cysteinate complex of osmium ion is also about 9.0. It shows that the sulphydril and carboxyl groups are the donor groups which take part in the formation of these metal-cysteine chelates. It is also known that Fe(II) prefers [275,276] coordination with the sulphydril and the carboxyl groups in cysteine. It is also known that in 1:3 Co(III)-cysteine chelate, the metal ion is coordinated to sulphydril and carboxyl groups [277,278].

The ΔH values reflect the changes in the number and strength of bonds, made and broken during a coordination reaction. The values of ΔH, therefore, are expected to throw light on the type of bonding between the metal ion and the ligand molecules. On comparing the values of ΔH of 1:3 Rh(III)-cysteine chelate and of 1:3 Rh(III)-2-mercaptopropanoic acid chelate, which are nearer to each other. This again concluded the coordination through sulphydril and carboxyl groups.

<u>I.R. Studies</u> :

The coordination of cysteine through sulphydril and carboxyl group was again confirmed by carrying out I.R. studies of solid complexes. The I.R. spectrum of cysteine gave ν_{N-H} band at 3000 and 3400 cm^{-1}, ν_{S-H} band at 820 and 2450 cm^{-1} and ν_{COOH} bands at 1590, 1470, 650 and 750 cm^{-1}. The bands obtained due to S-H were completely disappeared in the I.R. spectra of the complexes and no change in the positions of N-H bands on complexation was observed. The I.R. spectra of the complexes gave the COO^- bands at 1640 and 1420 cm^{-1}. Such type of observations have also been reported in case of amino-acid complexes that antisymmetric frequencies increase and symmetric frequencies decrease. The bands due to $\nu_{(M-O)}$ and $\nu_{(M-S)}$ were obtained at 420 and 350 cm^{-1} respectively, in the spectra of both the complexes.

Thermal Analysis :

Thermogravimetric analysis of both the complexes indicated the absence of water molecules.

Electronic Spectra :

The electronic spectrum of Rh(III) complex gave two spin-allowed bands at 19100 and 25500 cm^{-1} corresponding to the transitions $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$ respectively, and a third spin-forbidden band involving singlet-triplet transition was observed at 14410 cm^{-1}. The values of 10 Dq, B, β, C and ligand field stabilisation energy (K cals $mole^{-1}$) were thus found to be 21445, 400, 0.55 , 2345 and 24.50 respectively.

Comparatively less is known about osmium complexes in high oxidation states. Os(VIII) has effective configuration $5d^0$ hence its complexes are expected to be diamagnetic. In our case also the value of magnetic moment (Table - 22) indicated the diamagnetic character of the complex. The electronic spectrum of this complex gave three bands at 26000, 28850 and 36000 cm^{-1}. All of these bands may be considered to have arisen due to charge transfer.

SECTION C

CHAPTER—II : Cysteine as an Analytical Reagent for the Spectrophotometric Determination of Osmium (VIII)

Most of the methods reported in the literature involve the prior extraction of osmium-reagent complexes in organic solvents, viz., 4-(4-aminophenyl) morpholine [279], 2-mercaptobenzimidazole [280], 1-(2-thiazolylazo)-2-naphthol [281], thiosalicylamide [282], tetramethyl thiouram disulphide [283] and N-benzoyl-o-tolyl hydroxylamine [284]. These methods are also very sensitive to variations in laboratory conditions and possible mechanical errors. More recently, 1,5-diphenylcarbazide [285], phenanthrene quinone monosemicarbazone [286], rhodamine [287], NN'-bis (hydroxymethyl) thiourea [288] and 3-hydroxy-2-methyl-1, 4-naphthaquinone monoxime [289] have been used for the spectrophotometric determinations of osmium(VIII) but are subject to a large number of interferences. Secondly the estimations by all these methods can be carried out in a very small range of concentrations. Cysteine provides not only a rapid and accurate method but has the advantage of being straight forward and less interfering. This method can also be used for the estimations in a larger range of concentrations.

