Studies on the Reactions of Common and Less Common Metals and Metal Ions of Unstable States with Ligands containing Nitrogen and Sulphur

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I certify that the work presented in this thesis was carried out by the candidate, Dr. A.U. Malik, is an original piece of research work, and has not been submitted for any other degree of this or other University.

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PREFACE

The research career of the author dates back to 1960 when he started research work in the field of inorganic chemistry. His earlier investigations dealt with the complexes of Cu(I and II), Cr(II and III), Mn(III), V(IV) etc., with aromatic hydroxy sulphonic acids, hydrazine and ethanol amines. On the basis of this work, the author was awarded the Ph.D. degrees in February, 1963. Since then he is actively engaged in research in the field of inorganic chemistry except for the period 1963-64 when he got interested in analytical chemistry and published some work on the estimations of vanadium and dissolved oxygen in water. The conventional analytical work, however, could not satisfy the academic urge for long and he decided to shift again to basic research on coordination compounds. The work incorporated in this thesis, therefore, includes only the results of his investigations on coordination complexes carried out independently in Aligarh during the period, autumn 1964- summer 1969.

The present work was initiated with the object of studying the nature, composition and structure and in some cases the kinetics and mechanism of the formation of simple and mixed transition metal complexes with sulphur and nitrogen containing ligands. Thus the major portion of the thesis, enmassed in chapters III, VII and VIII, deals with mixed ligand complexes of Cu(I), sulphur and nitrogen ligated complexes of Pd(II), and substitution reactions of square planar complex, $[Ni(tu)_4]Cl_2$. The chapters I,II,IV give an account of the synthetic work on Cu(I) complexes with heterocyclic amines, substituted thioureas and 2, mercaptobenzthiazole. The results of the complexes of rare earths with substituted thioureas and 2,mercaptobenzthiazole are incorporated in chapters V and VI.

It will not be out of place if a few salient and noteworthy features of these investigations are enumerated. It may be pointed out that through these studies emphasis has been laid upon the syntheses of new complexes and the nature of bonding involved (as envisaged on the basis of I.R. and other studies). The kinetics and mechanism studies on copper(I) complexes are perhaps first of their kind and are likely to extend our horizon of knowledge of the chemistry of copper(I). The work on Ni(II) and Pd(II) complexes deals with some hitherto uninvestigated systems and opens further avenues for elaborate researches in this direction. Relatively a few complexes of 'f' orbital metals with sulphur containing ligands have been reported. The work on rare earths discussed here merely gives an account of the coordinating potentialities of sulphur ligands, viz., thioureas and 2,mercaptobenzthiazole toward these metals. No claim for extensiveness in these studies has, however, been made.

During this period, numerous publications have appeared relating to the studies described in this manuscript and it was not possible to refer to all the work. A few books,

monographs and review articles have been of immense help during the preparation of the manuscript of the thesis. The books worth mentioning are 'Mechanism of Inorganic Reactions by Basolo and Pearson; Inorganic Reaction Mechanism by Edwards; Advanced Inorganic Chemistry by Cotton and Wilkinson; Modern Aspects of Inorganic Chemistry by Emeleus and Anderson; Transition metal chemistry edited by Carlin; Progress in Inorganic Chemistry edited by Cotton; Advances in Inorganic and Radiochemistry edited by Emeleus and Sharpe; Physical methods in Heterocyclic Chemistry edited by Kartizky. Annual reports of chemical society, quarterly reviews and chemical reviews were also consulted at various stages during the writing of this thesis.

The author acknowledges his thanks to Prof. A.R.Kidwai, former Head of the Chemistry Department and Dr.S.M.F. Rahman, present Head of the Chemistry Department for encouragement and providing facilities during the course of this work. He is specially indebted to Dr. Rehman for giving unqualified assistance and useful suggestions from time to time. He is also thankful to Prof. Mohsin Qureshi for his interest in the work.

The author feels obliged to Dr. Naseer Ahmad for conducting far i.r. spectra of the samples in his laboratories at Lousiana State University, U.S.A. I also express my deep appreciation to Dr. M.M. Khan and Dr. Omar Farooq for their painstaking labour by correcting the manuscript and checking the references.

In the last but not the least I would like to thank Prof. W.U. Malik, Head of the Department of Chemistry, University of Roorkee, for inspiration and whole hearted encouragement during the whole span of this work, and his criticism and cogent comments on the work.

Finally, the author expresses his deep sense of gratitude to Prof. J.N. Chaterji, Head Chemistry, Patna University; Prof. R.C. Paul, Head Chemistry, Punjab University, and Head Chemistry, I.I.T. Kanpur, for supplying i.r. spectra of the complexes, magnetic susceptibility and chemical analysis data.

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4. Rate studies on the substitution reactions of tetrakis (thiourea palladium(II) chloride with some amino acids.

5. Studies on mixed ligand complexes of oxotitanium(IV).

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7. Studies on the interaction of copper(I) halides with 2, mercaptobenzthiazole.

8. Coordination compounds of palladium(II) with substituted thioureas.

9. Studies on the composition and structure of the complexes formed by the interaction of tetrakis(thiourea) nickel(II) chloride with heterocyclic amines.

10. Kinetics and mechanism of the substitution reactions of tetrakis(thiourea) nickel(II) chloride with heterocyclic amines.

11. Interaction of tetrakis(thiourea) palladium(II) chloride with heterocyclic amines and the kinetics and mechanism of the formation of mixed ligand complexes.

12. Studies on the interaction of some rare earths with 2, mercaptobenzthiazole.

13. Mixed ligand complexes of copper(I), Part IV. Interaction of 1,10 phenanthroline with tris(tu) copper(I) chloride and iodides.

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GENERAL INTRODUCTION

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The field of coordination chemistry, initiated by Alfred Werner and nourished by eminent inorganic and physical chemists like Jørgensen, Pfeiffer, Tschugaev, Ley, Bodlander, Jaeger, Mann, Bjerrum, Leden, Chernyaev and his group of Russian chemists, Ray, Feigel, Prodinger, Schwarzenbach, Calvin, Bailer, Nyholm, Chatt and several others, has witnessed spectular developments in the last two decades. Several factors have been responsible for these advancements. The gradual development of the valence bond theory, and further the ligand field and molecular orbital theories combined with the introduction of new analytical techniques such as infra red and ultra-violet spectroscopy, nuclear magnetic and electron spin resonance, nuclear quadrapole resonance, X-ray absorption, Mössbauer effect etc., has immensly helped in correlating the structural and configurational aspects of complexes with their physical properties. This in turn has opened new avenues for basic and applied research. Basic chemical applications, therefore, now include use of metal catalysts or chelate protective groups in the preparation of organic compounds, synthesis of inorganic compounds of predetermined properties, and the introduction of some new industrial processes like Zeigler-Natta polymerisation, the hydroformylation process and the Wacker olifine oxidation, and a better understanding of life process.

To incorporate the various aspects of modern inorganic chemistry mentioned above in the form of a short review would require great space and will also be the out of tune from the present investigations, it, therefore, seems reasonable to elaborate only those aspects which are pertinent to the problem, under study. A discussion of the modern valence concepts, and a survey of the chemistry of Cu(I), Ni(II) and Pd(II) and their substitution reactions, coordinating abilities of rare earths and, an account of the coordinating and chelating properties of sulphur and nitrogen containing ligands, have been included in this review.

1. Valence Theories:

Sidgwick's concept[1a,1b] of E.A.N. and later eleboration of the fact that the ligand species would be one which has a pair of electrons for sharing, is still the starting point for modern valence theories.

Since 1950, the crystal field theory, the molecular orbital theory and their admixture, the ligand field theory have been widely used to explain the behaviour of coordination compounds. The crystal field theory first proposed by Bethe[2] in 1929, was successfully applied to explain the magnetic properties of the transition metal ions by Schlapp and Penney[3] and by Van Vleck[4]. The theory was further strengthend by Hartmann[5] who used it to explain the so called d-d spectra of the complexes in the visible range. Orgel[6] was the first to give its usefulness for explaining the stability of coordination compounds of transition elements. Crystal field theory emphasizes, the effect of the external electrical field, due to the ligands, on the energy levels of the d orbitals of the central atom or ion. These orbitals split into groups of different energy and nature of the splitting determines the electronic population of the various orbitals and, by implication, the magnetic and spectral characteristics of the central atom. A further area where crystal field theory provides a very direct prediction is in the distortion of regular coordination arrangements. It predicts which electronic configuration will be energetically favourable for distortion. Such predictions have been extensively verified from X-ray determinations of the structure of complex ions.

The application of molecular orbital theory to coordination compounds was first made by Van Vleck[7] in 1935. The ligand and metal orbitals which are used to build up the molecular orbitals are combined to form new linear combinations which satisfy some symmetry requirements. In the event a given atomic orbital overlaps appreciably with only one other atomic orbital, the pair may be regarded as a localised molecular orbital, holding as many as 2 electrons. This would correspond to the usual conception of chemical bond. The d orbitals of the central metal ion which do not point towards the ligands become non bonding molecular orbitals e.g., orbitals in which the electrons have the same energy as they posses prior to coordination. Thus, the d_{xz},d_{yz} and d_{xy} are non bonding molecular orbitals for an octahedral complex, while for a square planar complex the non bonding orbitals are $p_z, d_{xz}, d_{yz}, d_{xy}$ and d_z2. For an n coordinated central ion there will be found n bonding orbitals e.g., orbitals having lower energy than they possess prior to coordination and n antibonding orbitals e.g., orbitals in which electrons possess higher energy than they possessed prior to coordination. The molecular orbital theory is most reasonable of the existing theories. It conveniently explains all type of bondings including π bonding. Furthermore, with a reasonable selection of atomic orbitals, the theory automatically includes all of the interactions which in the valency bond theory would require the inclusion of a large number of reasonance forms.

The nature of the chemical bond in coordination compounds has also been explained currently on the basis of (i) electrostatic theory and (ii) valence bond theory. Although each theory has its own advantages and a single theory cannot be applied convincingly to all types of coordination compounds.[8a,8b] However, the approach of molecular orbital theory is so far more logical and convincing.

2. Nucleophilic Reactivity:

The effectiveness of a nucleophilic reagent, nucleophilic reactivity is often defined in terms of the basicity (H) of the nucleophile (towards the proton on water) and polarizability (P) which is a measure of the ease of distorting or removing the electrons in the nucleophile.[9] The polarizability is calculated from the molar refraction (R), the electrode potential (L_n) or the electronegativity.

Edwards[10] correlated these terms by the equations:

$$\log (k/k_o) = \alpha P + \beta H$$
$$\log (k/k_o) = \alpha E_n + \beta H$$

where (k/k_o) is the rate relative to water, P is defined as log (R_N/R_{H_2O}), H is a function of basicity (pK_a + 1.74), $E_n = E^o$ + 2.60, where E^o is the standard potential for the process:

$$2Y \rightleftharpoons Y_2^{2+} + 2e$$

For water, H and E_n are zero, α and β can be determined experimentally from a series of related reactions.

The correlation of basicity with nucleophilic character may be understood by aligning the substitution reaction:

$S - X + Y \longrightarrow Y - S + X$ (where Y is a nucleophile, $S — X$ is the substrate, and X is the leaving group) with an acid-base reaction. The basicity of Y (and similarly of X) is measured by the acid-base reaction.

$$Y + H_3O^+ \longrightarrow YH^+ + H_2O$$

Obviously, to the extent the substrate atom S has a localised positive charge similar to that of a proton, the basicity of the nucleophile would play the main role and the rate of substitution will be correlated with basicity.

Some of the important coordinating groups such as thiourea, triphenyl phosphine and iodide are more nucleophilic than their basicities would warrant and this excessive reactivity is ascribed to polarizability.[11]

In general, those nucleophiles that are strongly basic are often not very polarizable e.g., F^- on tetrahedral phosphorus. Conversely, a large polarizable nucleophile may not be very basic e.g., thiourea, iodide ion. This situation is further exemplified by considering the stability order of the halide ions in presence of different cations. With Be^{2+}, Ti^{4+} the order is $F^- > Br^- > I^-$ and with cations such as Ag^+, Cu^+ and Hg^{++} the order is reversed e.g., $I^- > Br^- > Cl^- > F^-$.[18]

The alteration of solvent is another factor that affects the order of nucleophilic reactivities.[12,13] In general, the most basic is often the most solvated in a protonic solvent such as water and alcohol. The poor nucleophility of F^- and good nucleophility of I^- may be explained on considering the order of binding of halide ions $F^- > Cl^- > Br^- > I^-$ in hydroxylic solvents through hydrogen bonding. The strong solvation of the ground state is one reason why F^- ion, the most basic halide ion, is a poor nucleophile whereas I^- ion is a good nucleophile in displacements on saturated carbon in aqueous solution. In solvents that cannot hydrogen bond (e.g., acetone, dimethyl formamide, (D.M.F.), the rate order is apparently reversed, for Cl^- ion reacts more rapidly than iodide.

It has been found that some nucleophiles such as peroxyanions and hydroxylamine show higher reactivities than those expected from their basicities and polarizabilities, such groups are characterised by the presence of one or more unshared electron pairs on an atom adjacent to the nucleophile atom. The excess reactivity shown by this class of reagents is called the 'alpha effect' as proposed by Edwards and Pearson,[9] with reference to the pair of electrons on the alpha atom. The magnitude of alpha effect may be estimated by the fact that perhydroxide ion OOH^- is several times more reactive than H^-, even though the OH^- ion is far more basic.

Some of the factors that influence reactivity of nucleophile have been listed by Jencks and Carruolo.[14] These include (a) hydrogen bonding (b) proton transfer and general acid catalysis (c) electrostatic effects (d) steric effects (e) resonance and (f) relative bond strengths to proton and other substrate atoms. These factors, although are of limited applicability than basicity, polarizability and solvent effects, but are important in special cases.

3. Hard and Soft Acids and Bases.

A convenient and useful way to classify metal ions and ligands is according to their order of polarizability.[15] In general, polarizable bases (or Lewis acids) are called soft bases (or acids) and non polarizable bases (or Lewis acids) are called hard bases (or acids). The above classification can be very well understood if we carry out the division of metals according to their tendencies: class (a) to form stable complexes with first ligand atom of each periodic group and, class (b) to form stable complexes with the ligand atom belonging to the second or subsequent member of each periodic group.[16a,16b]

For class (a) metal ions the order of stability is

$F^- > Cl^- > Br^- > I^-$

$O \gg S > Se > Te$

$N \gg P > As > Sb > Bi$

For class (b) metal ions, the order of stability is

$F^- < Cl^- < Br^- < I^-$

$O \ll S \sim Se \sim Te$

$N \ll P > As > Sb > Bi$

In general, class (a) metal ions are Lewis acids of small size and high positive oxidation states, prefer to bind to small, non polarizable ligands (containing least polarizable atom of a group) such as F^-, O_2 and H_2O, whereas class (b) metal ion, are Lewis acids of large size and low positive oxidation states, prefer to bind large, polarizable ligand (containing most polarizable atom of the group) such as I^-, R_2S and olefines. Class (a) Lewis acids are called hard acids and class (b) Lewis acids are known as soft acids. As a rule, soft acids always prefer to combine soft bases and hard acids prefer to combine hard bases.

According to the π bonding theory of Chatt,[17a,17b] the soft acids, class (b), have invariably closely held outer d orbital electrons which can form π bonds by donation to suitable ligands. Such ligands contain atoms having empty d orbitals acting as acceptor orbitals such as P, As, S and I. Unsaturated ligands such as CO and isonitriles would also act as acceptors of metal electrons by the use of empty orbitals provided the molecular orbitals formed are not too unstable. In class (a) Lewis acids, ligand atoms such as O and F could form bonds in the opposite sense, by donating electrons from the ligands to the empty orbitals of the metal. Thus the soft acids (class b) are potential d-p electron donors via π bonds. The hard acids are potential π bond acceptors. These effects are, in addition to σ bonding interactions.

4. General Considerations on Sulphur containing Ligands (especially thiourea and related compounds).

Ligands containing oxygen or nitrogen as donor atoms and ligands such as halide ion, cyanide ion and unsaturated compounds such as olefines,cyclopentadiene, carbon mono xide etc. have so far been studied in much detail. Ligands containing sulphur have less extensively investigated although in recent years considerable interest has been shown in sulphur ligands.

From a consideration of an electrostatic model[18,19] the coordinating ability of a unidentate ligand depends not only on its electronegativity but on total dipole moment, μ. Thus the large size and small permanent dipole moment of H_2S (μH_2S, 1.1D, μH_2O, 1.9D) reduces its coordinating ability below that of water for ions of low field strength. However, H_2S is more polarizable than water (molar refractivity of donor atoms, H_2O: 3.7 cc., H_2S: 9.5 cc) and with ions of high field strength(Cu^+, Ag^+, Hg^{++} etc.),

H_2S coordinates readily and protons are forced off to give insoluble sulphides. Whereas both the permanent dipolement and coordinating ability decrease in the series $H_2O > ROH > R_2O$, the reverse holds good for sulphur, both dipolement and coordinating ability increase in the order: $H_2S < RSH < R_2S$. Moreover, although polarizability is decreased by alkyl substitution, the decrease is much less (5%) in going from H_2S to R_2S than the corresponding decrease (24%) in going from H_2O to R_2O.[20]

Leaving aside a few potential ligands[21a,21b] e.g., NO_2^-, 2,2' bipyridyl, o-phenanthroline, dimethyl glyoxime etc., oxygen and nitrogen have no orbitals available to accept electrons from suitably placed d orbitals on the metal atom. However, sulphur has vacant d orbitals which can be used for $d_\pi - d_\pi$ bonding, this usually occurs with latter transition metals in their normal oxidation states, Pd(II), Pt(II), Hg(II) etc., and with the early transition metals in their lower oxidation states, (Mo(0), W(0), Re(I) etc.). The extent to which such π bonding occurs is mere speculation but it does occur with ligands containing sulphur. Low spin d^8 ions, Pd(II), Pt(II), Ni(II), and Au(III), and d^{10} ions, Cu(I), Ag(I), Au(I) and Hg(II) have the highest formation constants with heavy halides (I^-, Br^-) and with sulphur ligands. Being typically (b) they form strong π bonds with soft ligands and also $d_\pi - d_\pi$ bonds by donation of a pair of electrons to the ligand.[15,17a,17b]

The polarizabilities of sulphur ligands decrease in the order: $S^{2-} > RS^{-} > R_2S$ and therefore, it is necessary to have a distinction between sulphide ion, mercaptide ion and thioether while considering the bonding properties of sulphur ligands. In the above order, not only the polarizabilities but the number of lone pairs also decrease. Williams[22] suggested that the principal difference between thiols and thioethers as ligands is that the former are highly polarizable but not as effective d_π electron acceptors as the latter. Thiols but not thioethers cause spin pairing in complexes of Co(II) and Ni(II). The ability to cause spin pairing in complexes of Co(II) and Ni(II) is confined to 'soft bases' which are relatively strong π acceptors. The polarizability of the ligand is, however, the more decisive factor.[23a,23b]

Livingstone[19] has given an excellent review on metal complexes of sulphur containing ligands and described the chemistry by dividing the ligands into the following categories: (i) sulphide ions (ii) negatively charged unidentate ligands such as thiols, sulphite ion, thiosulphate ion and thiocyanate ion (iii) neutral unidentate ligands such as thioethers, thiourea, thio acetamide, thiobenzamide, triphenyl phosphine sulphide and dimethyl sulphoxide (iv) sulphur containing chelating agents such as thioether, thiol, alkyl xanthates, dialkyl-dithiocarbamate, thio derivatives of β diketones and β ketoesters and α dithiols. The present discussion, however, will be limited to thiourea and related ligands.

Thioureas act as soft bases and unidentate neutral ligands, forming strong complexes with class (b) metals particularly with d^{10} configuration e.g., Cu(I), Ag(I), Au(I) and Hg(II). In thiourea, sulphur atom unlike the nitrogen has vacant d orbitals, the latter may be used as d_{π} acceptor orbital and therefore, the possibility of $d_{\pi}-d_{\pi}$ bond formation is not excluded. Another important characteristic with thiourea is its tendency to reduce some metals from higher oxidation states to lower oxidation states e.g., Cu(II) to Cu(I), Au(III) to Au(I), Pt(IV) to Pt(II), Ce(IV) to Ce(III), and Te(IV) to Te(II), and stabilising the lower oxidation state. This is not surprising since thiourea being highly polarized molecule and having sulphur atom with acceptor d orbitals, should have tendency to create conditions so as to make the metal ions favourable for coordination and this may be achieved by making the size of the ions larger and reducing the positive charge. This is ofcourse not necessarily be true with all the ions since factors such as configuration of the metal, redox potential of the system and other environmental factors also play key roles in the stabilization of the oxidation state of a particular metal ion.

Thiourea forms complexes in which the coordination number of the metal ion usually varies from 2 to 4 and in a few cases the formation of higher coordinate species (> 4) are also reported. Complexes with coordination number two are reported with Ti(IV), Ag(I), Au(I), Hg(II) etc. A coordination number of three is reported for Cu(I). There are numerous examples of 4 coordinate species. The structures of a number of thiourea complexes have been determined by X-ray analysis and infra red studies.

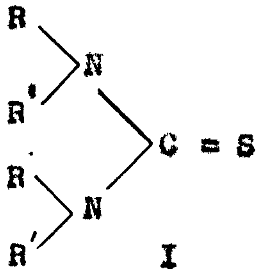
The nickel atom in $[Ni(tu)_4Cl_2]$ where tu = thiourea, is surrounded by four sulphur atoms at 2.45A° and two chlorine atoms are at 2.4A° in the trans octahedral sites.[24] The structure of high spin compound has also been determined.[25] Ni-S is found to be 2.1-2.3A° in the diamagnetic form whereas in 6-coordinate complex it is 2.4-2.6A°. This is in accordance with the ligand field theory which predicts that stronger field producted by the ligands closer to the nickel will cause the eg electrons to pair in the d_{z^2} orbitals, so producing a diamagnetic complex with no close neighbours in the z-direction.

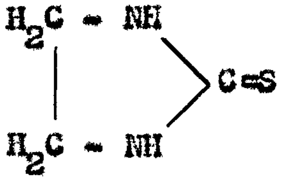
The compound, $[Ni(tu)_2(NCS)_2]$, is octahedral and polymeric, the sulphur atom of each thiourea molecule is bound to two nickel atoms.[26] The compounds, $[M(tu)_2(NCS)_2]$, (M = Mn, Co, Cd etc.), are isostructural with $[Ni(tu)_2(NCS)_2]$.[24] In the compound, $(Ni(py)_2(tu)_2Cl_4)$ (py=pyridine), the sulphur atoms of two of the four molecules are probably bridging as in thiocyanate complexes.[27]

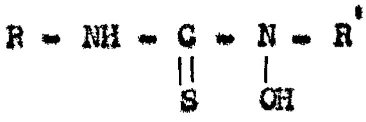
The compound, $[Cd(tu)_2Cl_2]$, is tetrahedral but $[Pb(tu)_2Cl_2]$ has a polymeric structure in which lead atom is 7-coordinate, being surrounded by 4 bridging sulphur atoms, 2 bridging chlorine atoms and one non bridging chlorine.[24] The complex, $[Mo(tu)_3Cl_3]$ [23a] has a magnetic moment of 3.71, but the complex, $[Mo_2(tu)_6Cl_6]$ has a moment of 0.59B.M. In the latter, two Mo octahedral are bridged by either 3 chlorine or 3 sulphur atoms (from the thiourea) and the low value of magnetic moment is ascribed to spin-spin coupling due to metal-metal interaction, either directly or via the bridging atoms.[28b]

Infra red spectra studies have shown that thiourea coordinates through sulphur not only with class (b) metals[29] but also with Sn(IV),[30] Pb(II)[31] and Te(II);[32] however, in $Ti(tu)_2Cl_2$ the coordination is through nitrogen.

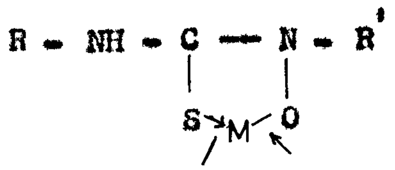
Complex of NN'-substituted thioureas(I), R=alkyl or aryl, R'=alkyl,aryl or H, has been extensively investigated.[33] Cu(I) and Ag(I) form complexes containing 1,2,3 or 4 molecules of ethylene thiourea (II).[34] Complexes of Cu(I) and Ag(I) are also known with other substituted thioureas.[35]


I


II


$R - NH - \underset{\underset{S}{\|}}{C} - \underset{\underset{OH}{|}}{N} - R'$

III


IV

Ni(II) forms an interesting series of complexes with substituted thioureas. The complexes, $[Ni(ntu)X_2]$ (where X=Cl, Br, ntu=1-(1-naphthyl)-2-thiourea) are tetrahedral, the paramagnetic compounds, $[Ni(ethu)_4X_2]$ (X=Cl, Br) are octahedral and have been isolated in cis and trans forms but the iodo complex is six coordinate[36] and is a rare example of tetragonal Ni(II) complex.[37]

NN'-diethyl thiourea, NN'-diphenyl thiourea and NN-diphenyl thiourea behave as bidentate chelating agents, bonded through both nitrogen atoms.[33] Bis chelate complexes of Co(II), Ni(II) and Cu(II) are formed by a number of NN'-diaryl-N-hydroxothioureas (III), the hydrogen of the OH group is replaced and the ligand is most probably coordinated through sulphur and oxygen[38] (IV).

5. Stabilisation of Lowest Valencies of Transition Metal (Formation of complexes with π-Acceptor (π acid) ligands).

In metals in their lower valency states the coordination between the ligand and the metal usually takes place by the donation of electrons from the filled orbitals of the ligand to the empty orbitals of the metal.[40a] Such a process will naturally lead to extensive charge accumlation around the metal with the result that the chances of covalent bonding diminish. However, there is one way in which the effect of charge accumulation can be minimised, namely, by a mechanism involving the transfer of charge from the metal ion back to the ligand. This usually takes place by the p_π or d_π orbitals on the ligands which act as acceptor orbitals and cannot be done by σ bonding since σ orbitals of all the ligands are filled. Such type of acceptor ligands are also called π acid ligands.[39a]

The important ligands which are found experimentally to stabilise the lower valency states of the transition metals are:

C_2H_4, CO, CN^-, PR_3, R_3As, $SC(NH_2)_2$, I^-, SCN^-, C_5H_5N, 2,2'-dipyridyl, o-phenanthroline etc.

Each of these ligands has acceptor levels for π electrons and is suitable for the stabilisation of lower valency states and other ligands though similar in each other way are less effective or incapable to stabilise these valency states. Thus phenanthroline, dipyridyl and thiourea with vacant d orbitals and arsines with empty d π orbitals are more effective than ethylenediamine or aliphatic amines in stabilising lower valency states.[40a]

It is now recognised that the qualitative order of various ligands in their ability to function as π acceptors is in the following order;[41,42,39b]

$NO \geqslant CO \sim RNC \sim PF_3 > PCl_3 \sim AsCl_3 \sim SbCl_3 > PCl_2(OR) > PCl_2R > PCl(OR)_2 > PClR_2 \sim P(OR)_3 > PR_3 \sim AsR_3 \sim SbR_3 \sim SR_2 > RCN > NR_3 \sim OR_3 \sim ROH > H_2NCOR.$

6. Dipyridyl and o-phenanthroline as π Acid Type Ligands.

2,2'-dipyridyl and o-phenanthroline form complexes with metal ions in their normal oxidation states e.g., +2, +3 etc. They are supposed to form strong σ donor bonds, supplemented by moderate degree of π bonding as is the case with all ordinary complexes with similar ligands. However, in contrast to nearly all of the other complexes formed by metal ions in normal oxidation states, the dipyridyl and o-phenanthroline complexes, generally of the type $(ML_2)^{n+}$ or $(ML_3)^{n+}$ where L is dipy or o-phen., can be reduced giving stable species with the same formulas but with charges of only +1, 0 or even -1. This is true for both transition and non transition metals[43,44] e.g., Ti(I), Ti(0), V(II), V(I), V(0), V(-I), Cr(II), Cr(I), Cr(0), Co(0), Cu(I), Fe(0), Zr(0), Mg(0), Be(0) etc.

There is no plausible explanation for the abnormal behaviour of these ligands to stabilise zero or negative oxidation states of the metals. However, the following approaches are worth mentioning although a convincing solution is yet to come.

According to Orgel,[40b] the source of stability of these complexes is due to synergic bonding in which electrons are transferred from the σ orbital on the nitrogen atoms to the empty d (e_g), s and p orbitals of the metal and from the d (t_{2g}) orbitals of the metal to the empty π molecular orbitals of the conjugate system. The acceptor properties of these amines, as indicated by their charge-transfer spectra, e.g., $(Fe(phen)_3)^{2+}$, $(Cu(phen)_2)^+$, do not seem to depend critically on the presence of the aromatic system, but rather than that of the 4 atom conjugate system.

$$HN = CH - CH = NH$$

The argument is not very convincing and moreover, not applicable to non d metal ions.

Another approach which Harzog[44] used in his communications consists of assuming that the ligand, dipy or o-phen, is always formally neutral, thus making the formal oxidation state of the metal equal to whatever charge is carried by the complex as a whole. Using this formulation, it must be assumed that the dipy molecules manifest their π acidity by absorbing electron density from filled metal orbitals into the π antibonding orbitals of the ring system.[39c] This view is perhaps suitable for the transition metals complexes but ofcourse without any direct support from e.s.r. or any other electronic spectral study, but for the non transition metal complexes it seems less appropriate than the following formalism.[45] In this approach, the metal atom is assumed to remain in its normal oxidation state, while the dipy groups are assumed to be reduced to radical anions, $dipy^{\pm}$, with the extra electrons occupying antibonding π^{*} orbitals. When the number of unpaired electrons is found to be less than the number of $dipy^{\pm}$ groups, there is sufficient $dipy^{\pm}$ - $dipy^{\pm}$ interaction to cause coupling of spins. Such formulations are equally applicable to o-phenanthroline complexes.

7. Heterocyclic Amines as Ligands-Some recent studies.

Amongst the nitrogen containing ligands, the complexes of pyridine and related compounds have been extensively studied and this is perhaps due to their ease of preparation and their relatively uncomplicated reaction mechanism. Beech[46] on the basis of magnetic[47] and spectral studies[48] classified these complexes into three main types:

i) Discrete, octahedral ML_4X_2 (L=pyridine or substituted pyridine, X=halogen or pseudo halogen). The X groups are axial.

ii) Discrete, tetrahedral ML_2X_2

iii) Polymeric, octahedral ML_2X_2 with bridging X groups.

Nelson and coworkers,[49a,49b] have studied the configurational equilibria: ML_4X_2 (octahedral) $\rightleftharpoons$ ML_2X_2 (tetrahedral) (L is pyridine or its alkyl substituted analogue), present both in the solution and in the solid state. It was found that the heat of reaction could not be correlated with the basicity but is dependent on the alkyl side chain in L. Thus, for the system $X = I$, $M = Ni^{2+}$; L=pyridine or 3-picoline in chloroform solution, enthalpy changes were + 23.8 and 21.7 Kcal/mol, respectively. Since the 3-methyl substituent directs charge on the 2,4 and 6 positions of the pyridine ring, it was inferred that metal to ligand π bonding must exist in these complexes and was inhibited by the presence of 3-substituent. Also the relative value of the equilibrium constant for the reaction with L=methyl pyridine, compared to L=pyridine, was found to depend on X and it was possible to arrange X in order of π bond (L to M) promotion.

$$NCS^- \ll Cl^- < Br^- < I^-$$

Irving and de Silva,[50] calculated the equilibrium constants for the reaction, $Ag^+ + 2HL^+ = AgL_2^+ + 2H^+$; L = pyridine or substituted pyridine. Jaffe and Doak[51] observed that enhanced stability in these complexes is reflected in changes from σ bonding to π bonding. Mortimor et al.,[52a,52b,52c,] have used differential enthalpimetric analysis to study the thermal decompositions of the complexes of the type ML_nX_2 (M = first transition series metal, L=quinoline, pyridine or a methyl pyridine, X=Cl, Br or I). For the reaction of the type ML_4X_2 (octahedral) $\rightleftharpoons$ ML_2X_2(tetrahedral) + 2L, similar conclusions to those of Nelson (loc.cit.) were reached regarding the extents of σ and π bondings.

Baxendale and George[53] studied the stepwise reaction of 2,2'-dipyridyl with Fe(II) and found that the order of stepwise equilibrium constants normally follows: $K_1(1.6\text{x}10^{-4}\text{mol}^{-1}\text{lit}^{-1}) > K_2 (<10^5) > K_3(2\text{x}10^7)$ and reversal in order for Fe(II)-dipy system is thought to be related to change in spin state of Fe(II)[54] which results in an increase stabilisation of the more substituted species. The overall equilibrium constant for the analogous reaction of Fe(III) with 2,2'-dipyridyl was found to be $1.6\text{x}10^{12}$ $\text{mol}^{-3}\text{l}^{-3}$. The smaller value compared with that obtained for the Fe(II) complex, is not unexpected since no stabilisation due to change in spin state is anticipated.

Dale and Banks[55] summarised the equilibrium constants data between divalent metal ions (except Ag^+) and o-phenanthroline. For the stepwise reactions:

$$M(aq)^{n+} + \text{o-phen.} \rightleftharpoons M(\text{o-phen})^{n+}_{aq}$$
$$M(\text{o-phen})^{n+}_{aq} + \text{o-phen} \rightleftharpoons M(\text{o-phen})^{n+}_{2aq}$$
$$M(\text{o-phen})^{n+}_{2aq} + \text{o-phen} \rightleftharpoons M(\text{o-phen})^{n+}_{3aq}$$

(where M is Ag, Mn, Cu, Zn or Cd, and n=1 (Ag) or 2 for other metals)

In most cases the order of the equilibrium constants was found to be : $K_1 > K_2 > K_3$ except M = Ag, for which K_3 was not recorded and $K_2 > K_1$. This reversal in K_1 and K_2 implies that the substitution sequence is different for Ag^+ than for other metal ions. The substitution in this case may take place either through linear coordination[56,57] in which o-phenanthroline acts as a unidentate ligand resulting in a linear N-Ag-N structure of enhanced stability or by bridging or polymerisation as observed for ethylene-diamine complexes of Ag(I) in the solid state.[58]

8. Linear Coordination of d^{10} Ion.

The formation of linear coordinated species (C.N.1 or 2) is well known in d^{10} configuration. The simple ionic theory, however, predicts that these large ions (Ag^+, Au^+, Hg^{2+}, Cu^+ etc.) should occur in higher coordinate species.[64]

An obvious expla-nation for linear coordination in d^{10} ion involves s-p covalent bonding in preference to ionic bonding. This explanation, has, however, got its exceptions, e.g., Zn^{++} and Cd^{++} where the order of s-p seperation is more or less the same. On the other hand a strong tendency of linear distortion is always associated with small d-s seperation (Table-1) with the result that extensive hybridization of d_{z^2} and s orbitals is made possible in case of Cu^+, Ag^+, Au^+ and Hg^{++} as against Cd^{++}, Zn^{++} and Tl^{+++}. According to Orgel " this is essentially because the mixing of d and s orbitals can lead to a charge distribution strongly favouring a linear arrangement by removing charge from the region between the ligand and the metal ion."[56,57]

TABLE - I.

Energies (e.v.) of lowest d^9s state above the d^{10} state

	Cu^+	Zn^{2+}	Ag^+	Cd^{2+}	Au^+	Hg^{++}	Tl^{3+}
d^9s	2.7	9.7	4.8	10.0	1.9	5.3	9.3

The mechanism of hybridisation of $d_z{}^2$ and s orbitals resulting in linear coordination may be explained on considering the fig.1. The electron pair initially in the d_z^2 orbitals occupies $\psi_1 \frac{1}{\sqrt{2}} (d_{z^2} - s)$ hybridised orbital giving a circular region of relatively high electron density, from which the ligands are somewhat repelled and regions above and below this ring in which the electron density is relatively low. Ligands are attracted to these regions. By further mixing of $\psi_2 = \frac{1}{\sqrt{2}} (d_z 2 + s)$ with the P_z orbital, two hybrid orbitals suitable for forming a pair of linear covalent bonds can be formed.

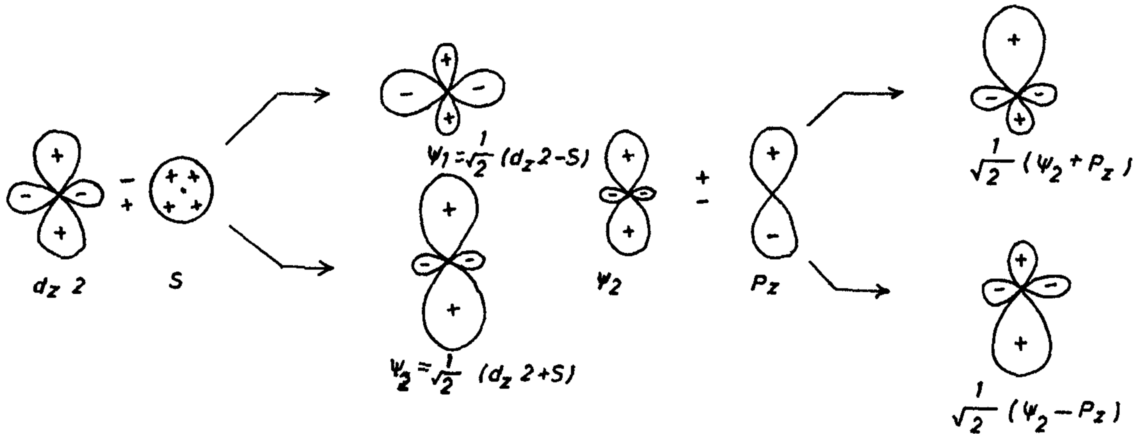


Fig.I

(Cotton and Wilkinson'Advanced Inorganic Chemistry' Wiley Eastern Private) Ltd. (1969) page 1042).

9. Some Aspects of the Chemistry of Copper(I).

The copper is the only member of first transition series giving some stable monovalent compounds. This characteristic is attributed to the higher second ionization potential of copper in comparison to other members[60] as evident from the ionization data given in the table II.

T A B L E - II:

I and II Ionization potential data of the first transition metals:

	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
First I.P.(e.v.)	6.11	6.56	6.83	6.74	6.76	7.43	7.90	7.86	7.63	7.72	9.39
Second I.P.(e.v)	11.87	12.80	13.57	14.65	16.49	15.54	16.18	17.05	18.15	20.29	17.96

Another criterion generally applicable to the phenomenon of the variable valencies in the transition metals, is the overall energy changes occurred during the formation of the compound in a particular valency state.[60] If the (endothermic) ionization energy is sufficiently compensated by the increased (exothermic) solvation energy or electrostatic lattice energy of the solid compound, that particular oxidation state may be favourable.

Copper(I) ion with a $3d^{10}$ configuration is colourless, insoluble, diamagnetic, and with zero ligand field stabilisation energy. The instability of Cu(I) is explained in terms of the following potential data.[61,62]

$$Cu^{+} + e = Cu\ ,\ E^{o} = 0.52V$$

$$Cu^{2+} + e = Cu^{+},\ E^{o} = 0.153V$$

Whence

$$Cu + Cu^{2+} = 2Cu^{+},\ E^{o} = -0.37V;\ K = \frac{(Cu^{2+})}{(Cu^{+})^{2}} = \sim 10^{6}$$

The relative stabilities of Cu(I) and Cu(II) will depend very strongly on the nature of anions or other ligands present, on the dielectric constant of the solution and on the nature of neighbouring atoms in a crystal. The fact that these factors play important role will be exemplified in the discussion in the proceeding paragraphs.

The potential data indicate that cooper(I) ion can exist in aqueous solutions in exceedingly low concentrations, and infact the compound like CuCl, CuBr and CuCN do exist in stable state in water but decompose readily to cupric state due to higher solution and lattice energies of the copper(II) ions.

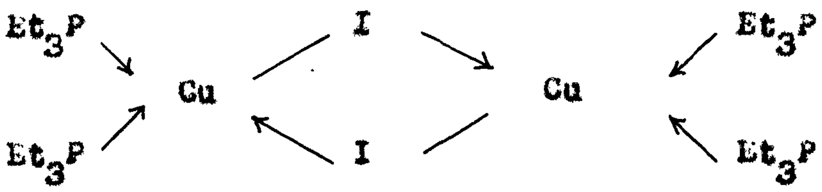
The equilibrium $2Cu^+ \rightleftharpoons Cu + Cu^{2+}$, can be displaced in either direction depending upon the nature of the anion or the ligand introduced and on the dielectric constantsof the media. The equilibrium, $[CuI_2(H_2O)_2]^- \rightleftharpoons [CuI_2(H_2O)_2]$ + e with a large negative E^o value, favoursa Cu^+ state in which iodide forms easily polarized strong covalent bonds. Similarly, in the equilibria :

$(Cu(CN)_2)^- = Cu^{2+} + 2CN^- + e$, $E^o = 1.1$, CN^- favours covalent bond formation and Cu(I) state is favoured. On the other hand, anions that cannot give covalent bonds or bridging groups such as ClO_4^- and SO_4^{--} or ligands having greater affinity for Cu(II) than Cu(I) or Cu(I)-L is less covalent than Cu(II)-L (L is a ligand) e.g., NH_3, ethylene-diamine, hydrazine etc., Cu(II) state is favourable.[61]

Another approach perhaps more logical and convincing regarding the stability of copper(I) complexes is based on the behaviour of Cu(I) ion as a soft acid. Cu(I) being a Lewis acid of large size and low oxidation state will prefer to bind large polarizable ligands such as I^-, R_3P, R_3As etc. (soft bases). As stated by Chatt (loc.cit) in his π bonding theory that soft acids contain loosely held d electrons which can form π bonds by donation to suitable ligands (soft bases). Thus there will always be tendency of copper(I) ions to form $d_\pi - p_\pi$ or $d_\pi - d_\pi$-bonds to ligand atoms with empty or vacant d orbitals, e.g., N, S, P, As, I etc. Infact copper(I) forms stable complexes with phosphines, arsines, thiourea, iodide and unsaturated ligands such as CO, C_2H_2, C_2H_4, propylene, butylene, butadiene etc.

The formation of halo complexes of copper(I) is another characteristic associated with copper(I) halides. Copper(I)halides are highly insoluble but, however, may be made soluble in presence of the excess of halide ions. Sufficient amount of work has been done on the behaviour of copper(I) halides in alkali halide solutions.[63a,63b,63c] The compounds more extensively studied are cuprous chloride and cuprous bromide. The complex species like CuX_2^-, CuX_3^{2-}, CuX_4^{3-} ($X = Cl^-$, Br) are found to exist in solutions. With the higher concentrations of halide ions the lower species such as CuX_3^{2-} form the main bulk.[64] Recently, the behaviour of copper(I) iodide in acetone-potassium iodide medium was studied and the main species present in the solution was found to be CuI_2^-.[65]

An interesting aspect related to the coordination chemistry of copper(I) is the lower coordination number exhibited by copper(I) complexes. In general, Cu^+ ion usually forms complexes with a coordination number one or two (NH_3, halides, pyridine and substituted pyridines, CN^- etc.), less commonly with a coordination number of three (thiourea) and the examples of tetra coordinated copper(I) are not very common (tris phosphines, tris arsines, dipy etc.). The small coordination number in Cu(I) complexes is related to the chracteristic of d^{10} ion with large size and low oxidation state favouring a linear coordination due to small d-s separation (Orgel, loc. cit). However, more interesting is the observation that there is always a tendency for copper(I) ion to achieve its coordination maximum.[66] There are numerous examples in literature to illustrate this characteristic of copper(I) complexes. The complex, $(C_2H_5)_3$ As CuI in which the apparent coordination number is two, the molecular weight determination indicates it to be a four fold polymer $(Et_3$ As $CuI)_4$.[67] The crystal structure of this complex consists of four copper atoms disposed at the apecies of a regular tetrahedron, in such a way that each copper atom is itself surrounded tetrahedrally by three iodine atoms (each shared with copper atoms) and an arsine molecule. Similarly, the compound CuI 2P $(C_2H_5)_3$ described by Argulow is a tetramer with the following structure.[66]



10. Some Aspects of the Chemistry of Ni(II).

The complex formation tendency of Ni(II) is well known. The main stereochemical species of the Ni(II) complexes may be described in terms of octahedral (C.N-6, para-magnetic μ_{eff} =3.0-3.3), tetrahedral (C.N-4, para-magnetic, μ_{eff}=3.45-4.0) and square planar (C.N-4, diamagnetic) structures. Pentacoordinate (diamagnetic) trigonal bipyramidal form is also known. All these complexes have characteristic electronic spectra and which can be interpreted in terms of d orbitals splitting under a particular ligand field usually governed by the spectrochemical series, the series for the common ligands is: $I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS < py \sim NH_3 < en < dipy < o\text{-}phen < NO_2^- < CN^-$ and is arranged according to the capacities of the ligands to cause splitting.[68]

Considering the distortion of d^8 system in a tetragonally distorted octahedral field bringing about a singlet-triplet spin state isomerism. The theoretical interpretation of this type of behaviour was given by Maki[69] for a weak ligand field and by Liehr and Ballhausen[70] for a strong ligand field.

The first convincing example of spin state isomerism was given by Carlin et al.,while studying dichloro tetrakis (N-N-diethyl thiourea) Ni(II) complex.[71] The complex is spin paired below 194°K but attains partial magnetism reversibly as the temperature is raised. The corresponding Br^- and I^- are diamagnetic at room temperature but Br^- becomes slightly paramagnetic at 373°K. The relative abundance of the triplet state among the two halides is that predicted by Maki and Ballhausen, and Liehr treatments of Ni(II) in D_{4h} symmetry, since the separation between the singlet and triplet states is the least for Cl^- which lies closest in ligand field strength to the substituted thioureas. Several other examples of spin isomerism are provided by $Ni(VPP)_2\,(NO_3)_2$[72] (where VPP is $P(Ph)_2CH{=}CHP(PH)_2$)

and Ni(TAAB)X_2[73a,73b] (where TAAB is tetra benzo (b,j,n) 1,5,9, 13-tetra azacyclohexadecane) complexes.