EXPERIMENTAL

Apparatus :

Absorbance measurements at varying wavelengths were recorded with a 'Unicam' SP-500 spectrophotometer using one cm.path length matched glass cuvettes. pH measurements were made with a expanded scale (solid-state) pH-823 ECIL pH meter.

Reagents and Solutions :

All the chemicals used were of analytical reagent grade. Osmium tetroxide obtained from Johnson Methey and Co. Ltd. (London) and cysteine hydrochloride from Koch-Light Laboratory Ltd. (England) were used as such. Acetic acid-sodium acetate buffers were used for pH adjustment. All the solutions were prepared in double distilled water. The solution of metal ions was standardised by reported methods [285,287].

DISCUSSION

Selection of the Wavelength :

Vösburgh and Cooper's method [290] was applied. The mixtures of the metal and the reagent in the ratio 1:5, 1:6, 1:8, 1:10 and 1:15 gave the absoption maxima at 370 nm providing a suitable wavelength to work.

Effect of pH :

The effect of pH on the stability and intensity of the colour was determined by preparing a series of mixtures containing metal and the reagent in the ratio of 1:5 and buffers with pH values varying from 2.0 to 6.8. The wavelength of maximum absorbance and the absorbance at the wavelength maximum remain unchanged between pH 4.0 and 5.2 and thus rigid control of the pH during colour formation is not necessary. A sodium acetate-acetic acid buffer of pH approximately 4.5 gives satisfactory pH control and does not interfere in the determination in any way.

Effect of the Reagent Concentration :

The effect of excess of the reagent on the intensity of colour was also studied and it was found that six fold excess of the reagent is required for full colouration.

Effect of Temperature and Light :

Under optimum conditions the colour intensity remains unaltered in the light and in the temperature range of 15 to 80°C.

Rate of the Reaction and Stability of the Colour :

The colour develops instantaneously on mixing the reactants and remains stable for more than ten days.

Beer's Law :

The system adheres to Beer's law in the range of 1.0 - 60 ppm of osmium(VIII) with an optimum range of 5.0 - 55 ppm of the metal as evaluated from a Ringbom's plot [291]. The molar absorptivity calculated over the range studied is 1429 ℓ mole^{-1}cm^{-1} and the mean sensitivity (Sandell method) [292] is 0.132 μg/cm^2.

Composition and Stability Constant :

The composition and stability constant of the complex as determined by Bjerrum's pH-metric method [261], are found to be 1:1 and 1.2589 x 10^9 respectively. Spectrophotometric methods could not be applied because of the precipitation in the solution containing osmium and cysteine ratio as 1:1.

Effect of Diverse Ions :

The interference caused by various cations and anions was also studied. Solutions containing a known quantity of Os(VIII) and varying amounts of diverse ions were prepared and the osmium was determined. K^+, Tl^+, NH_4^+, Rb^+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+}, Sb^{3+}, Bi^{3+}, Ru^{3+}, Rh^{3+}, Ir^{3+}, Zr^{4+}, Sn^{4+}, Pt^{4+}, Mo^{6+}, W^{6+}, Se^{6+}, Te^{6+}, Cl^-, Br^-, I^-, NO_2^- , NO_3^-, ClO_4^-, CO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-} and PO_4^{3-} do not interfere in the determination even when present in five fold excess. Interference caused by the following ions could be eliminated by the addition of the reagents given in parenthesis. $Cu^{2+}(S_2O_3^{2-})$, $Ag^+(I^-)$. Ni^{2+} ions are tolerated if their concentration is less than osmium ions. However, the presence of

Cr^{3+} seriously interfere.

Recommended Procedure :

A solution containing osmium(VIII) is treated with a suitable masking agent as necessary, six or more than six fold excess of an aqueous solution of cysteine is added and the volume is brought to about 60% of the final volume by adding distilled water. The pH of the solution was then adjusted to about 4.5 by adding a buffer solution, dilute to the requisite volume with distilled water and then the absorbance is measured at 370 nm against water blank.

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