The presence of Ni(II) with two different stereochemistries in a unit cell of a complex molecule has been reported in a number of cases. The complexes exhibit two types of behaviours, one in which the metal ion has the same coordination and same set of attached ligands but different stereochemistries and other in which the metal ion produces two different coordination numbers and hence different stereochemistries within the unit cell.[74]

Kilbourn, Powell and Derbyshire[75] isolated two crystalline forms of the complex compound dibromo bis (benzyl diphenyl phosphine) Ni(II), one red and diamagnetic, the other green with two unpaired electrons (μ_{eff}=2.7 B.M.). On the basis of X-ray studies of green complex, they showed that there are 4-coordinated atoms in the unit cell, one Ni(P(Ph.CH_2) Br_2 is square planar and two Ni(P(Ph.CH_2) $Ph_2)_2$ Br_2 units are tetrahedral. When allowance was made for only two of the three Ni atoms being high spin, the moment of the tetrahedral Ni atoms was calculated to be 3.3 B.M., in good agreement with the values generally observed for nickel in pseudo tetrahedral environment. Since the square and tetrahedral structures of a complex differ chiefly in the angles subtended by ligand atoms at the metal atoms, Powell[75] suggested the term interallogon (allos-different, gonia-angle). An example of the second type of isomerism is provided by the yellow form of the Lifschilts compound, bis-(meso-stibene diamine)

Ni(II) dichloroacetate.2/3 C_2H_3OH, 4/3 H_2O. The magnetic, spectral and x-ray studies of the complex indicate a magnetic moment of 2.58 B.M. at room temperature and the unit cell contains both 6 -coordinate and 4-coordinate Ni atoms in the ratio 2:1.[76a,76b]

A large number of Ni(II) complexes which are diamagnetic in the solid state are found to be paramagnetic when dissolved in a variety of solvents, without decomposition. Such a phenomenon was explained on the basis of solute-solvent interactions thus depending upon the character of the solvent. In most polar solvents, a strong ligated atom such as nitrogen or oxygen is present and this may exercise a moderate perturbation with a resultant change in the coordination number and spin state of a particular species.[77]

Several diamagnetic bis (salicylaldimine) Ni(II) complexes were found to be fully paramagnetic (μ_{eff}=3.0-3.2 BM) in pyridine solution, a phenomenon which Wills and Mellon[78] attributed to the formation of 6-coordinate pyridine adducts. Basolo and Matoush, were later on able to isolate the pyridine adducts. Similar behaviour was observed in water, py and acetonitrile for the nickel complexes of the macro-cyclic ligand.[79] It was suggested that the origin of paramagnetism in all these cases is solvent dependent and may be represented by the equilibria:

$$\text{Solvent} + \text{planar (diamagnetic)} \rightleftharpoons \text{pseudo octahedral(paramagnetic)}$$

Later studies particularly by Sacconi[80,82a,82b] and Holm[81] and their coworkers conclusively proved that solvent is not the necessary condition for the development of paramagnetism. Sacconi[90] on the basis of dipolemoment studies and Holm[81] on electronic spectral grounds showed that bis-(N alkyl-salicyaldimine) Ni(II) complex when dissolved in inert solvent like benzene, no tetrahedral species are present in significant concentrations although the solution is paramagnetic. Sacconi and coworkers[82a,82b] further observed that besides in solutions, paramagnetism also occurs in the molten state. On the basis of these detailed investigations they arrived at the conclusion that experimental evidence can only be accounted by the two models (i) molecular association (solute-solute interaction) and (ii) planar-tetrahedral equilibria.

The studies on Ni(II)-N-n-alkyl salicylaldimine complexes, Ni(II)-N-aryl substituted complexes[88,89] and Ni(II)-β diketone complexes[90,91] provide some of the best examples related to anomalous magnetic behaviour of Ni(II) complexes arises by solute-solute interaction. An early indication that the anomalous magnetic moment of bis(N-methyl salicyldimine) Ni(II) in solution might be due to molecular association was provided by the isolation of a coloured, paramagnetic (μ_{eff}=3.2 B.M.) form of the complex by heating the diamagnetic form to 150-200°C.[83,84] In contrast to diamagnetic isomers, the paramagnetic form was observed to have a very low solubility in organic solvents. This suggested that 6-coordination is attained by the stacking of the planar units in a manner that the oxygen atoms of adjacent molecules interact axially with the metal ions.[83,85,86] In terms of solute-solute interactions Ni(II)-n-alkyl salicylaldimine complexes have been studied to the greatest extent. The evidence for solute association was provided by the observations: simultaneous increase in magnetic moment with increasing concentration, n.m.r. contact shifts, molecular weight in chloroform and benzene as well as by spectral data.[81] Solute association in solutions of the higher N-n-alkyl substituted analogues is apparently less, these being monomeric and diamagnetic at ordinary temperatures.[87] N-methyl complex is infact the best example of solute-solute interaction model.

As stated above the main reasons for abandoning the mechanism involving the equilibria planar(diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) in solution were the paramagnetism shown by bis-(N-methyl salicylaldimine) Ni(II) in non-conducting solvents and absence of tetrahedral species. One great difficulty in regard to the conclusive recognition of the presence of planar tetrahedral equilibria for solutions of diamagnetic complexes for many years was the fact that the stereochemical species had not been characterised spectrally till 1959.[92] However, with the isolation and characterisation of planar and tetrahedral forms of (benzyldiphenyl phosphine) Ni(II) halides and related complexes, the planar $\rightleftharpoons$ tetrahedral equilibria model was again revived.[93-95]

These complexes exhibit moments between 0 and 2.9 B.M. in benzene solutions. Although the planar $\rightleftharpoons$ tetrahedral model failed to explain the paramagnetism of bis-(N-methyl salicylaldimine) complex in solution, however, it was found to be suitable for accounting some of the properties of N-aryl substituted salicylaldimines complexes and infact the paramagnetism of α-branched N-alkyl substituted complexes appears predominently due to the presence of tetrahedral species.[96] Holm and Chakravorty[97] studied a series of bis-(o-hydroxynaphthaldimine) nickel(II) complexes and observed their magnetic behaviour as a function of ring substituent and R (alkyl) group, both in solid and in solution. The anomalous moments in solution have been found to arise from a planar $\rightleftharpoons$ tetrahedral equilibria. Spin density calculations were performed and thermodynamic data were obtained by the use of n.m.r. contact shift methods. A number of similar examples of Ni(II) complexes with nitrogen and/ or oxygen donor systems showing configurational equilibria involving planar $\rightleftharpoons$ tetrahedral and in a few cases octahedral $\rightleftharpoons$ square planar via 5-coordinate paramagnetic form, have been cited in recent chemical literature.[98,99,100]

A brief survey of the recent chemistry of Ni(II) complexes described above leads undoubtly to believe that the anomalous magnetic behaviour of Ni(II) complexes is one of the most fascinating problems in coordination chemistry. The mechanism namely, spin state isomerism, solvent-solute and solute-solute interactions and configurational equilibria are although quite capable to explain the observed facts but, however, they are subjected to change as new informations are uncovered or new concepts in this area of chemistry are developed.

11. Chemistry of Palladium(II) Complexes:

At this stage it will be worthwhile to discuss briefly the stereochemistry of Pd(II) complexes and to give certain salient features for comparison to its lower analogue, Ni(II).

Palladium(II) and Nickel (II) have similar chemical characteristics. There is extensive tendency to form square planar complexes although Pd(II) is kinetically less labile than Ni(II) (Pt(II) is inert) as is evident from numerous kinetic data.[101,102] Ni(II) is commonly six coordinate, Pd(II) like its Pt(II) analogue is commonly 4-coordinate square planar and only in special circumstances five and six coordinate species are formed. The fact that the tendency to form square planar complexes increases from Ni(II) to Pt(II) may be attributed to increase π bond strength in heavier metals due to the ability of their more extended orbitals (d_{xy},d_{zx},d_{yz}) to overlap better with ligand π orbitals.[103]

Although Pd(II) species are predominently square planar, there are indications that additional weaker bonds may be formed in the vacant octahedral sites. In solutions, the vacant sites may be occupied by solvent molecules,[104] and in catalytic reactions of these metal complexes or in ligand displacement reactions, initial attack presumably occurs in the axial positions. The dimethyl glyoxime complex, $Pd(DMGH)_2$ is an example of axial interactions in crystalline compounds between stacked square units. Unlike Ni(II) complex, the Pd(II) complex dissolves in bases again indicating additional coordination.[105]

$$Pd(DMGH)_2 + OH^- = \left[Pd\ (DMGH)_2OH^-\right]$$

There is also evidence of interaction of certain atoms of ligands bound to the metal with axial positions. The crystalline complex, trans-PdI_2 (PMe_2Ph_2) in which the α hydrogen of the phenyl groups of the coordinated phosphine occupy axial positions, the trans axial position being occupied by an iodine atom of an adjacent molecule[106,107] with the formation of quasi 7 coordination complex. Basolo and Baddley[108] studied the substitution reactions of $[Pd(Et_4dien)\ Cl]^+$ with various reagents and found that the complex reacts rather slowly ($t_{\frac{1}{2}}$ =6 min), an example of the steric hind-rance, the ethyl groups block off the axial positions of the plane to give a quasi octahedral structure a position which is frequently observed in chloro ammine Co(III) substitution reactions whereas the corresponding reactions with unsubstituted $(Pd(dien)\ Cl)^+$ are exceedingly rapid.

Like Ni(II) but less frequently, complexes with a trigonal bipyramidal structure have been obtained for Pd(II). Tris (o-diphenyl arsinophenyl) arsine (QAS), for example, gives the salts of the type $Pd(QAS)\ X)^{+}X$ which act as 1:1 electrolyte in solution.[109] With bis (o-diphenyl arsinophenyl) phenyl arsine (TAS), a 5 coordinate complex $PdI_2(TAS)$ is obtained but this dissociates in nitro benzene to give $(Pd(TAS).^{++}$ [110]

12. Coordination Chemistry of Rare Earth Ions.

The coordination chemistry of rare earth metal ions is not extensively investigated while compared to d block transition metal ions, this is evident from the scanty references available in chemical literature. Prior to 1950, the only approach to the coordination chemistry of rare earths was in connection with the separation of lanthanide ions from each other. However, during the last ten years or so considerable interest has been shown in this area of coordination chemistry due to the advancements in analytical techniques and enrichment in the field of theoretical chemistry in general.

Compared to d-type transition metals, the lanthanides form a few complexes, and are obtained only with strong chelating agents containing highly electronegative donor atoms e.g., oxygen. So it is not surprising to find a majority of rare-earth complexes belonging to oxygen containing ligands. The fact that the electronic configuration does play an important role in the rare earth complex formation can be exhibited by the following considerations.

The formation and stability of a coordination compound of a 3d metal ion are related to the participation of the d electrons in the metal-ligand bond through hybridisation of metal electronic orbitals and overlapping of the hybrid orbitals with the appropriate ligand orbitals. The 4f electrons present in rare earth metal ions are effectively shielded by electrons in subsequent 5s and 5p orbitals and thus unable to interact with ligand orbitals. If rare earth ligand bonding is to occur, the hybridisation must involve normally with unoccupied high energy 5d, 6s and 6p orbitals and hybridisation of this type can be expected only with strong coordinating ligands.[111] Such type of bond formation should be highly electrostatic in character and the complex species formed by these cations (rare earth) should resemble more closely with those of alkaline earth metal ions, Ba^{2+}, Ca^{2+} and Sr^{2+} rather than that derived from the d block transition metal ions.[111-113] The absence of significant interaction between ligand and 4f orbitals is supported by magnetic,[111,114,115,116] and spectral measurements.[114,117,120] It has been observed that complexing groups have only nominal effects upon the magnitude of the permanent magnetic moments of the tripositive ions or upon the positions of their sharply defined, characteristic absorption bands in the ultraviolet and visible regions. Indirectly this is evidence for the ionic model, as is also the absence of π bonding. On the other hand, the possibility of covalent interactions cannot be completely excluded.

The lanthanide ions, in any oxidation state are large (radii:0.85-1.06) compared with those of transition elements (e.g., Cr^{3+} and Fe^{3+} with radii of 0.60-0.65Å) forming most stable complexes. Strongly electrostatic attractions between rare earth metal ions will, therefore, be small in comparison to d block transition metals, but will increase in magnitude from cation to cation for a given oxidation state as cation radius decreases, and for a given metal as cation charge increases. The said view point is confirmed by the observations: (a) the relatively small overall stabilities of the known complex species (b) generalised increase in stability with decreasing size of positive cation for species containing a common ligand and (c) the increase in stability for a given ligand with cation charge (e.g., Ce^{3+} to Ce^{4+}, Eu^{2+} to Eu^{3+}).

Summing up the above factors it may be concluded that the rare earths have reduced tendency to form complexes, the situation is here comparable to that existing in alkaline earth metal chemistry, where possible coordinated bonds are not strong enough to cause the metal ion to leave the solvation layer and enter into the complex.[121] The 'chelate effect' overcomes this deficiency as is evident from the study of stable complexes of rare earths where a large majority belongs to chelate complexes.

Chelating agents increase the free energy change of the reaction through an entropy effect, a common feature of all chelation processes. The fact that entropy effect[122] is operative in rare earth metal chelate is substantiated by a number of thermodynamic measurements[123-127] which show that in many cases the entropy contribution of the free energy change of the process is the determining factor and the enthalpy term is very small or even opposed to the formation of the complex.

A big majority of rare earth metals chelates are formed by chelating agents containing oxygen as a donor atom and in a few cases nitrogen donor is also found to be active. The chelates with β diketone series of ligands such as acetyl acetone, dibenzoyl methane and thionyl trifluoro acetone have been much studied, they have the stoichiometry $M(\beta \text{ diketone})_3$ and generally crystallised with solvents. The chelate species in these cases is usually inner complex type. The water soluble chelates formed by hydroxy acids, aminoacids and polyamine polycarboxylic acids are extensively reported. The latter give simaltaneously more than a single metal chelate ring involving a given metal ion, are most stable and probably the best characterized species. Although most of the chelates contain tripositive rare earth metal ions but a significant number are also derived from Eu(II) and Ce(IV), the two tripositive ions that are most stable in aqueous solution. These complexes have 6-coordinated octahedral structures in which coordination numbers greater than six, are also reported.

The tripositive rare earth ions have little tendency to form halocomplexes.[128] The fluoro salts containing tetra positive Pr, Nd, Tb and Dy are of particular importance in exemplifying the stabilization of this oxidation state by highly negative charged F^- ions.[129]

Due to the high positively charge character the lanthanides have little or no tendency to form complexes with π bonding ligands. The absorption spectra of solutions of certain rare earth metal laurates in mesitylene have been interpreted[129] as indicating some association of the cations with hydrocarbon through π electrons supplied by the latter, but there is no confirmatory evidence. Similarly, complexes with o-phenanthroline and 2,2'-dipyridyl are also known such as, $[\mathrm{phen_2MCl\ (H_2O)\ Cl_2}]$, $[\mathrm{(Phen_3M)\ (SCN)_3}]$ and $[\mathrm{dipy_2M(H_2O)_n}]$.[132] The cyclopentadiene gives salts cyclopentadienides such as $[\mathrm{M\ (cp)_3}]$ and $[\mathrm{M\ (cp)_2Cl}]$.[130,131]

There are numerous experimental evidences[133] which indicate the formation of complex species in which the coordination is larger than six. Thus the solid compound, $\mathrm{M(BrO_3)_3\ (H_2O)_9}$ contains the grouping $\mathrm{M(H_2O)_9^{3+}}$, which has a trigonal prismatic geometry with the water molecules opposite the re-ctangular faces.[134] The compound, $\mathrm{M\ (SO_4)_3.9H_2O}$ contains the grouping $\mathrm{M(H_2O)_6O_6^{9-}}$, which amounts to two interpenetrating prisms and requires a coordination number of eight.[135] The formation of $\mathrm{M(diket)_4}$ as the piperidine salt requires a coordination number of atleast eight.[136] The ability of certain complex species to add additional ligands e.g., to form $M(HEDTA)(IMDA)$,[137] $M(NTA)_2$[138] or $M(HEDTA)(OH^-)$ [139,140] also indicate coordination numbers larger than six. The insolubility of some lanthanide tropolonate also suggests cross linkages leading to coordination number exceeding six.[141] Recent crystal structure studies indicate ten coordination in the compound $HM(EDTA)(H_2O)_4 \cdot 3H_2O$[142,133], nine coordination in the ion $[La(EDTA)(H_2O)_3]^-$[142,133] and eight coordination in $[Eu(acac)_4]^-$.[143]

Problem Under Investigation:

The thesis deals with the syntheses, structural studies and behaviour in solution of some new complexes of transition metals.

The complexes synthesised are those of copper(I), nickel(II), palladium(II) and some rare earth metal ions with nitrogen and sulphur containing ligands. The nitrogen containing ligands include π delocalised systems such as pyridine and substituted pyridines e.g., picolines, lutidines, quinolines, acridine etc. The potential π acceptor ligands 2,2'-dipyridyl and o-phenanthroline have also been used in these studies. Amongst the sulphur containing ligands only neutral unidentate ligands, thiourea and substituted compounds e.g., isopropyl, benzyl, naphthyl, diphenyl, allyl and o-tolyl thioureas have been used for the present investigations. Some complexes of 2-mercaptobenzthiazole with copper (I) and rare earths have also been synthesised.

The main emphasis has been laid on the mixed ligand complexes of Cu^{+}, Ni^{2+} and Pd^{2+}. Some of the systems in this field have not been sufficiently explored especially those of copper(I). The studies in solution have been carried out with these mixed ligand compounds and detailed mechanisms have been put forwarded.

The kinetic studies are based on the potentiometric and spectrophotometric measurements and wherever possible the stereochemical evidence has been provided by the synthesis/or the preparation, of a particular substituted complex by adopting various paths.

The structural aspects in these studies are limited to the investigations on the geometry and the bonding in these complexes.

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CHAPTER - I:

COORDINATION COMPOUNDS OF CUPROUS CHLORIDE AND IODIDES WITH HETEROCYCLIC AMINES.

Coordination Compounds of Cuprous Chloride and Iodides with Heterocyclic Amines.

Pyridine and related compounds have been found to be potential ligands for complex formation due to the presence of highly nucleophilic heterocyclic nitrogen. The coordination takes place either through σ bond or $p_{\pi} - d_{\pi}$ bond and complex ion formation with metals both in their higher and lower oxidation states thus becomes possible. A survey of the existing literature would, however, reveal that reactions of ligands ranging from simple pyridine to complex many membered alkaloids[9,10] with normal valence ions, viz., Ni(II)[1,2], Cr(II & III)[3,4], Cu(II)[5], Ag[6], Rh[7], Ir[8] etc., have been studied, but very little has been done to know about the nature of the complexes formed with metals in their lower oxidation states. Investigations in these directions were considered worth undertaking. For this purpose copper(I) was chosen as a typical example.

The scope of the work on the coordination chemistry of copper(I) is limited due to the instability of copper(I)compounds as well as due to their insolubility and smaller affinity for these ligands. The meagre references available on the complexes of copper(I) speak of the inadequacy of the work done in this field and therefore, more systematic and extensive studies are warranted in this direction. The work described in the following pages deals with the studies on copper(I) complexes with a number of heterocyclic amines, using method of potentiometric titrations (with a $Cu^{++} + e \longrightarrow Cu^{+}$ couple), chemical analysis, magnetic measurements and I.R. studies.

EXPERIMENTAL:

A. Copper(I) Chloride-Heterocyclic Amines Complexes

a) Preparation of the complexes:

To a solution of cuprous chloride in potassium chloride an excess of amine (in acetone) was added with constant shaking. The product so obtained settled readily, was filtered on a sintered funnel, washed several times with small aliquots of distilled water and finally with absolute alcohol. The product was then dried in vacuo in a nitrogen atmosphere.

b) Composition and Properties of the Complexes:

Magnetic susceptibility measurements were carried out at 30°C with a Gouy magnetic balance with temperature adjustments. All the complexes were found to be diamagnetic

Unstable Complexes*

1. CuCl - pyridine : Light yellow changes to green
2. CuCl - 2,picoline: Light yellow changes to green
3. CuCl - 4,picoline: Yellow changes to green
4. CuCl - isoquinoline: White changes to green

* Composition determined by potentiometric method

Stable Complexes*

1. CuCl-3,picoline, Cu(3 pic)Cl. Deep yellow product, decomp. temp. 119°C. Calcd. for C_6H_7N CuCl: C-37.5, H-3.6, N-7.3, Cu-33.1, Cl-18.5. Found: C-37.1, H-3.2, N-7.3, Cu-33.2, Cl-18.4.

2. CuCl-2,4 Lutidine, Cu(2,4L)Cl. Light yellow product, decomp.temp. 211°C. Calc. for C_7H_9CuCl: C-40.8, H-4.4, N-6.8, Cu-30.8, Cl - 17.2. Found: C-40.4, H-4.2, N-6.7, Cu-30.9, Cl-17.1.

3. CuCl-Quinoline, Cu(Q)Cl. Yellow product, decomp.temp. 242°C. Calc. for C_9H_7N CuCl: C-47.3, H-3.1, N-6.1, Cu-27.85, Cl-15.6, Found: C-46.9, H-3.0, N-6.1, Cu-27.7, Cl-15.5.

4. CuCl-Acridine, Cu(Ac)Cl. Red crystals, decomp.temp. 210°C. Calc. for $C_{13}H_9N$ CuCl: C-56.1, H-3.2, N-5.0, Cu-22.8, Cl-12.8. Found: C-55.4, H-3.0, N-4.9, Cu-22.4, Cl-12.6.

5. CuCl-Piperidine, Cu(pip)Cl. Red product, decomp.temp. above 360°C. Calc. for $C_5H_{10}N$ CuCl: C-32.8, H-5.5, N-7.65, Cu-34.7, Cl-19.4, Found: C-32.5, H-5.3, N-7.7, Cu-34.8, Cl-19.5.

*Abbreviations used for the ligands: py-pyridine, pic-picoline, L-lutidine, Q-quinoline, I.Q-isoquinoline, Ac-acridine, pip-piperidine. C,H and N analyses were carried out by Australian Microanalytical Service, Division of Organic Chemistry, University of Melbourne, Australia. Copper was estimated iodometrically while chlorine was determined gravimetrically as AgCl.

Reagents

Cuprous chloride was prepared by the method recommended by Keller and Wycoff.[11] Solutions of copper(I) chloride were prepared in concentrated potassium chloride and were estimated gravimetrically by precipitating Cu^+ ions as cuprous thiocyanate.

Pyridine (Baker analysed reagent), 2,3 and 4 picolines, 2,4 and 2,6 lutidines (all E.Merck Products) quinoline and isoquinoline (light products) and acridine (B.D.H. product) were used. The solutions of the reagent were prepared in doubly distilled water, and where the reagents were insoluble in water, water-acetone and water-ethanol mixtures were used as solvents.

Potentiometric Measurements:

Potentiometric titrations were performed by using a Pye precision potentiometer (type 7568), employing saturated calomel and Pt, as reference and indicator electrodes ($Cu^+ \rightleftharpoons Cu^{++} + e$ couple), respectively.

Direct titrations (CuCl in the cell) were performed using varying concentrations of amines and cuprous chloride solutions. Concentrations of some of the solutions (CuCl and amines) together with the points of inflexions, obtained from the potentiometric titration curves are given in table 1.

TABLE -1:

Potentiometric titrations of copper(I) chloride and heterocyclic amines.

Original conc. of Cu^+ (in the cell)	Conc. of amine added (in moles/litre)	Vol. of amine consumed at the point of inflexion.
10 cc(1×10^{-1}M)	5.7×10^{-2}(3,pic)	17.1 cc
10 cc(8.77×10^{-2}M)	2.73×10^{-2}(2,6L)	4.1 cc
10 cc(8.77×10^{-2}M)	7.11×10^{-2}(Ac)	9.8 cc
10 cc(8.77×10^{-2}M)	1.12×10^{-2}(pip)	7.2 cc

(Vide Fig.1)

B. Copper(I) Iodide-Heterocyclic Amines Complexes

Solution of cuprous iodide was prepared by dissolving the reagent in a concentrated solution of KI. The resulting cuprous iodide was then treated with an excess of amine (in ethanol), the complex precipitated and settled readily. The product was filtered, washed several times with distilled water and ethanol, and dried in vacuo over CaO. The dried product was then dissolved in acetone and after a few days, crystals appeared which were separated from the supernatant liquid, soaked with filter paper and dried in vacuuo. In some cases several crystallisations were required.

Composition and properties of copper(I) iodide complexes.

All the complexes were found to be diamagnetic, soluble in organic solvents but insoluble in water.

Analytical data[*]

1. CuI-pyridine, Cu(py)I. Amethyst crystals, decomp. temp. 190°C. Anal. Found for C_5H_5N CuI: C-22.1 (22.3), H-2.2 (1.8), N-5.0 (5.2), I-46.8 (47.1) and Cu-23.4 (23.6).
2. CuI-2,picoline, Cu(2,pic)I. Light brown crystals, decomp. temp. 155°C Anal. Found for C_6H_7N CuI: C-24.8 (25.4) H-2.5 (2.5), N-4.5 (4.9), I-44.3 (44.8) and Cu-22.4 (22.4).

3. CuI-3,picoline, Cu(3,pic)I. Light brown crystals, decomp.temp. 150°C. Anal. Found for C_6H_7N CuI: C-24.7(25.4), H-2.2(2.5), N-4.6(4.9), I-44.2(44.8) and Cu-21.7(22.4).
4. CuI-4 picoline, Cu(4 pic)I. Dark brown crystals, decomp. temp.240°C. Anal. Found for C_6H_7N CuI: C-24.7(25.4), H-2.3(2.5), N-4.6(4.9), I-44.1(44.8) and Cu-22.1(22.4).
5. CuI-2,4 lutidine, Cu(2,4L)I. Light buff crystals, decomp.temp. 145°C. Anal. Found for C_7H_9N CuI: C-27.6(28.2), H-2.8(3.0), N-4.6(4.8), I-41.8(42.7) and Cu-20.7(21.0).
6. CuI-2,6 lutidine, Cu(2,6L)I. Brownish black crystals, decomp.temp. 145-150°C. Anal. Found for C_7H_9N CuI: C-27.7 (28.2), H-2.8(3.0), N-4.3(4.8), I-41.6(42.7) and Cu-20.7 (21.0).
7. CuI-quinoline, Cu(Q)I. Light yellow product, decomp.temp. 155°C. Anal. Found for C_9H_7N CuI: C-32.7(33.8), H-2.3(2.2) N-4.1(4.4), I-39.6(39.7) and Cu-19.6(19.9).
8. CuI-isoquinoline, Cu(I.Q)I. Dark yellow product, decomp. temp.204°C. Anal. Found for C_9H_7N CuI: C-32.2(33.8), H-2.3(2.2), N-3.9(4.4), I-39.[illegible](39.7) and Cu-19.7(19.9).
9. CuI-piperidine, Cu(pip)I. Dirty white product, decomp. temp.175°C, Anal. Found for $C_5H_{10}N$ CuI: C-20.8(21.9), H-3.6(3.6), N-4.7(5.1), I-44.8(45.9) and Cu-22.8(23.1).
10. CuI-acridine, Cu(Ac)I. Brick red crystals, decomp. temp.335°C, Anal. Found for $C_{13}H_9N$ CuI: C-38.1(40.5), H-2.2(2.3), N-3.4(3.8), I-34.2(34.3) and Cu-16.9(17.2).

11. CuI-o-phenanthroline, Cu(o-phen)I. Red crystals, decomp.temp.260°C. Anal. Found for $C_{12}H_8N_2$ CuI: C-37.1 (38.9), H-2.3(2.2), N-7.7(7.56), Cu-17.1(17.1), I-33.9 (34.2).

12. CuI-2,2' dipyridyl, Cu(dipy)I. Dark pink crystals, decomp.temp.270°C. Anal. Found for $C_{10}H_8N_2$ CuI: C-34.7 (34.6), H-2.5(2.4), N-7.9(8.1), Cu-18.4(18.4), I-36.7 (36.6).

*Calculated values are given in brackets.

C,H and N analyses were carried out by Australian Microanalytical Service, University of Melbourne, Australia. For copper and iodide estimations, the complex was dissolved in dil. HNO_3 and estimations of copper and iodine were preformed separately. Copper was estimated iodometrically by first precipitating as copper sulphide and dissolving the latter in dil. HNO_3. Iodide was estimated as AgI.

Infra red Spectra of Copper(I)-Heterocyclic Amines Complexes.

Apparatus: Infra red spectra of copper(I) chloride-heterocyclic amines complexes were recorded with a double beam Perkin Elmer spectrometer, type 221, equipped with NaCl gratings and using nujol mull. The spectra of copper(I) iodide-heterocyclic amines were recorded with a Perkin Elmer '237' recording spectrometer, employing the standard KBr technique using spectral grade KBr.

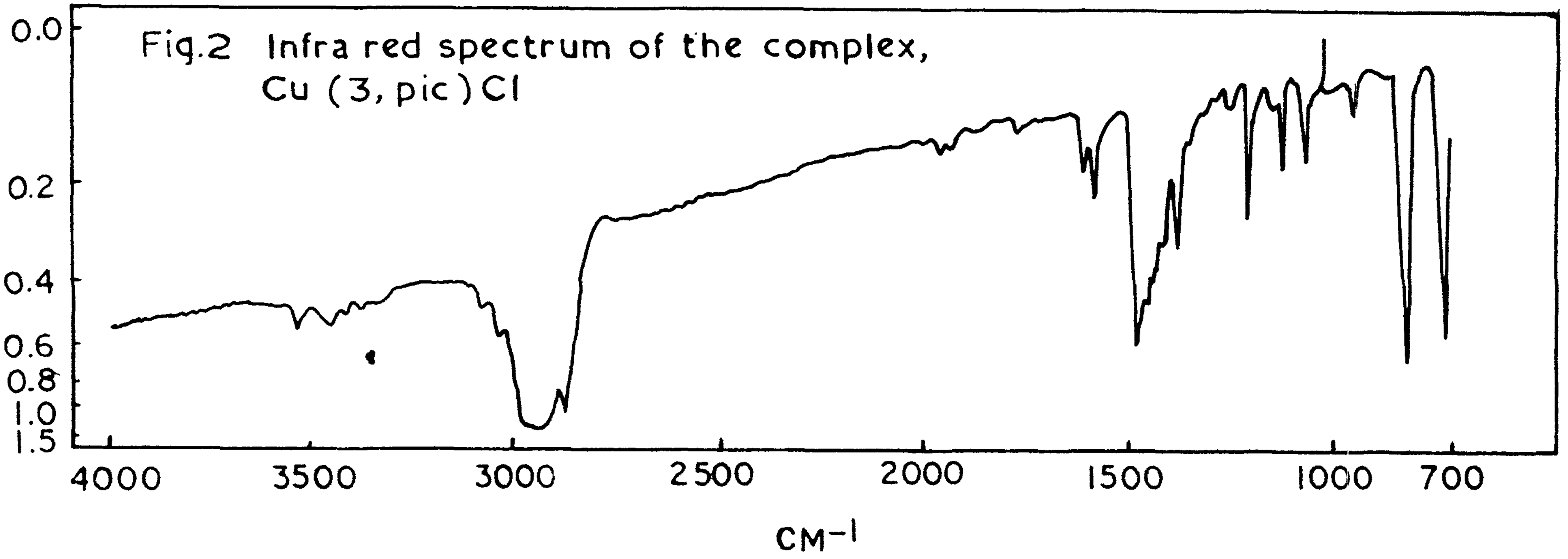

Fig.2 Infra red spectrum of the complex, Cu (3, pic) Cl

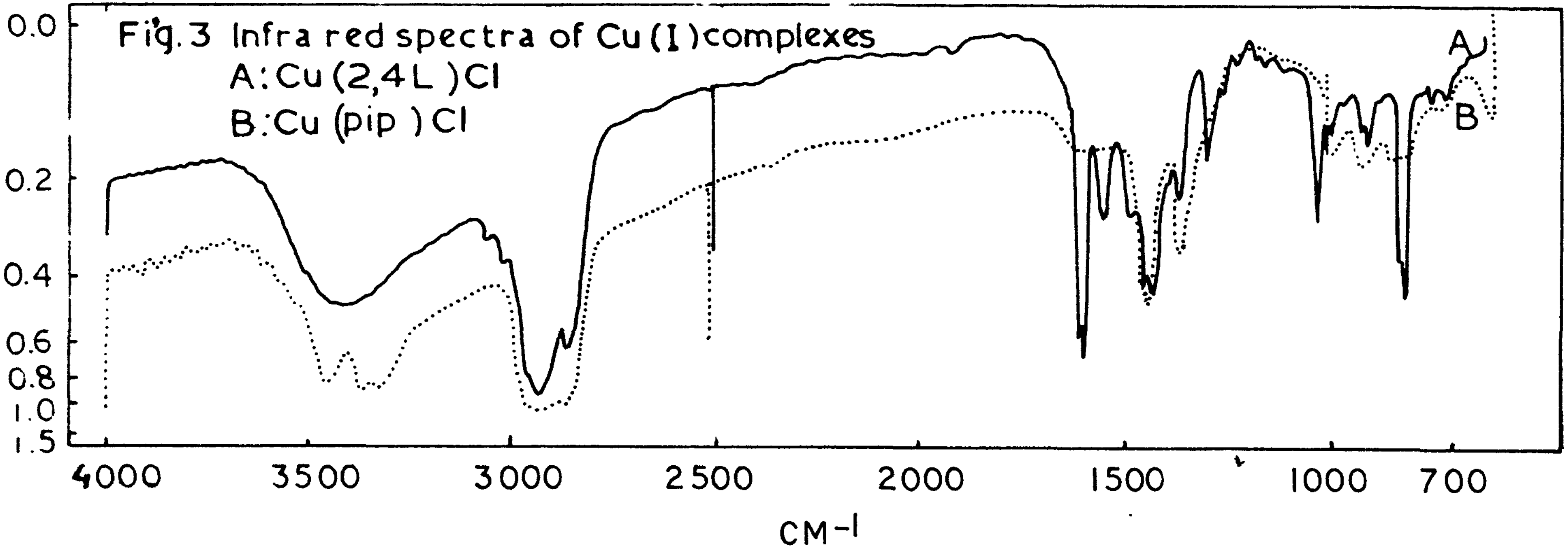

Fig.3 Infra red spectra of Cu (I) complexes

A: Cu (2,4L) Cl

B: Cu (pip) Cl

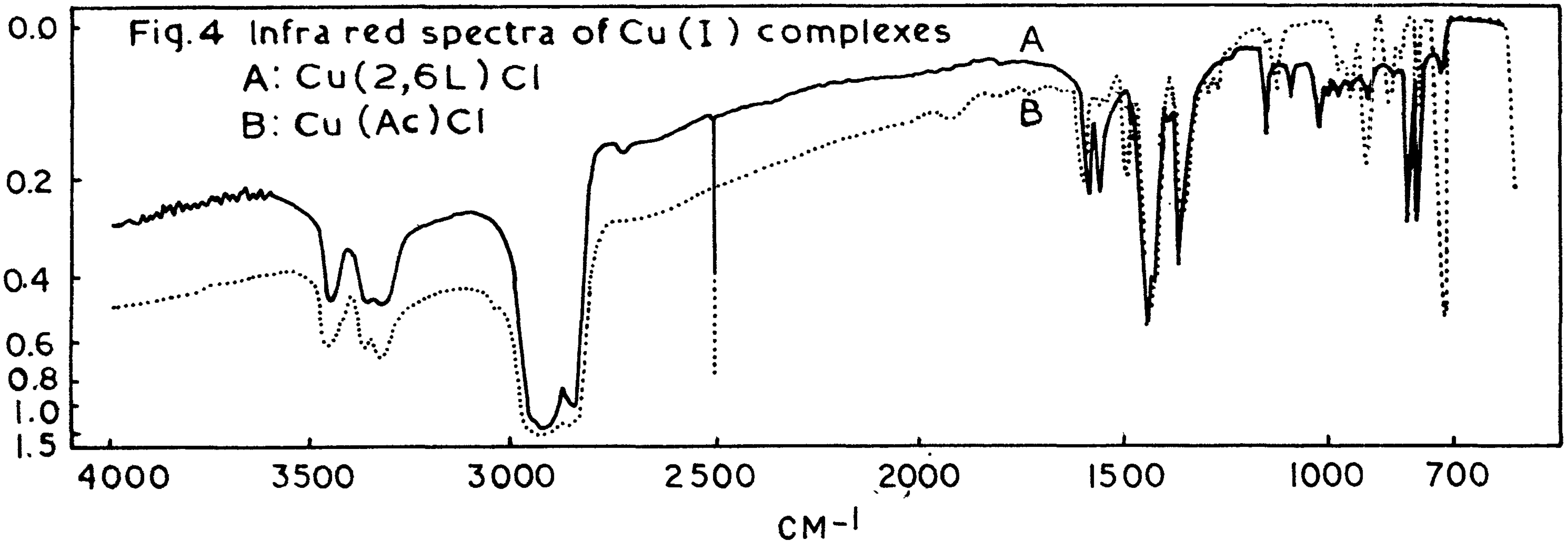

Fig.4 Infra red spectra of Cu(I) complexes

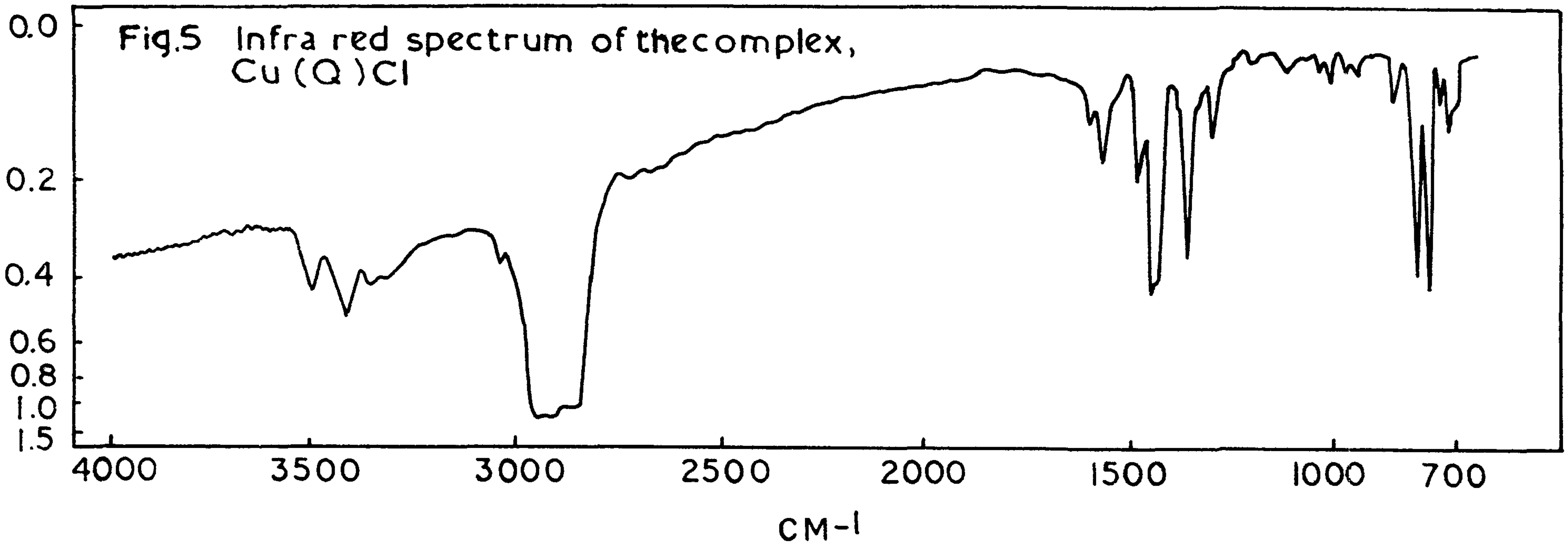

Fig.5 Infra red spectrum of the complex, Cu (Q) Cl

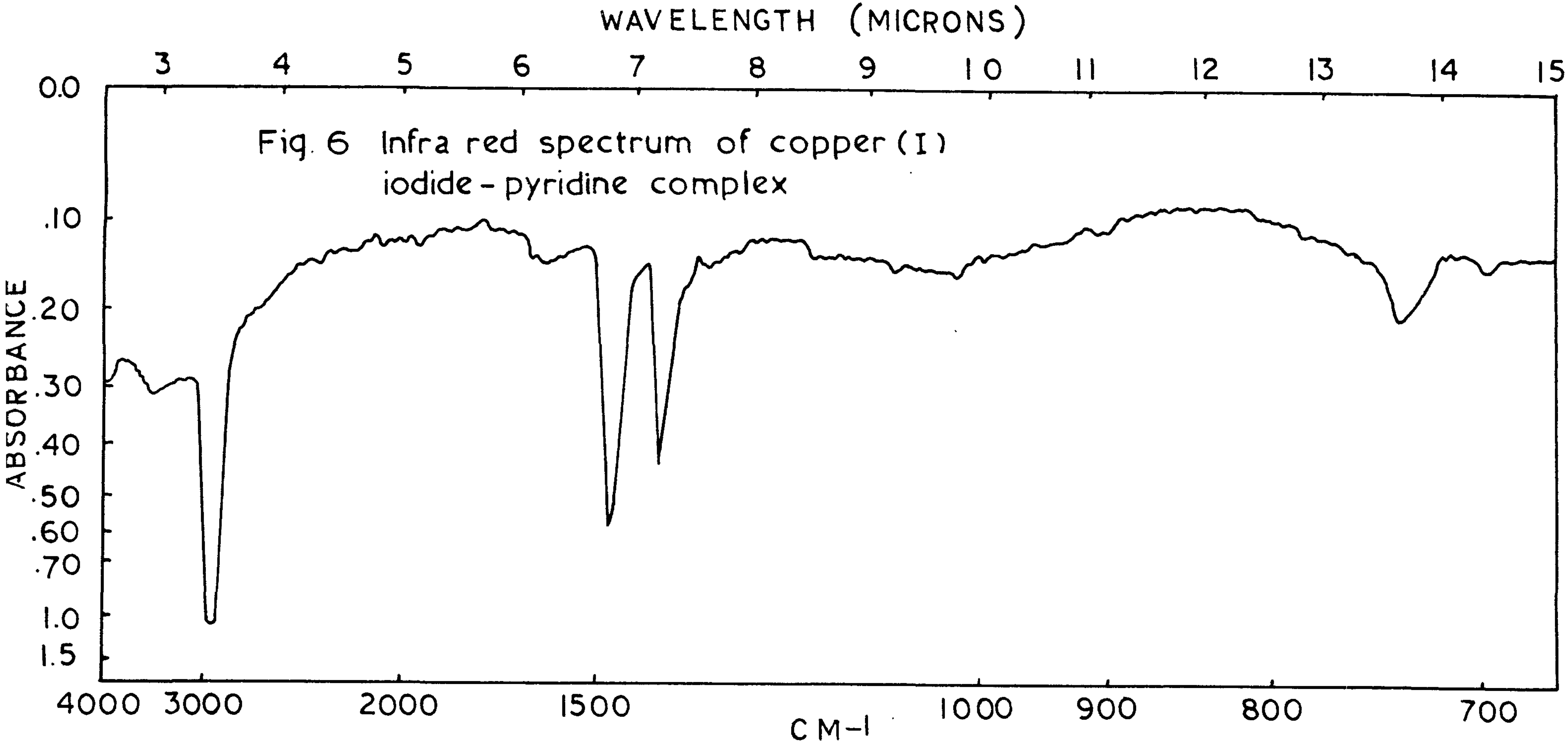

Fig. 6 Infra red spectrum of copper (I) iodide - pyridine complex

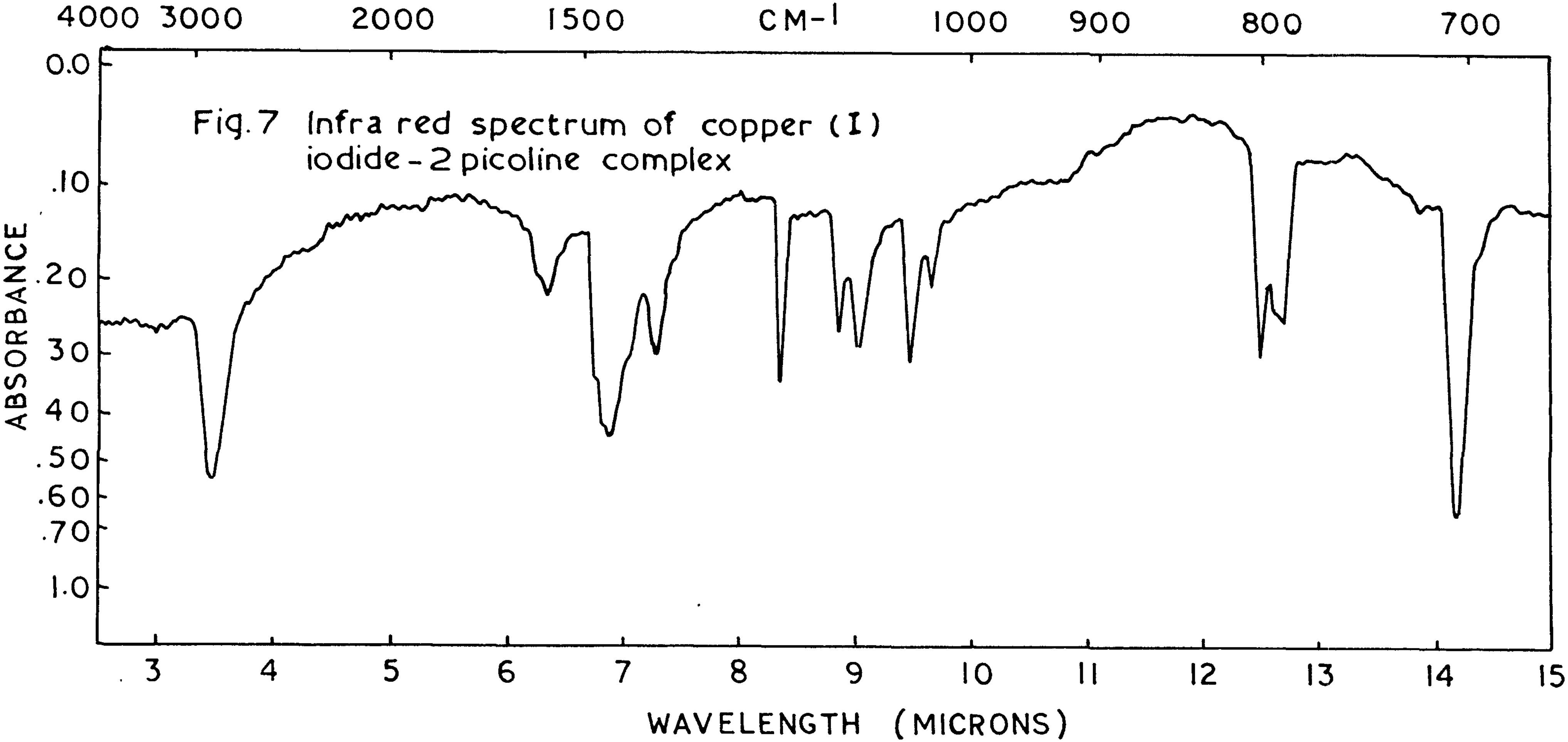

Fig. 7 Infra red spectrum of copper (I) iodide-2 picoline complex

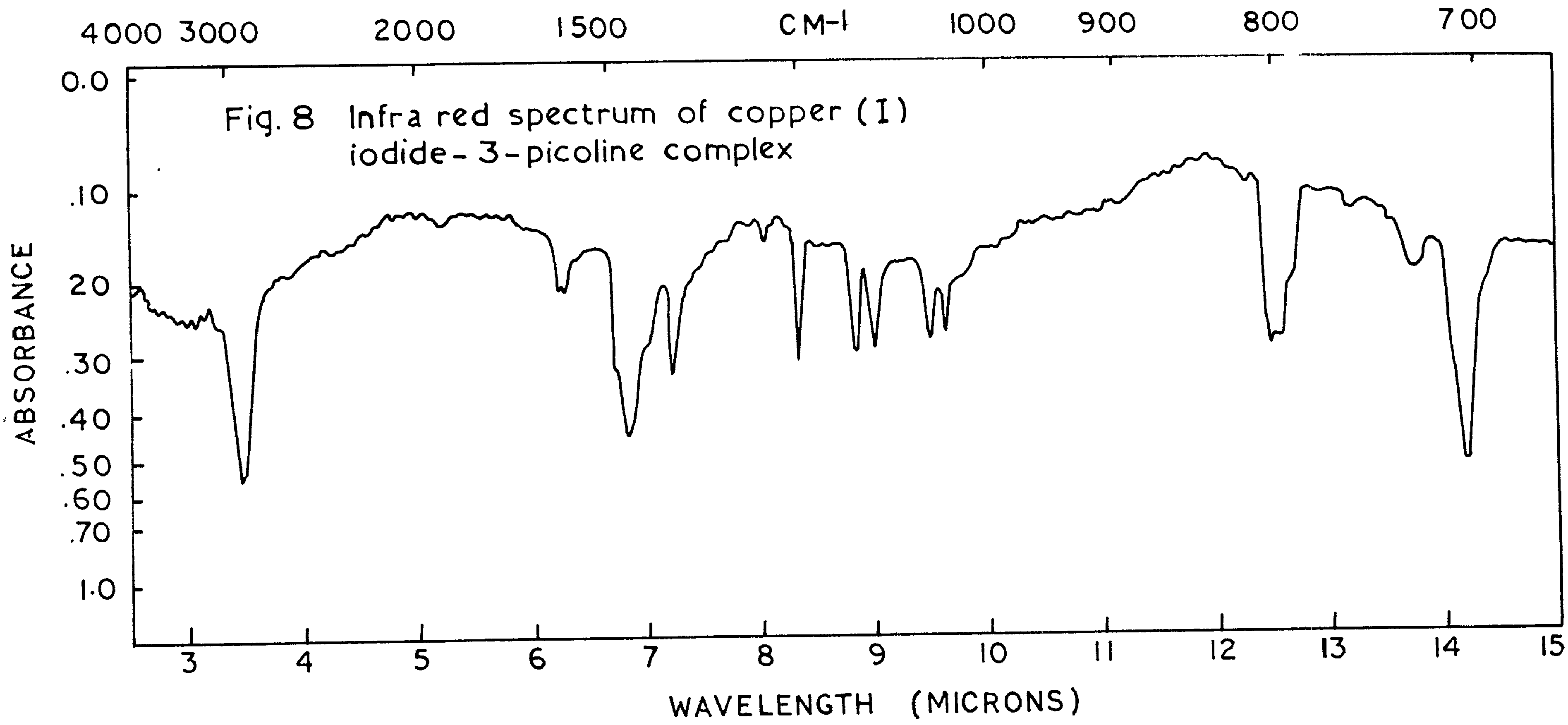

Fig. 8 Infra red spectrum of copper (I) iodide-3-picoline complex

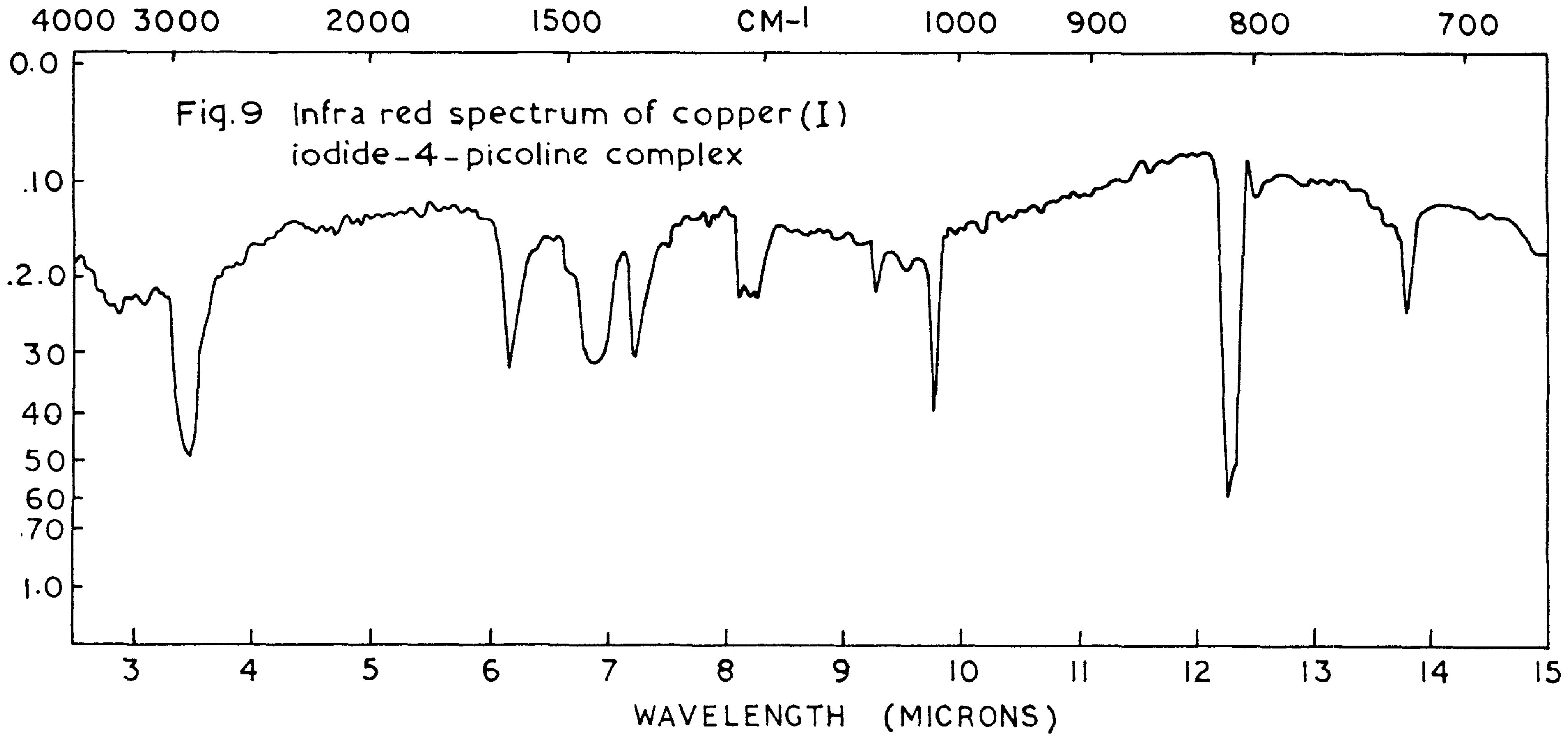

Fig.9 Infra red spectrum of copper(I) iodide-4-picoline complex

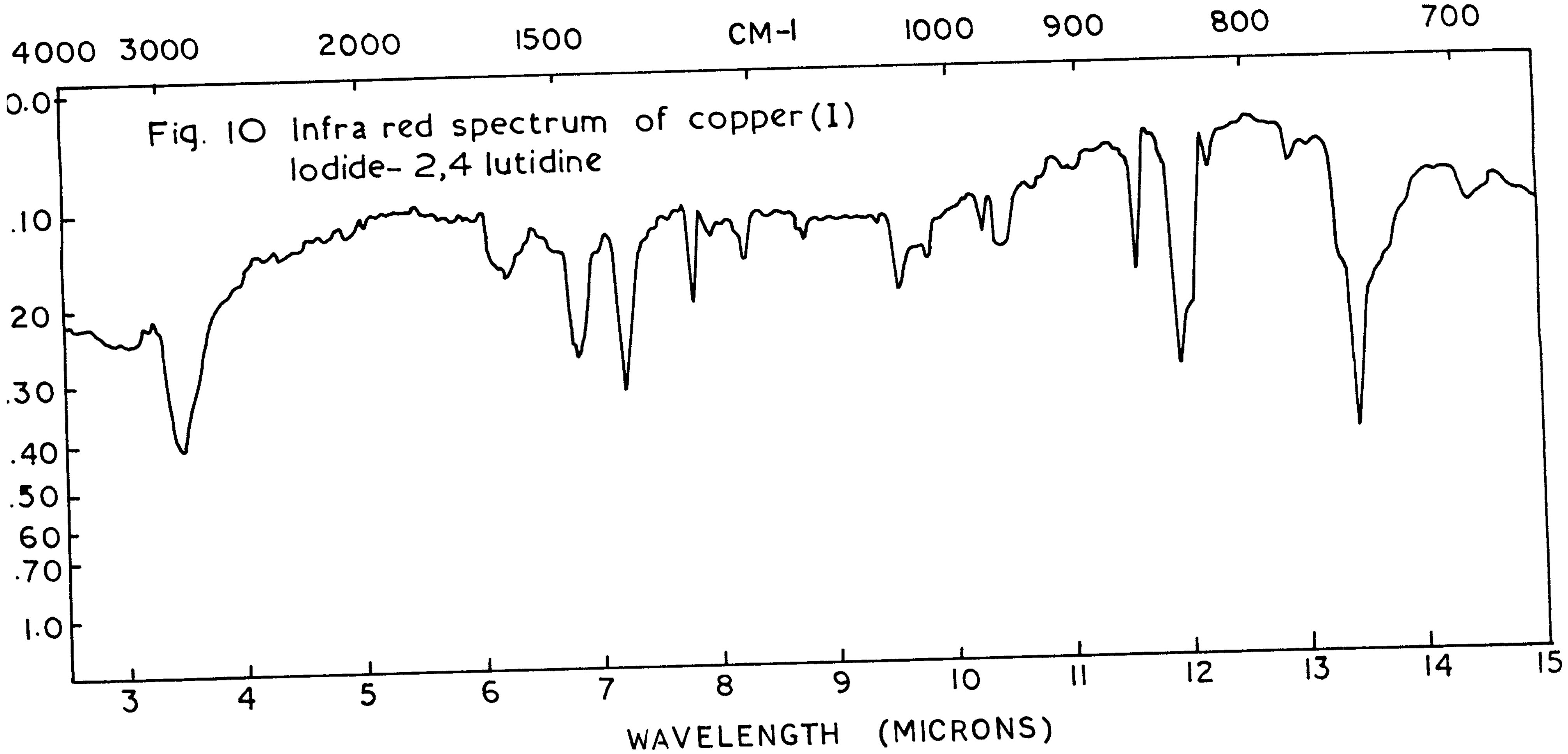

Fig. 10 Infra red spectrum of copper(I) Iodide- 2,4 lutidine

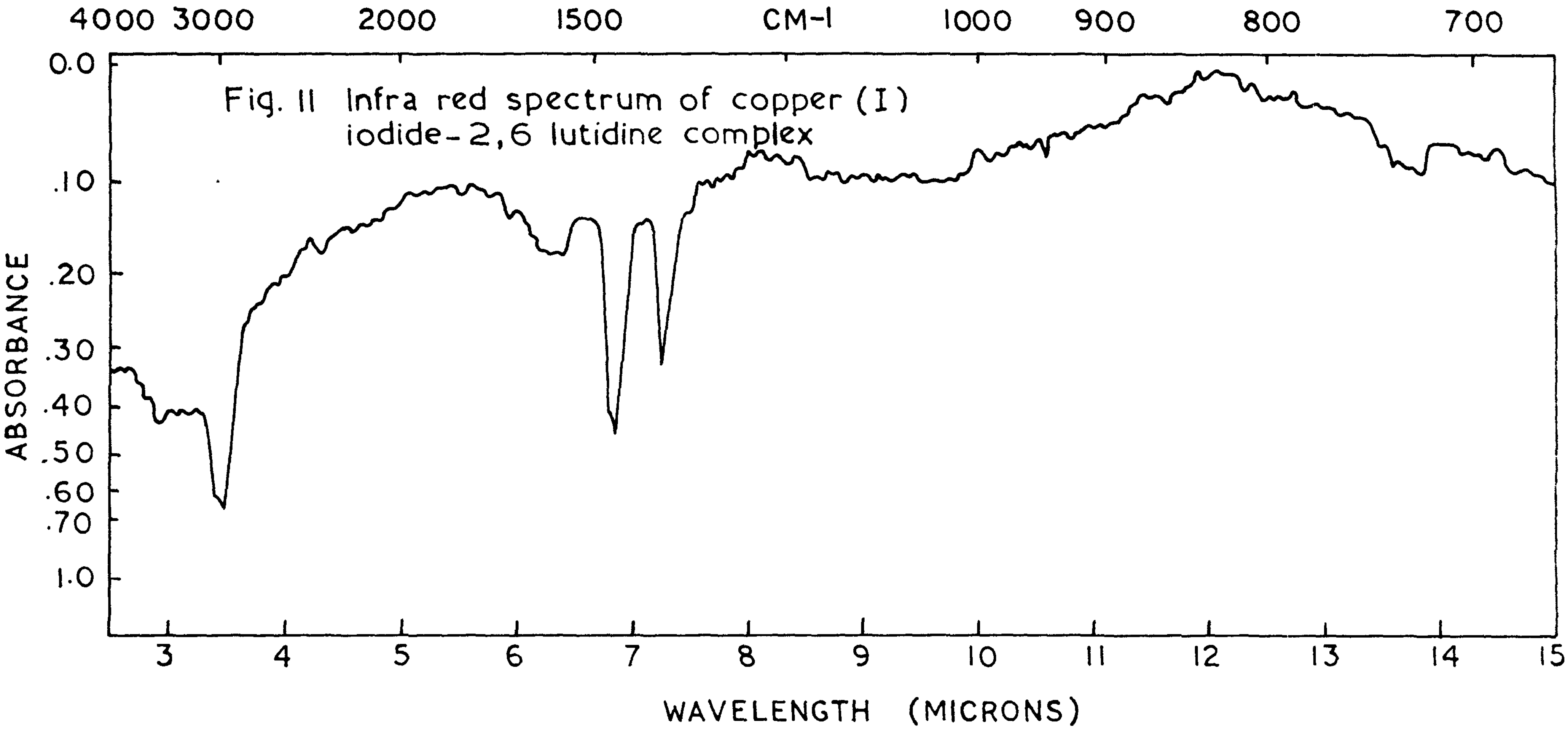

Fig. 11 Infra red spectrum of copper (I) iodide-2,6 lutidine complex

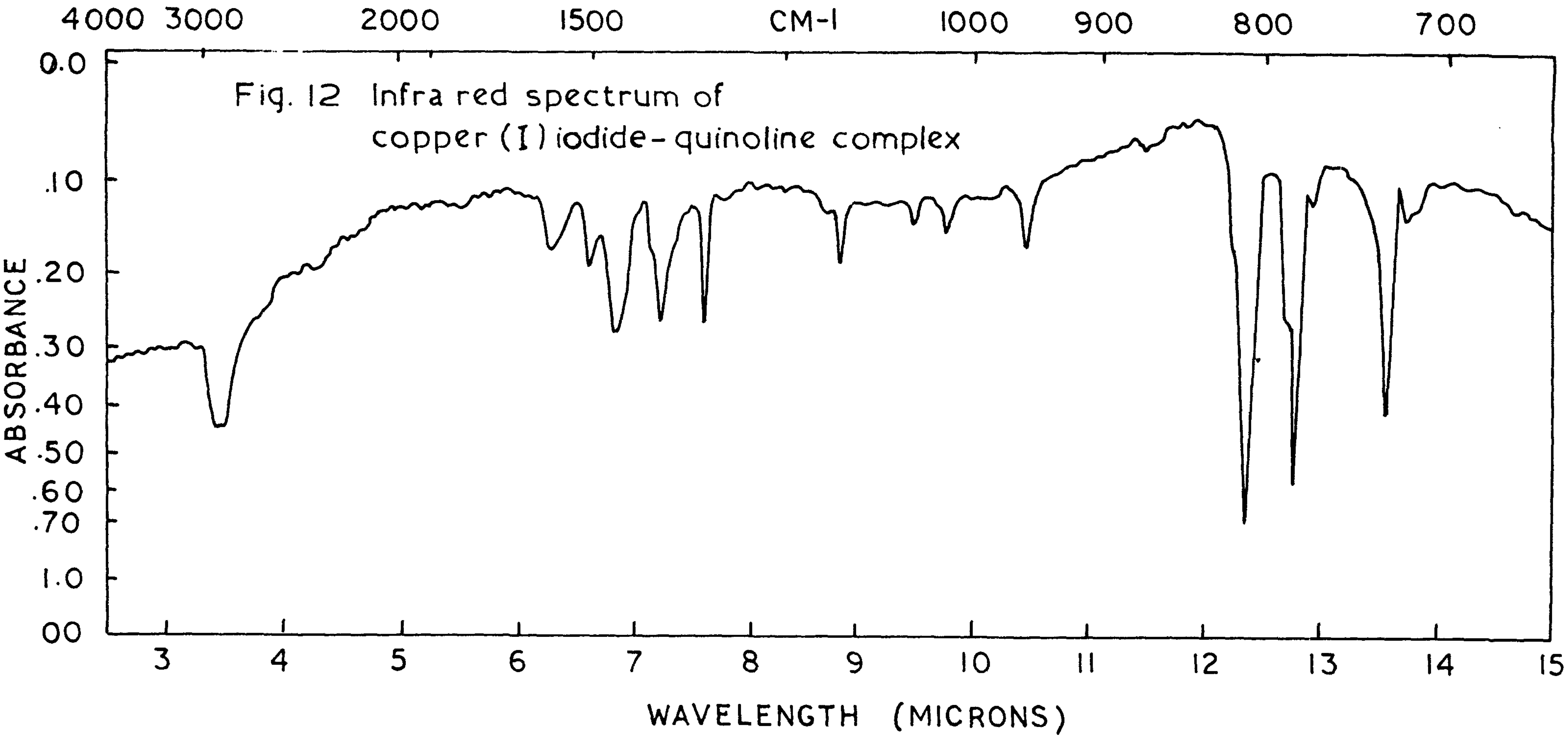

Fig. 12 Infra red spectrum of copper (I) iodide-quinoline complex

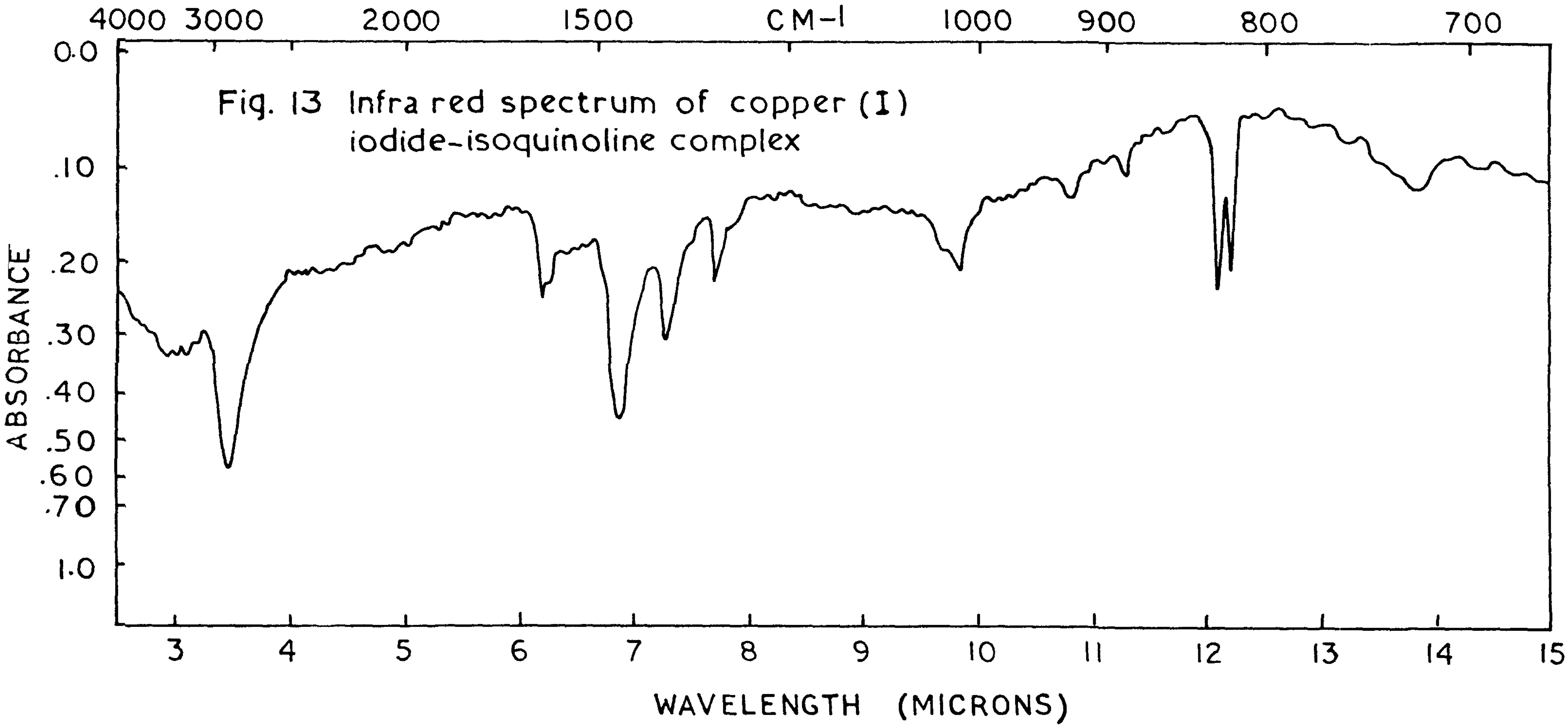
Fig. 13 Infra red spectrum of copper (I) iodide-isoquinoline complex

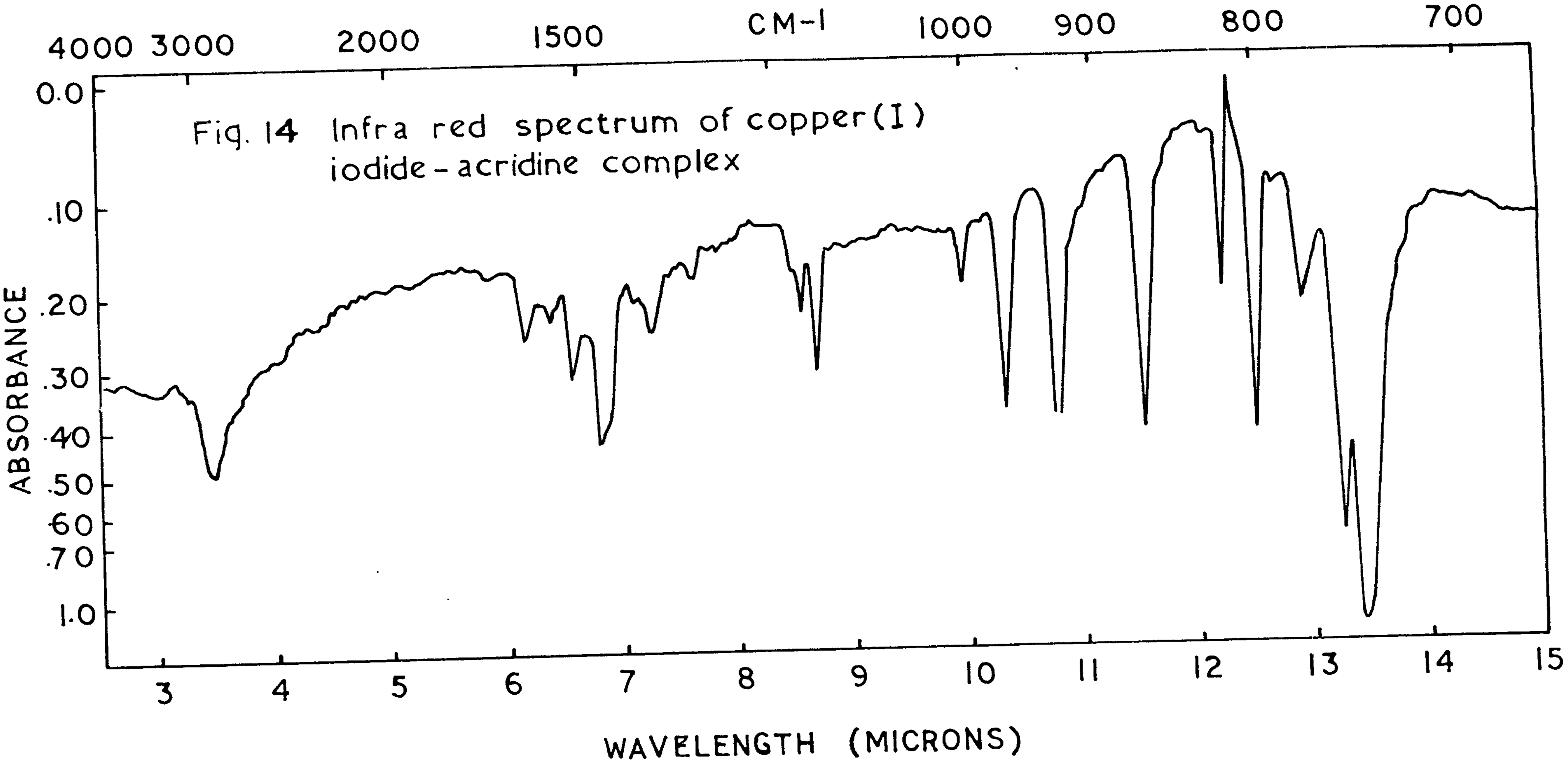

Fig. 14 Infra red spectrum of copper(I) iodide-acridine complex

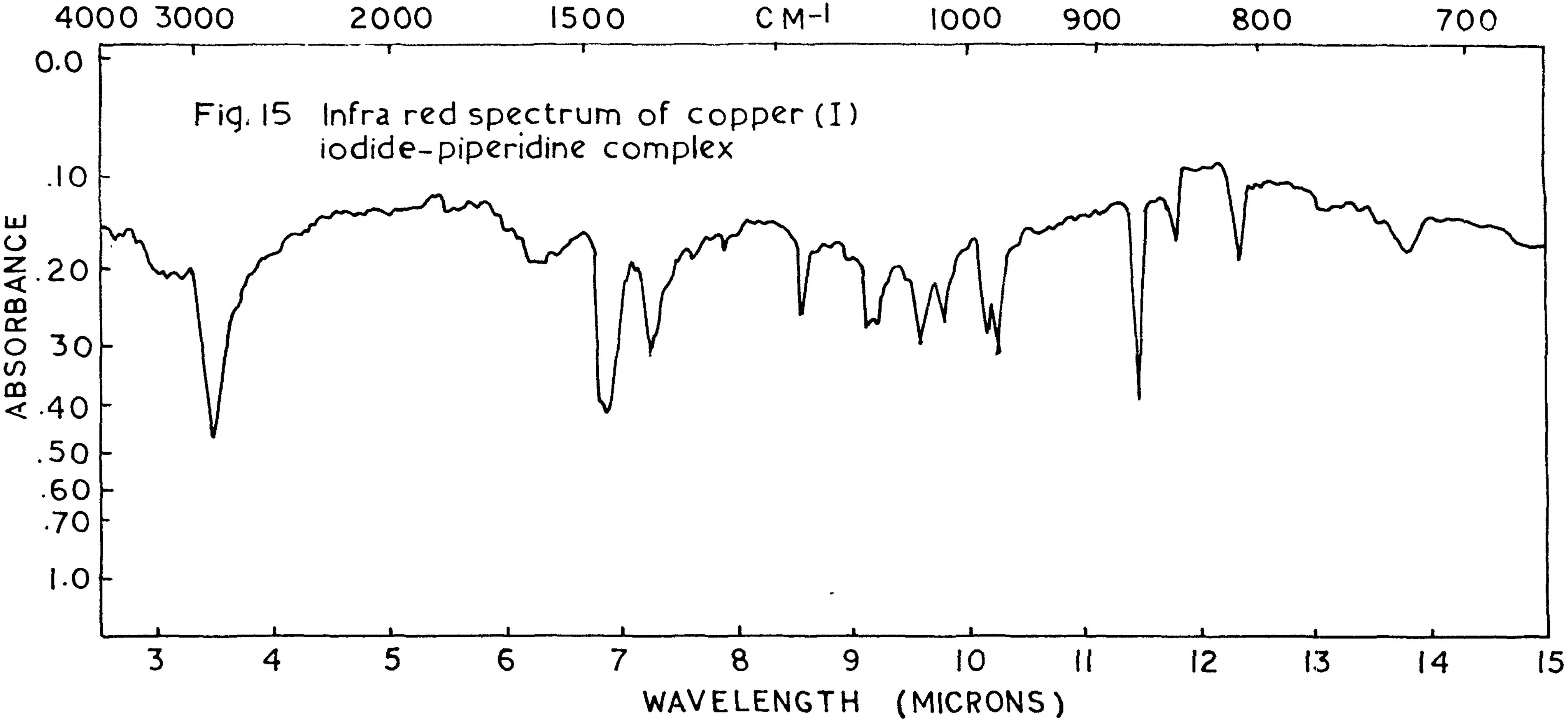

Fig. 15 Infra red spectrum of copper (I) iodide-piperidine complex

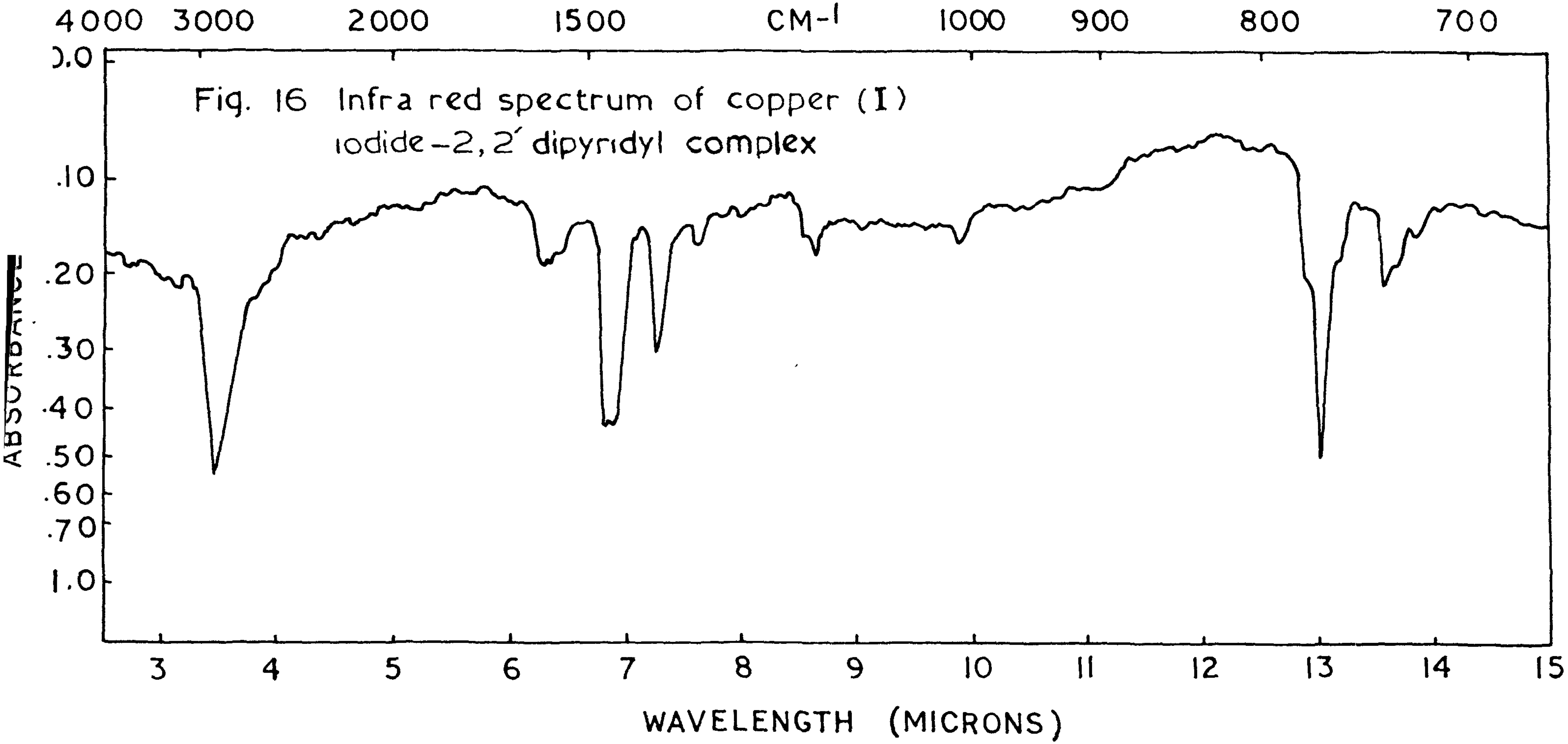

Fig. 16 Infra red spectrum of copper (I) iodide-2,2′ dipyridyl complex

Infra red absorption frequencies (700 cm^{-1}—3,000 cm^{-1}) of the complexes arising from the coordinated amines are as follows:

1. Cu(3pic)Cl: 715(v.s), 805(v.s), 935(m), 990(m), 1020(m), 1055(s), 1115(s), 1125(m), 1195(v.s), 1335(m), 1370(s), 1475(v.s), 1575(s), 1595(s), 2900(s); (Fig.2).
2. Cu(2,4l)Cl: 730(m), 755(m), 820(v.s), 910(m), 925(m), 995(w), 1030(s), 1160(w), 1230(m), 1265(v.s), 1295(s), 1365(m), 1390(w), 1435(s), 1455(s), 1485(m), 1550(s), 1600(s), 1615(s), 2910(s);(Fig.3A).
3. Cu(2,6L)Cl: 730(m), 790(v.s), 810(v.s), 830(v.w), 865(m); 925(m), 990(m), 1030(m), 1110(m), 1155(m), 1370(s), 1460(v.s), 1575(m), 1610(m), 2950(s); (Fig.4A).
4. Cu(Q)Cl: 730(m) 740(m), 805(v.s), 815(s), 865(m), 955(m), 980(m), 1020(m), 1050(m), 1335-40(m and b), 1205(m), 1310(m), 1370(v.s), 1455(v.s), 1500(s), 1580(m),1590(m), 1615(m), 2900(s); (Fig.5).
5. Cu(Pip)Cl: 710(m), 825(m & b), 860-865(m & b), 920(m), 985(m),1365(s), 1450(s), 2920(s); (Fig.3B).
6. Cu(Ac)Cl: 725(v.s), 780(m), 795(m), 815(v.s), 830(m), 845(w), 860(m), 920(s), 955(m), 985(w), 1000(b and m), 1140(m), 1290(m), 1305(m), 1370(s), 1460(v.s), 1510(s), 1545(m), 1565(m), 1615(s), 2900(s); (Fig.4B).

7. Cu(py)I: 735(m), 1380(s), 1470(v.s), 2900(v.s); (Fig.6).

8. Cu(2 pic)I: 785(m), 800(s), 1035(m), 1055(s), 1110(s), 1130(s), 1200(v.s), 1375(m), 1475(v.s & b), 1580(m), 2860(s); (Fig.7).

9. Cu(3 pic)I: 715(v.s), 760(w), 805(s&b), 1040(m), 1050(m), 1110(s), 1130(s), 1200(v.s), 1335(s), 1470(s), 2900(v.s); (Fig.8).

10. Cu(4 pic)I: 735(m), 815(v.s), 1020(v.s), 1075(m), 1220-1240(m & b), 1380(s), 1450(s), 1620(s), 2900(v.s); (Fig.9).

11. Cu(2,4L)I: 745(v.s), 775(w), 820(w), 835(s), 865(s), 1050(m), 1280(s), 1380(s), 1470(v.s), 2900(s); (Fig.10).

12. Cu(2,6L)I: 725(v.s), 1440(v.s), 1550-1575(w & b), 2900(s); (Fig.11).

13. Cu(Q)I: 740(s), 785(v.s), 810(v.s), 955(m), 1145(m), 1310(s), 1375(s), 1470(m), 1600(m), 2900(m); (Fig.12).

14. Cu(I.Q)I: 820(s), 830(s), 1300(m), 1375(m), 1460(s), 1625(m), 2900(s); (Fig.13).

15. Cu(Ac)I: 745(v.s), 755(sh), 775(m), 800(s), 820(s), 870(v.s), 930(v.s), 965(v.s), 1005(m), 1150(s), 1160(w), 1375(w), 1470(v.s), 2860(v.s), 2850(m); (Fig.14).

16. Cu(pip)I: 725(w), 815(m), 860(m), 875(v.s), 930(s), 990(m), 1020(w), 1050(m), 1085(w & b), 1400(m), 1460(v.s), 1475(s), 2900(v.s); (Fig.15).

17. Cu(dipy)I: 770(v.s), 1400(s), 1460(m & b), 1580-1620(b&w), 2900(s); (Fig.16).

18. Cu(o-phen)I: 765(s), 835(v.s), 970(m), 1125(m), 1225(m), 1410(v.s), 1450(m), 1500(m), 1620(m), 2950(w).

*Intensities abbreviations:

s-strong, v.s-very strong, w-weak, v.w-very weak, m-medium, b-broad, sh-shoulder.

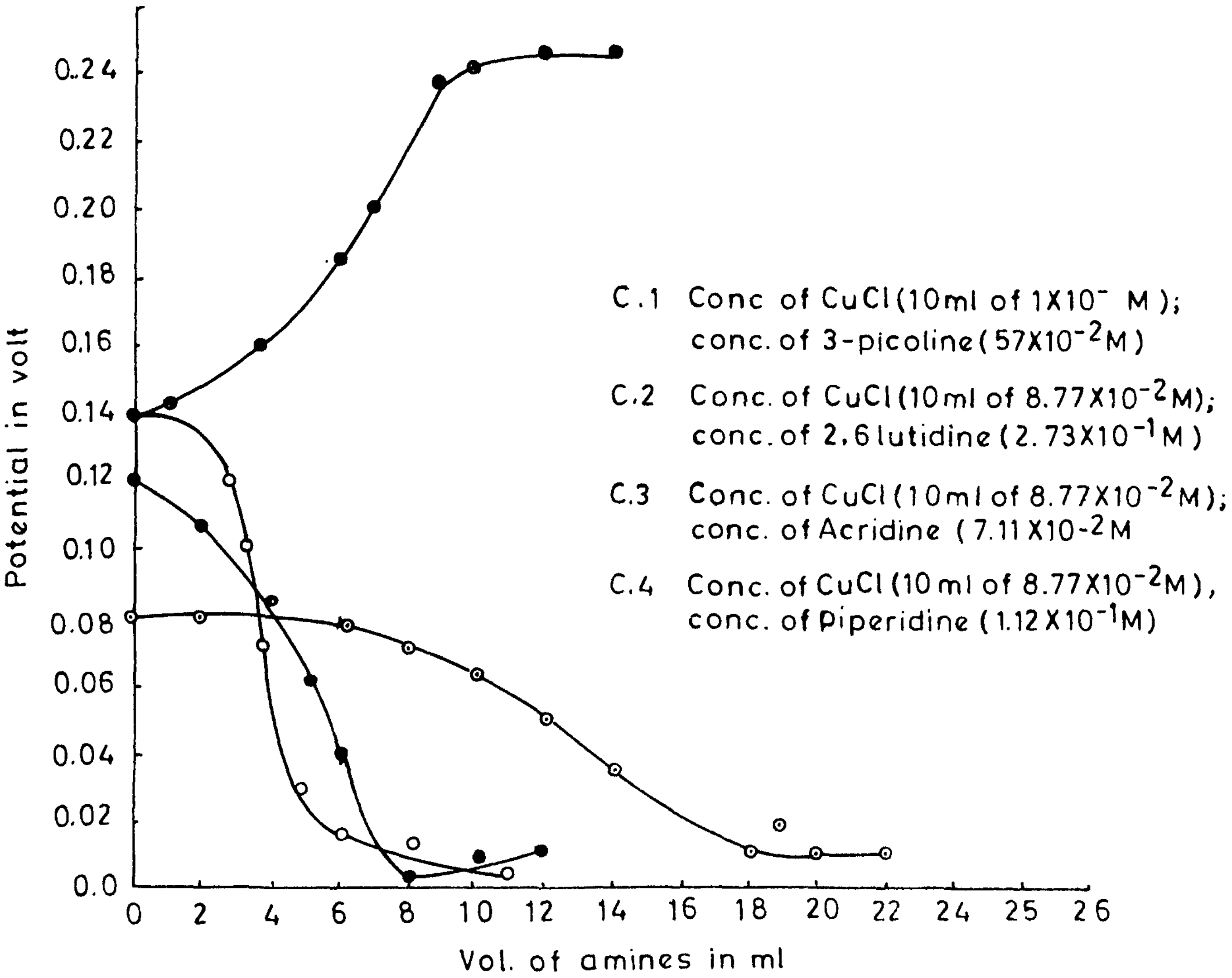

Fig. 1 Potentiometric Titrations

(Amines as titrants)

(Vide table 1)

RESULTS AND DISCUSSION

Complexes of Copper(I) Chloride with Heterocyclic Amines

The complexes of cuprous chloride with heterocyclic amines may be divided into two categories: (i) unstable complexes, e.g., with pyridine, 2 picoline, 4 picoline and isoquinoline, the composition of these complexes could only be determined by the potentiometric method. On addition of above mentioned amines to a cuprous solution there is formation of coloured complexes py(light yellow), 2 pic (light yellow), 4 pic (yellow) and I,Q(white), but the colour changes to green on keeping for sometime or during washing or drying; (ii) stable complexes, e.g., with 3 picoline, 2,4 and 2,6 lutidines, quinoline, acridine and piperidine. The composition of these complexes was determined both by chemical analysis and potentiometric titrations. The results of potentiometric titrations carried out, by employing Cu(I) $\rightleftharpoons$ Cu(II) + e couple, indicate a ratio 1:1 for the complexes (Fig. 1). The chemical analysis of the isolated products also gives the same ratios. The complexes formed with 3-pic (deep yellow), 2,4,L(light yellow) 2,6L(white), Q(yellow), pip(red) and Ac(red) are quite stable in dried state. The complexes are insoluble in water but soluble in acetone and alcohol, and slowly oxidise on standing for a long time. All the complexes were found to be diamagnetic as expected from Cu(I) species.

The unstable nature of copper(I) chloride complexes with heterocyclic amines may be attributed to: (i) presence of weak covalent Cu — Cl bond in these complexes[12] (ii) weaker π bonding capacities of the ligands and (iii) the greater affinity of these ligands for Cu(II).[13] The fact that above factors play an important role is further exemplified on considering the formation of stable Cu(I) iodide complexes with these ligands e.g., pyridine, picolines, quinolines, lutidines etc., and formation of stable copper(I) chloride and iodides complexes with better π bonding bidentate ligands such as 2,2' dipyridyl and o-phenanthroline.

Complexes of Copper(I) Iodide with Heterocyclic Amines:

Copper(I) iodide forms 1:1 complexes with pyridine (amethyst), 2 picoline (light brown), 3 picoline (light yellow), isoquinoline (dark yellow), piperidine (dirty white), acridine (brick red), 2,2' dipyridyl (dark pink) and o-phenanthroline(red). These complexes are very stable, remain unchanged even after keeping for more than a year, insoluble in water but soluble in organic solvents. All the complexes were found to be diamagnetic as expected for Cu(I) compounds.

The stability of these complexes[12] may be attributed firstly, to strong covalent bond between copper(I) and iodide which is a characteristic of a small group of metal ions e.g., Cu(I), Ag(I), Au(I), Cd(II), Hg(II), Pd(II) because here besides electrostatic forces the π bonding also contributes to the stability of the system. Moreover, the strong coordination of the nucleophilic nitrogen with the low positively charged Cu^+ and the presence of highly polarised I^- very close to the coordination sphere make them stable. Comparing with the corresponding Cu(I) chloride complexes, the conditions in the latter are not so favourable hence there is always a tendency of copper(I) chloride complexes to oxidise into Cu(II) species.

The formation of only monocoordinate complexes in these cases may be explained on considering the weak π bonding capacities of the heterocyclic amines. This property would restrict greater coordination due to the excessive charge accumulation around the copper(I) ion. Another important factor which contributes to the formation of monocoordinate species in copper(I), is the inherent tendency of $Cu^+(d^{10})$ ion to exhibit linear coordination due to small d-s separation[16].

<u>Infra red spectra of Cu(I) chloride and iodides complexes with heterocyclic amines.</u>

In figures 2 to 16, are given the infra red spectra of copper(I) chloride and copper(I) iodide complexes with heterocyclic amines.

The i.r. spectra of the complexes were studied on the assumption that while comparing with those of corresponding amines there occur no major changes in the spectra of the latter on coordination.[14,15] The following regions were found to be of special interests as regards to the study of the coordinated amines:

1. 1400-1600 cm^{-1} (ring CC,CN stretching vibrations): There are two marked changes in this region on complexation: (i) reduction in the number of bands, and (ii) shifts to higher frequences. There is no simple interpretation of these changes and it is difficult to correlate the nucleophilic order of the ligands amines with the shifts in wave lengths because of the presence of several bands in this region, however, the explanation that these changes occur mainly due to the strong polarisation of the aromatic ring caused by the coordination of Cu^+ to heterocyclic nitrogen does not seem unlikely. While comparing the spectra of copper(I) chloride complexes with those of iodide complexes, it is found that the above mentioned changes in ring CC,CN stretching vibrational modes are more distinct in the latter, indicating thereby the stronger bonding in the iodide complexes than the corresponding chloride complexes. In table 2, are given the spectral data for amines and their complexes in the region, 1400-1600 cm^{-1}.

TABLE -2:

Infra red spectral data for amines and coordinated amines in the region of ring CC,CN stretching vibrations.

3 picoline: 1580(s), 1480(v.s), 1450(s), 1415(v.s)
Cu(3pic)Cl: 1595(s), 1575(s), 1475(v.s)
Cu(3pic)I : 1470(s)
2,4lutidine: 1600(v.s), 1560(v.s), 1480(v.s), and 1445(v.s)
Cu(2,4L)Cl: 1615(s), 1600(s), 1550(s), 1455(s), 1435(s),
Cu(2,4L)I : 1470(v.s)
pyridine : 1439(s), 1486(s), 1534(v.s), 1600(s), 1636(m)
Cu(py)I : 1470(v.s)
2,2'dipyridyl: 1430(m), 1470(v.s), 1580(m)
Cu(dipy)I : 1460(m and b).

2. Ca. 800 cm^{-1}(CH out of plane ring deformation vibrations):

In majority of the complexes, this region is marked by three observed changes on coordination : (i)shifting to higher frequencies,(ii) reduction in the number of bands, and (iii) increase in the intensities of the bands. The changes are less marked in case of copper(I) chloride complexes. The changes in out of plane deformation vibrations may very well be explained in the light of the following factors;[12] (a) the strong nucleophilic character of heterocyclic amines and presence of vacant p_{π} orbital, resulting in the strong coordination, (b) strong

Cu-X bond due to the presence of vacant d orbital (Cl $<$ I), and (c) presence of highly polarised iodide ion. In case of cuprous chloride complexes, the factors (a) and (b) contribute most to the stabilities of the complexes whereas in cuprous iodide complexes all the three factors come into picture, resulting in the greater charge distribution and stability to the system and bringing about more distinct changes in CH out of plane deformation vibrations. Some of the i.r. spectral data are given in table 3 to illustrate the point:

TABLE -3:

i.r. frequencies of copper(I) complexes in the region of CH, out of plane deformation vibrations.

pyridine	: 702(v.s), 744(s), 810(w)
Cu(Py)I	: 735(m)
3-picoline	: 708(v.s), 783(v.s)
Cu(3pic)Cl	: 805(v.s), 795(v.s)
Cu(3pic)I	: 715(v.s), 715(v.s), 805(s & b)
2,4lutidine	: 817(v.s), 754(m), and 727(s)
Cu(2,4L)Cl	: 820(v.s), 755(w) and 730(m)
Cu(2,4L)I	: 745(v.s), 835(s), 865(s)
2,6 lutidine	: 775(v.s), 729(m), 716(m)
Cu(2,6L)Cl	: 830(v.w), 810(v.s)
Cu(2,6L)I	: 725(v.s)
2,2'dipyridyl	: 740(m), 760(v.s)
Cu(dipy)I	: 770(v.s)

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CHAPTER - II:

COORDINATION COMPOUNDS OF COPPER(I) HALIDES WITH SUBSTITUTED THIOUREAS

Coordination Compounds of Copper(I) Halides with Substituted Thioureas.

The metal complexes of thiourea are well known and many valuable references on them are available in the existing chemical literature.[1-5] The possibility of thiourea and related compounds as potential coordinating ligands can be very well understood on considering their high nucleophilities and availability of vacant d orbitals in sulphur which may also act as an acceptor d orbital. The latter has been usefully employed in the stabilisation of lower valence states of metals, e.g., Ag(I)[6], Cu(I)[7], Pd(II)[8] etc. Another interesting aspect of thiourea is its existence in canonical thioketo and thioenol forms. This has led to the possibility of coordination through nitrogen or sulphur (depending upon the metal and environment) and greater stability of the complexes.

In recent years, many investigations have been in progress on thiourea and substituted thiourea complexes covering various aspects of coordination chemistry, e.g., composition, crystal structure, stereochemistry, i.r. and n.m.r. spectra, and studies on ligand substitution on metal-thiourea complexes.[9-14] The infra red spectroscopy is found to be an important tool for assessing the nature of coordination bond in the complexes. The infra red spectra of a large number of metal-thiourea complexes have been studied and bonding is established.

The earliest reference available on the reaction of copper(I) with thiourea dates back to 1903 when Rosenheim and Loewstamm[15] isolated the complexes. Since then many investigations are in progress covering thiourea as well as substituted thioureas complexes.[16,3]

The work described here consists of the studies on the composition of copper(I) chloride and iodides complexes with substituted thioureas such as diphenyl, di-isopropyl, naphthyl, o-tolyl, benzyl and allyl thioureas. Besides chemical analysis, the composition of the complexes has been established by potentiometric method using $Ag-Ag_2S$ electrode. The nature of the coordination has been established on the basis of i.r. spectra of the complexes.

* * * *

EXPERIMENTAL

Copper(I) Complexes with Substituted Thioureas

Preparation of Copper(I)Chloride-Substituted Thiourea Complexes:

To a solution of cuprous chloride (in 2M KCl) was added an excess of substituted thiourea with constant stirring. The whole mixture was refluxed for 30-45 mts. over a water bath. The white product which settled down, was separated and filtered through a sintered funnel. The product was then washed several times with water and small aliquots of acetone to remove KCl and excess of complexing reagent, respectively. The whole mixture was then transferred to a flask and 100 ml of acetone were added to it. The mixture was heated over a water bath for about 20 mts. The hot reaction mixture was then passed through a filter paper and the light coloured filtrate was collected and kept for crystallisation in a vacuum desiccator when the crystals of the product appeared after a few days.

Analytical Data*

1. CuCl-diphenyl thiourea complex.

Bis (D.P.T.U.) copper(I) chloride. Light yellowish brown crystals, m.p. 140°C. Anal. Calc. for $C_{26}H_{24}N_4S_2$ CuCl: C-56.1, H-4.3, N-10.0, S-11.5, Cu-11.5, Cl-6.4. Found: C-53.3, H-4.6, N-9.4, S-11.1, Cu-11.3, Cl-6.3.

2. CuCl-naphthyl thiourea complex.

Bis (N.T.U.) copper(I) chloride. Dirty yellow crystals, m.p. 225-226°C. Anal. Calc. for $C_{22}H_{20}N_4S_2$ CuCl: C-52.5, H-3.9, N-11.1, S-12.7, Cu-12.7, Cl-7.5. Found: C-48.3, H-3.6, N-11.1, S-13.0, Cu-12.6, Cl-7.6.

3. CuCl-diisopropyl thiourea complex.

Bis (D.I.P.T.U.) copper(I) chloride. Light yellow crystals, m.p. 265°C. Anal. Calc. for $C_{14}H_{32}N_4S_2$ CuCl: C-40.1, H-7.6, N-13.3, S-15.3, Cu-15.1, Cl-8.5. Found: C-40.9, H-8.4, N-31.1, S-15.3, Cu-15.2, Cl-8.4.

4. CuCl-benzyl thiourea hydrochloride complex.

Mono(B.T.U.) copper(I) chloride. Brownish product, m.p.300°C. Anal.Calc. for $C_8H_{11}N_2S$ $CuCl_2$: C-31.8, H-3.6, N-9.0, S-10.1, Cu-21.1, Cl-23.5. Found: C-30.9, H-4.3, N-9.2, S-10.3, Cu-21.0, Cl-22.8.

5. CuCl-allyl thiourea complex.

Mono(A.T.U.) copper(I) chloride. Yellowish white crystals, m.p.215°C. Anal. Calc. for $C_4H_8N_2S$ CuCl: C-22.2, H-3.7, N-13.0, S-14.8, Cu-29.5, Cl-16.5. Found: C-21.3, H-3.7, N-12.0, S-14.2, Cu-29.5, Cl-16.5.

6. CuCl-o-tolyl thiourea complex.

Mono(T.T.U.) copper(I) chloride. Brownish black product, m.p.300°C. Anal.Calc. for $C_8H_{10}N_2S$ CuCl: C-36.2, H-3.8, N-10.6, S-12.1, Cu-24.0, Cl-13.4, Found: C-34.3, H-3.7, N-10.5, S-12.1, Cu-23.8, Cl-13.2.

Abbreviations used for the ligands

1. s-diphenyl thiourea: D.P.T.U. 2. naphthyl thiourea: N.T.U. 3. di-isopropyl thiourea: D.I.P.T.U. 4. benzyl thiourea hydrochloride: B.T.U. 5. allyl thiourea: A.T.U. 6. o-tolyl thiourea: T.T.U.

C, H, N and S analyses were carried out by the Australian microanalytical service, University of Melbourne, Australia.

Copper was estimated iodometrically, and chlorine gravimetrically as AgCl.

Reagents: A.T.U. and D.I.P.T.U. (E.Merck products), N.T.U., T.T.U. and D.P.T.U. (B.D.H.products) and B.T.U.(Light products) were used during the experiments. The reagents were purified by crystallisation from acetone. The solutions of the substituted thioureas were prepared in acetone.

Cuprous chloride was prepared by the method recommended by Keller and Wycoff.[20] Solutions of cuprous chloride were prepared in concentrated KCl.

Potentiometric measurements: The potentiometric titrations were carried out with the help of a 'PYE' precision potentiometer (No.7568, sensitivity: 10^{-6} volt) with lamp scale arrangement. The titration cell used was an 'H' shaped glass

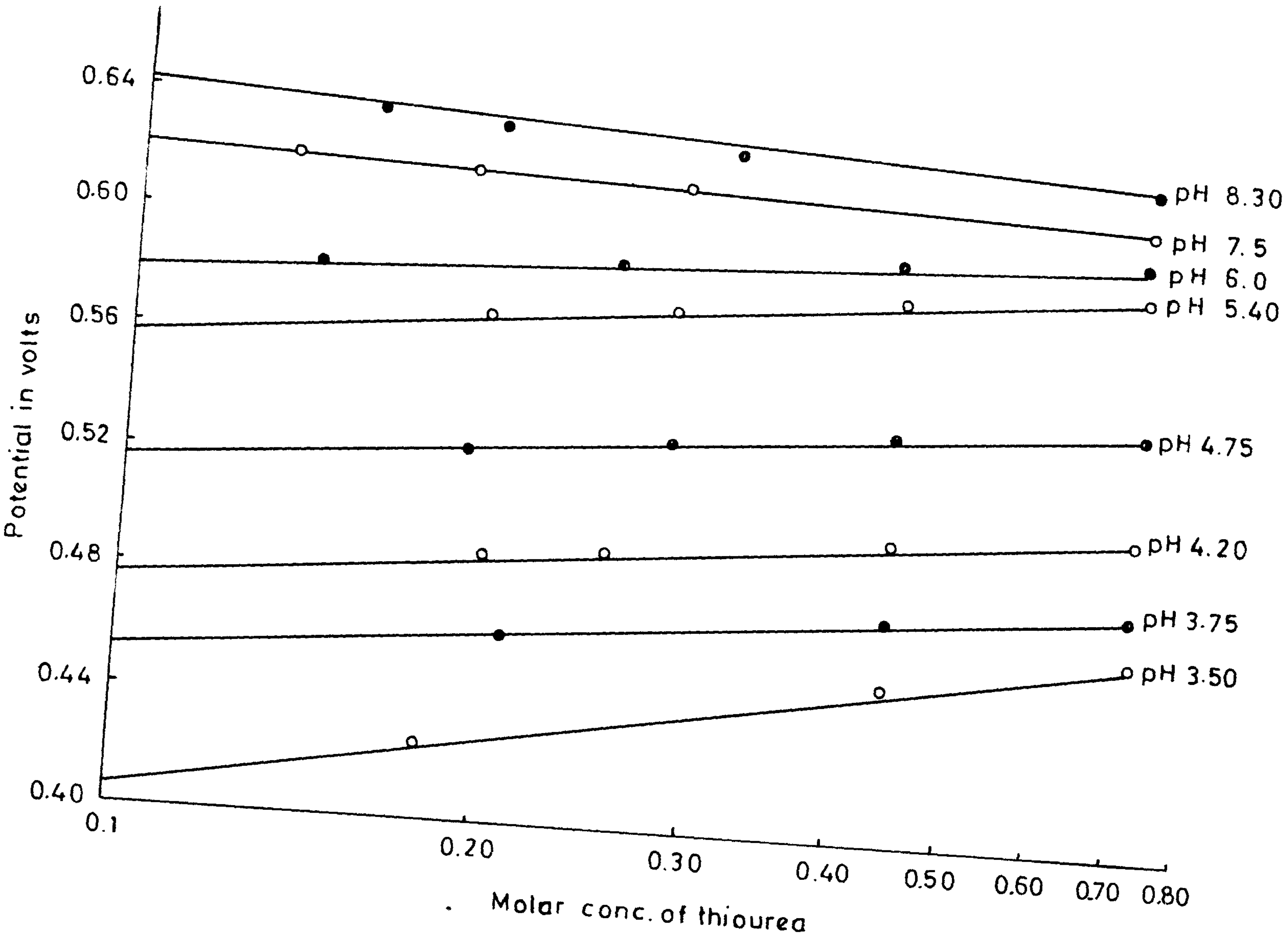

Fig. 1 Plot For Thiourea At Different pH Values
(Potential Vs. Log [tu])
(Logarithmic scale)

vessel with sintered glass partition. The electrodes used were $Ag-Ag_2S$ as an indicator and saturated calomel as a reference.

Preparation of Silver-Silver Sulphide Electrode: The electrode was prepared by passing a current of H_2S in distilled water having a silver deposited platinum wire dipped in it. The silver was deposited on Pt wire by using potassium argentocyanide solution and carrying out electrolysis for 8 hours using a current of 0.5 m a. Silver deposited platinum wire after coming in contact with H_2S water for about an hour got a uniform brown coating of Ag_2S.

The behaviour of $Ag-Ag_2S$ electrode in thiourea (tu) and substituted thioureas was studied by carrying out potential measurements. The potential of the solutions of thiourea and substituted thioureas was measured in the pH range of 2.0 to 8.0. The plots of log (tu) against E.M.F. gave straight lines in the pH range 3 to 8.3 showing thereby that $Ag-Ag_2S$ electrode could be used as a reversible electrode in the moderately acidic to feebly basic range. The behaviour is not met with in the higher pH range e.g., above 8.0. The acidic pH of the solution of substituted thiourea (in acetone) was maintained by adding acetic acid. Typical plots of log(tu) vs. E.M.F. at different pH's are given in Fig.1.

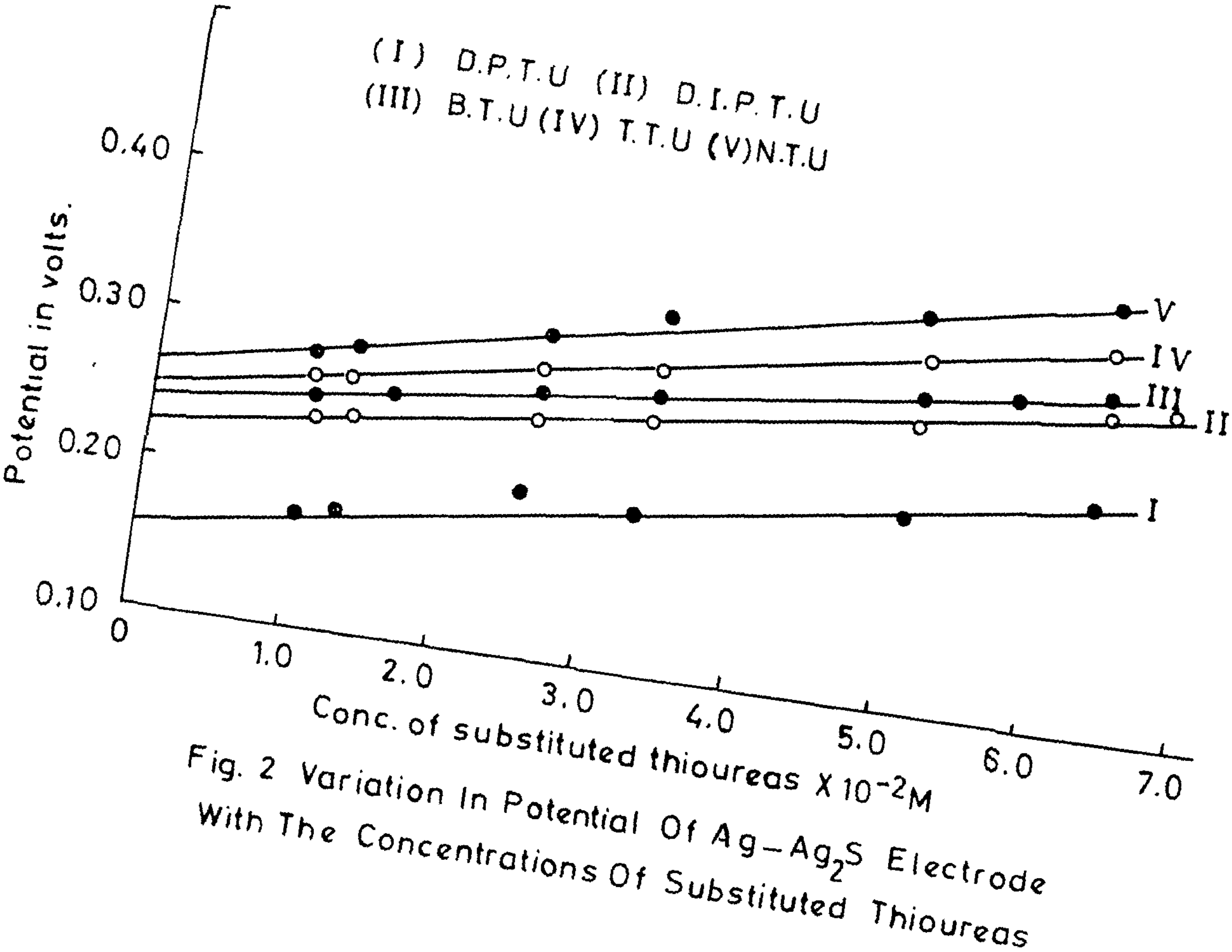

Fig. 2 Variation In Potential Of $Ag-Ag_2S$ Electrode With The Concentrations Of Substituted Thioureas

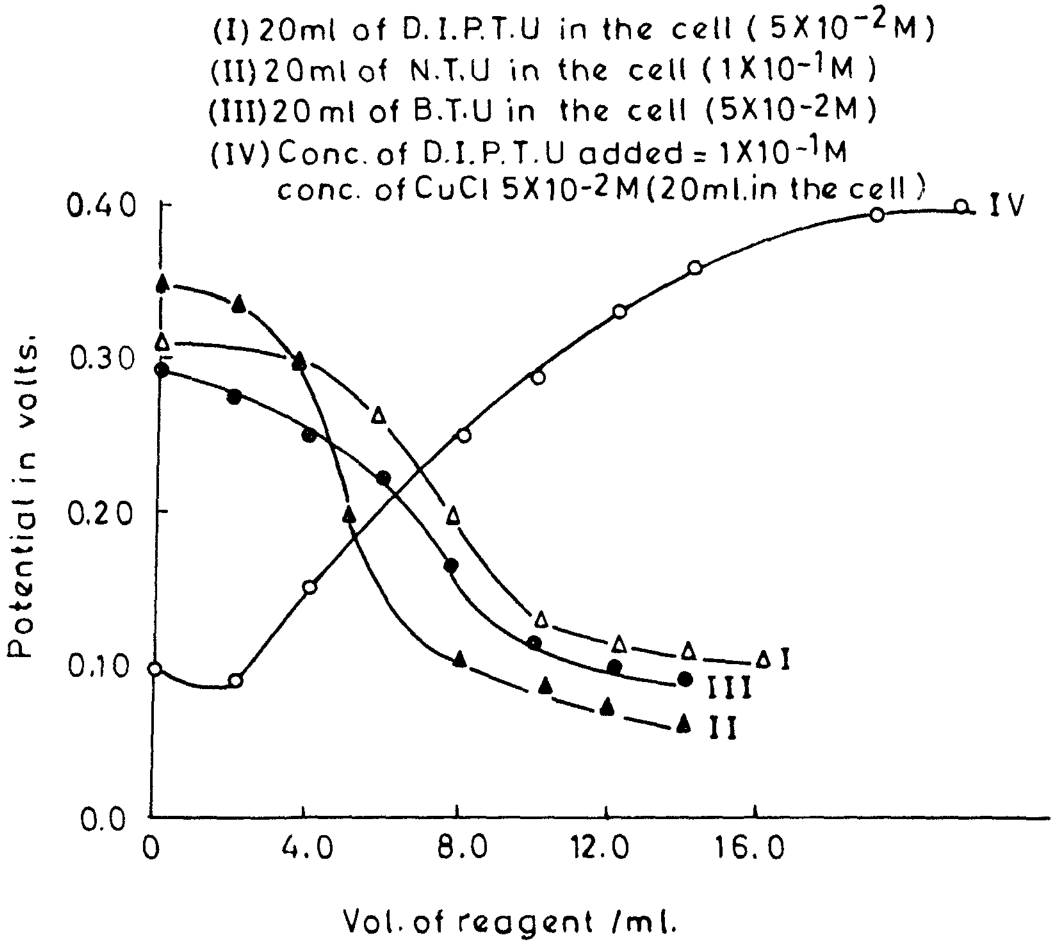

Fig. 3 Potentiometric Titrations

(Copper (I) Chloride And Substituted Thioureas)

Conc. Of CuCl Added = 5×10^{-2} M

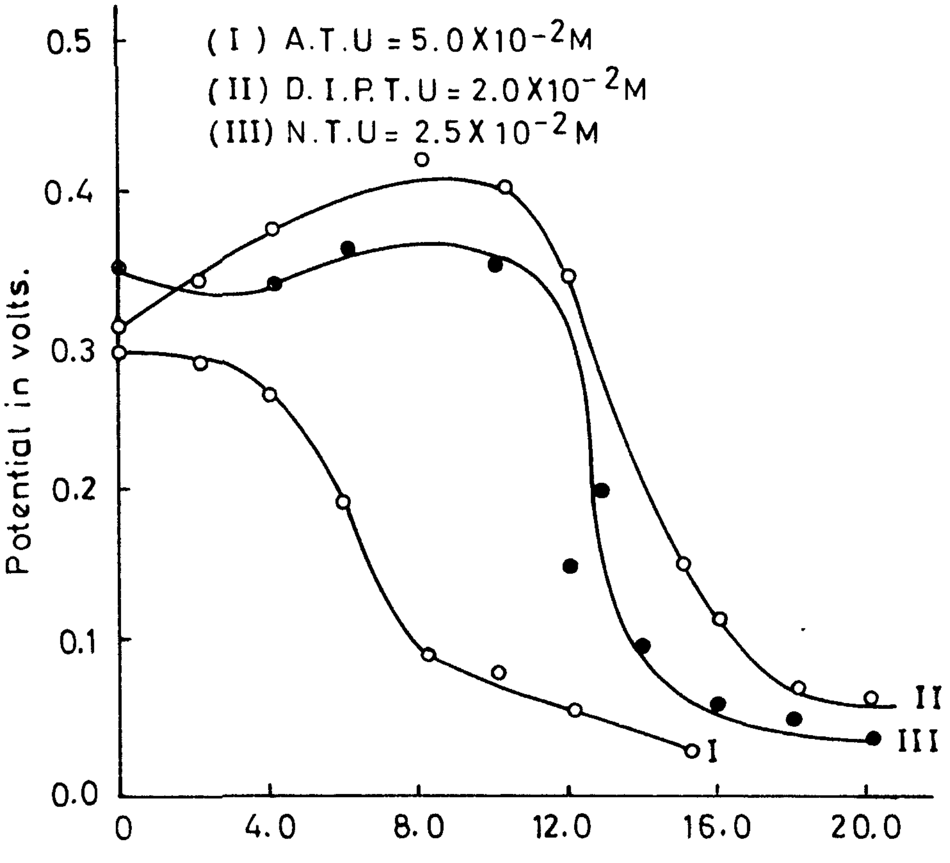

Fig. 4. Potentiometric Titrations
(Copper (I) Iodide And Substituted Thioureas)
Conc. Of Cu_2I_2 Added = 5.0×10^{-1}M
Substituted Thioureas (20ml. In Cell.)

TABLE - 1.

Variation in potential of the Ag-Ag_2S electrode with the concentrations of substituted thioureas (pH 3.5)

Conc. x10^{-2}M	D.P.T.U.	T.T.U.	D.I.P.T.U.	B.T.U.	N.T.U.
1.0	0.175	0.2630	0.2450	0.2550	0.2716
1.25	0.1831	0.2640	0.2480	0.2621	0.2760
2.5	0.2091	0.2960	0.2615	0.2851	0.320
3.125	0.2085	0.2050	0.2715	0.2850	0.3530
5.0	0.2341	0.3361	0.2980	0.3133	0.3581
6.25	0.2555	0.3612	0.3215	0.3310	0.3880

(Vide Fig.2)

Potentiometric titrations :- The composition of copper(I)-substituted thioureas complexes was determined by carrying out potentiometric titrations employing Ag-Ag_2S as an indicator electrode. Both direct (thioureas in the cell, and CuCl and CuI as titrants) and reverse (CuCl and CuI in the cell, and thioureas as the titrants) titrations were performed using varying concentrations of the reagents. Some of the typical titration curves are given in figures 3 and 4.

II. Copper(I) Iodide-Substituted Thioureas Complexes: An excess of substituted thiourea solution (in acetone) was added to a saturated solution of cuprous iodide in concentrated KI. The whole mixture was shaken thoroughly with a magnetic stirrer for about 15 mts, and then treated with a large volume of acetone, warmed slightly over a water bath and then filtered. The filtrate was evaporated slowly over a water bath and the dried mass so obtained was washed several times with small aliquots of water and absolute alcohol to remove KI and excess of the complexing reagent, respectively. The washed mass was then dried with ether and then dissolved in tetrahydrofuran, concentrated and kept for crystallisation. After about 24 hours, crystals of the complex appeared.

Analytical Data:

1. CuI-diphenyl thiourea complex.

Tris (D.P.T.U.) copper(I) iodide. Yellow crystals. Anal.Calc. for $C_{39}H_{36}N_6S_3$ CuI: C-52.4, H-4.1, N-9.6, S-11.0, Cu-7.3, I-14.5. Found: C-51.3, H-3.9, N-9.5, S-10.9, Cu-7.3, I-14.2.

2. CuI-naphthylthiourea complex.

Tris (N.T.U.) copper(I) iodide. Brownish black crystals. Anal.Calc. for $C_{33}H_{30}N_6S_3$ CuI: C-49.7, H-3.8, N-10.6, S-12.05, Cu-8.0, I-15.9. Found: C-48.3, H-3.7, N-10.4, S-11.9, Cu-7.9, I-15.8.

3. CuI-o-tolyl thiourea complex.

Tris (T.T.U.) copper(I) iodide. Dark brown crystals. Anal.Calc. for $C_{24}H_{30}N_6S_3$ CuI: C-40.6, H-4.4, N-12.3, S-14.0, Cu-9.3, I-18.55. Found: C-39.8, H-4.4, N-12.2, S-13.9, Cu-9.2, I-18.3.

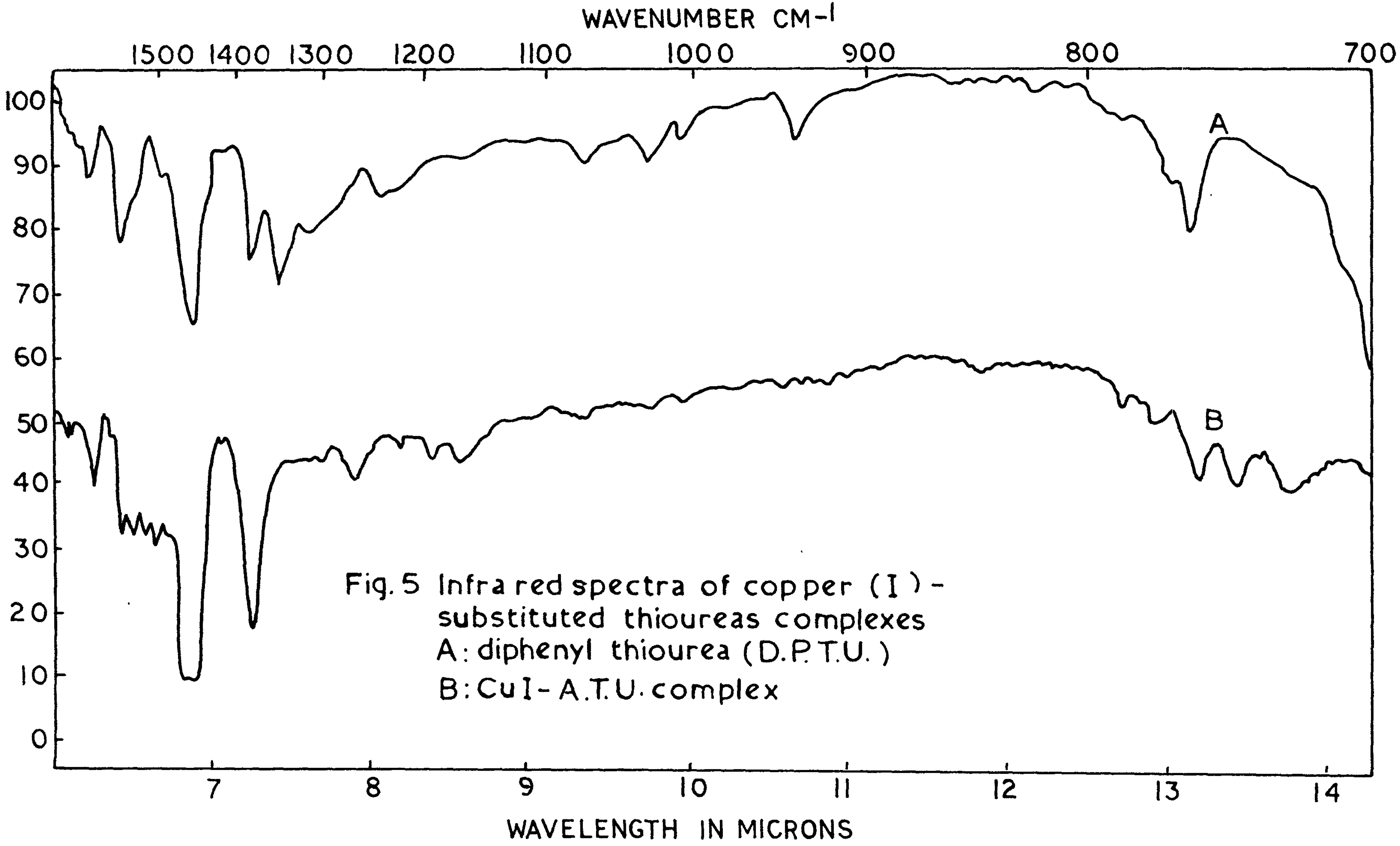

Fig. 5 Infra red spectra of copper (I)- substituted thioureas complexes
A: diphenyl thiourea (D.P.T.U.)
B: CuI-A.T.U. complex

4. CuI-allyl thiourea complex.

Tris(A.T.U.) copper(I) iodide. Light yellow crystals. Anal. Calc. for $C_{12}H_{24}N_6S_3$ CuI: C-26.7, H-4.45, N-15.6, S-17.8, Cu-11.8, I-23.3. Found: C-25.9, H-2.4, N-15.3, S-17.8, Cu-11.5, I-23.1.

5. CuI-di-isopropyl thiourea complex.

Tris(D.I.P.T.U.) copper(I) iodide. Dark amethyst crystals. Anal. Calc. for $C_{21}H_{48}N_6S_3$ CuI: C-37.6, H-7.15, N-12.5, S-14.3, Cu-9.5, I-18.9. Found: C-37.1, H-7.2, N-12.3, S-14.1, Cu-9.5, I-18.6.

C,H,N and S analyses were carried out by the Australian Microanalytical Service, Melbourne. Copper and iodine were estimated as described in case of cuprous iodide-heterocyclic amines complexes (chapter I).

Infra Red Spectra of Copper(I)-Substituted Thiourea Complexes:

The infra red spectra were recorded (in the range: 3 to 16 u) with a Beckman IR-5 spectrophotometer, using KBr pallets. The apparatus was checked by polystrene films and carbontetrachloride.

The infra red frequencies of the substituted thioureas and their copper(I) complexes are given as follows:

1. D.P.T.U: 700(s), 760(s), 940(m), 1000(w), 1030(w), 1075(w), 1250(w), 1360(s), 1380(m), 1450(s), 1560(s). (Fig.5A)
2. Cu(D.P.T.U.)$_2$Cl: 695(m), 745(s), 760(m), 1170(w), 1200(w), 1270(w), 1380(m), 1530(v.s), 1580(s), 1600(s). (Fig.5B)

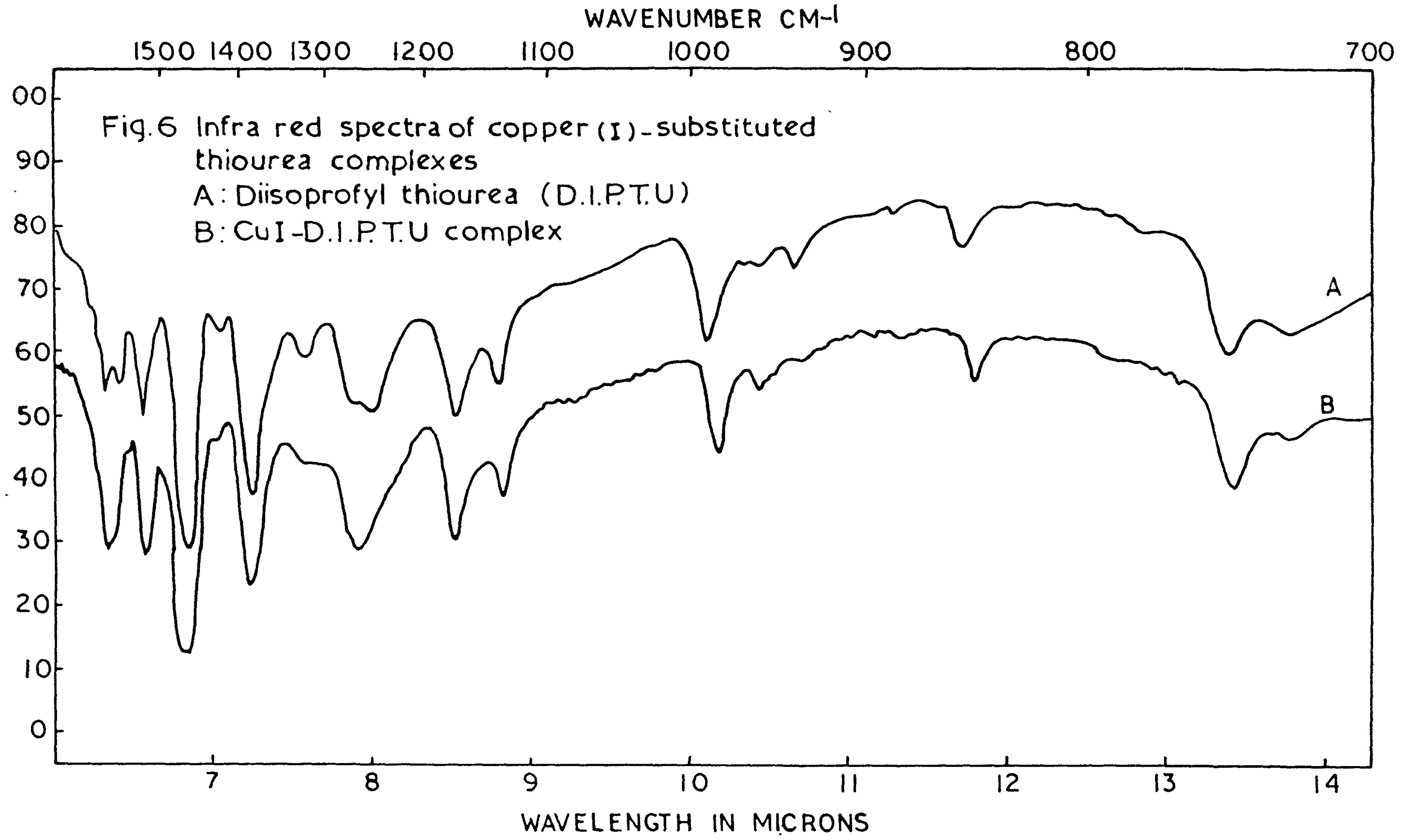

Fig.6 Infra red spectra of copper (I)-substituted thiourea complexes
A: Diisoprofyl thiourea (D.I.P.T.U)
B: CuI-D.I.P.T.U complex

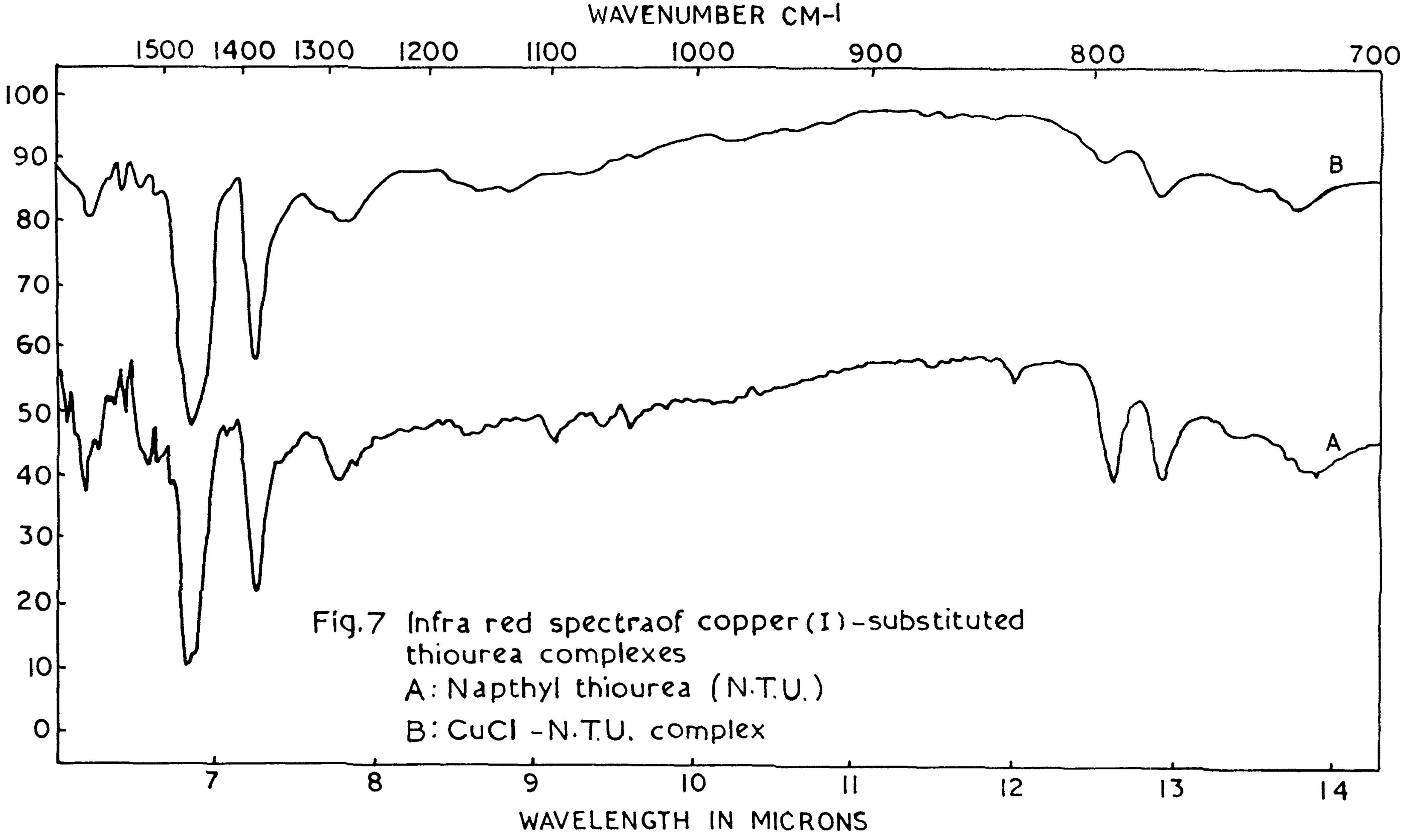

Fig.7 Infra red spectraof copper(I)-substituted thiourea complexes
A: Napthyl thiourea (N.T.U.)
B: CuCl -N.T.U. complex

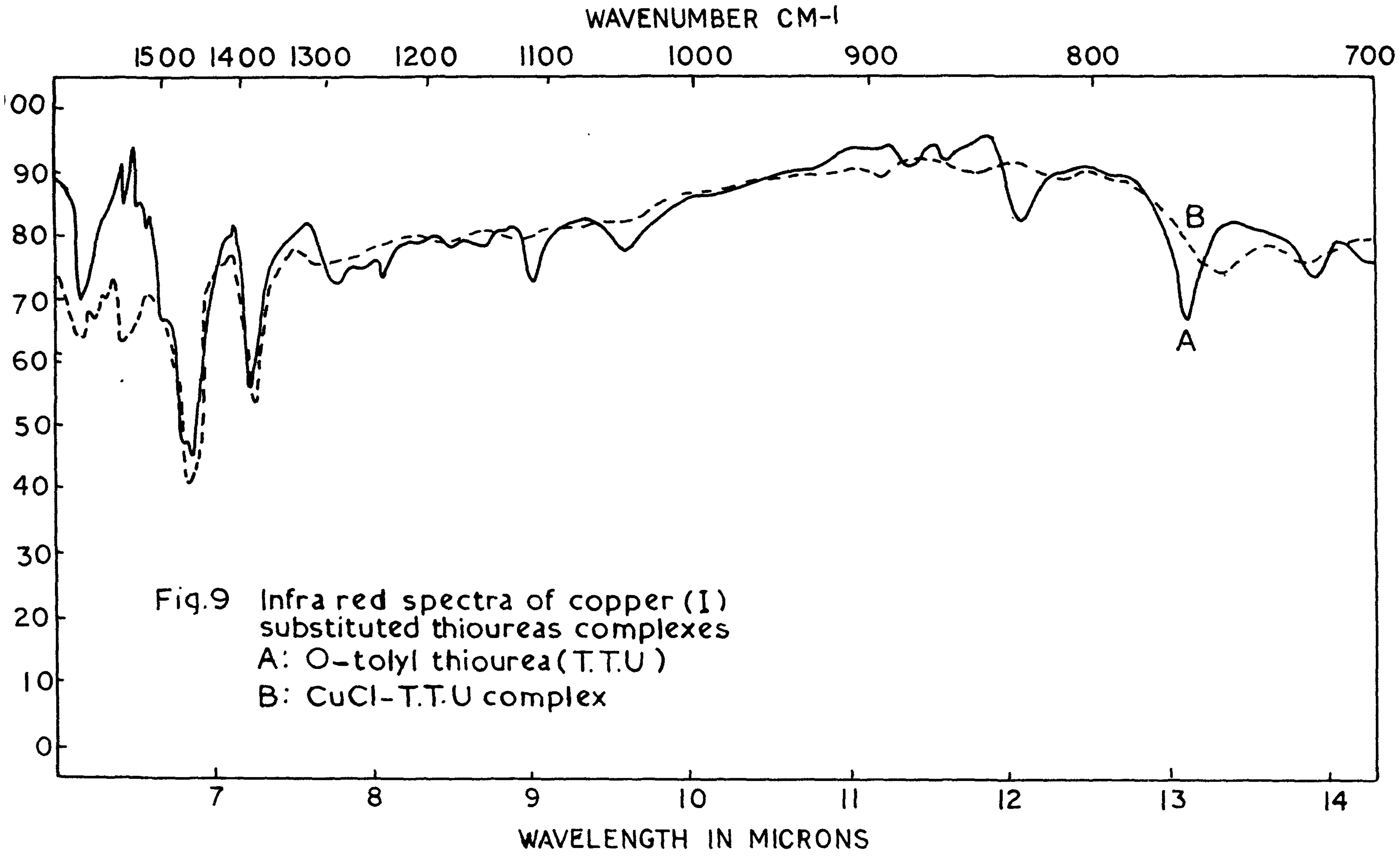

Fig.9 Infra red spectra of copper (I) substituted thioureas complexes
A: O-tolyl thiourea (T.T.U)
B: CuCl-T.T.U complex

3. Cu(D.P.T.U.)$_3$I; 700(s), 740(s), 950(m), 1170(w), 1200(w), 1270(w), 1375(v.s), 1530(s), 1570(s), 1600(s).

4. D.I.P.T.U; 750(s), 850(m), 980(v.s), 1120(s), 1165(s), 1240(s), 1310(m), 1360(m), 1410(m), 1520(s), 1550(v.s).(Fig.6A)

5. Cu(D.I.P.T.U.)$_2$Cl: 745(s), 845(w), 955(w), 980(m), 1120(s), 1160(s), 1260(m), 1380(s), 1520(s), 1560(s).

6. Cu(D.I.P.T.U.)$_3$I: 740(s), 840(w), 980(m), 1120(s), 1165(s), 1260(m), 1380(s), 1570(s). (Fig.6B)

7. N.T.U.: 745(m), 775(s), 790(s), 830(s), 870(s), 915(w),955(w), 980(m), 1010(w), 1060(m), 1085(v.s), 1160(sh),1200(w),1260(s), 1380(m), 1520(w), 1630(s). (Fig.7A)

8. Cu(N.T.U.)$_2$Cl: 725(w&b), 765(s), 795(v.w), 1290(m&b),1390(v.s) 1520(w), 1530(v.w), 1630(w), 1730(w), (Fig.7B).

9. Cu(N.T.U.)$_3$I: 720(w), 750(s), 1290(m&b), 1390(s), 1540(s), 1630(s).

10. A.T.U.: 740(s), 775(m), 935(s), 945(sh), 970(w), 995(m), 1070(s), 1130(m), 1250(s), 1320(s), 1400(m), 1540(s), 1630(s).(Fig.8A)

11. Cu(A.T.U.)Cl: 765(s), 910(v.w), 925(m), 995(w), 1280(sh), 1390(s), 1510(v.w), 1580(s), 1630(s).

12. Cu(A.T.U.)$_3$I: 775(s), 910(v.w), 925(m), 995(w), 1380(s), 1580(s), 1630(s). (Fig.8B)

13. T.T.U. : 715(m), 760(s), 855(w), 870(w), 1090(m), 1110(m), 1230(w), 1255(w),1280(w), 1490(s), 1520(w),1540(m), 1610(s). (Fig.9A)

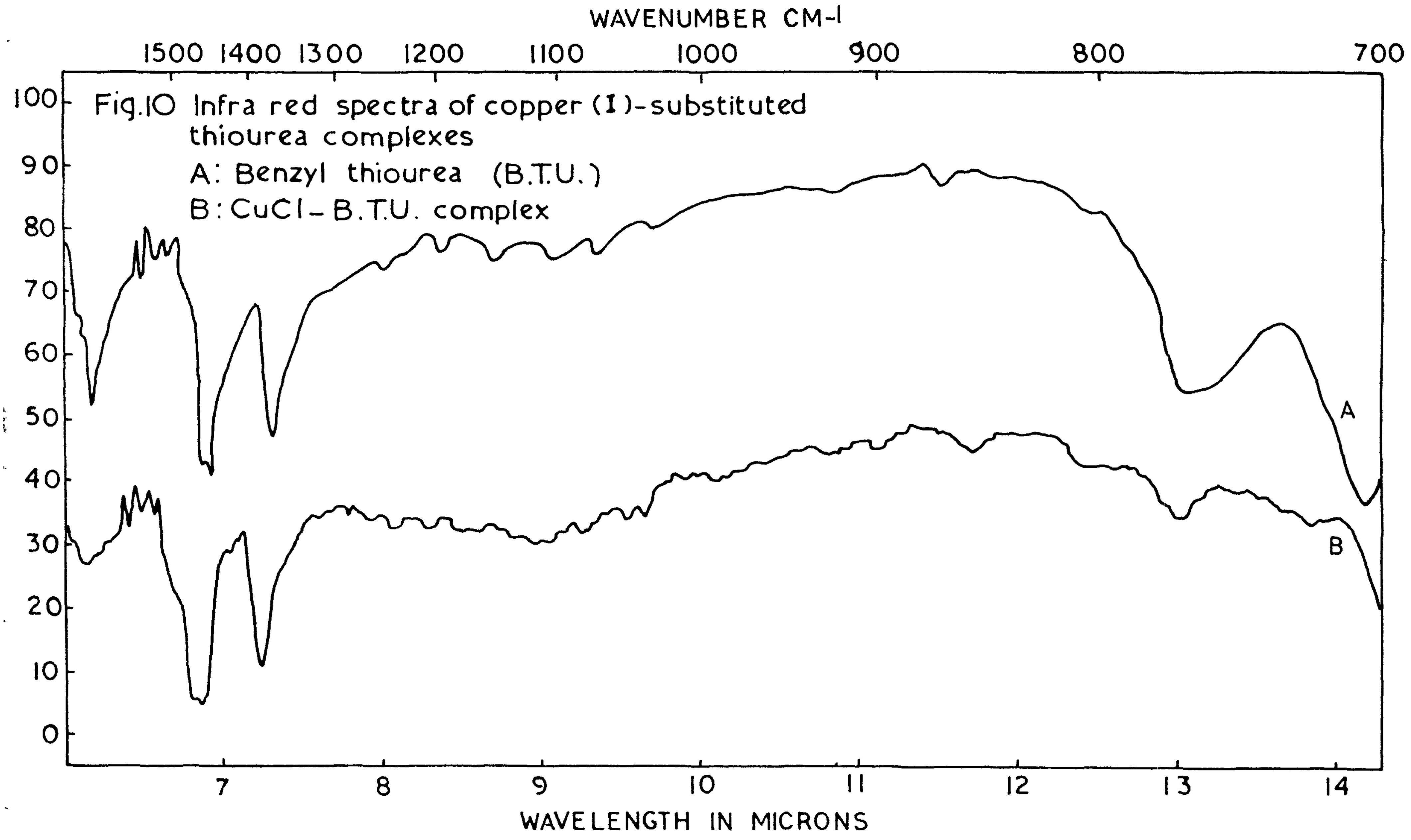

Fig.10 Infra red spectra of copper (I)-substituted thiourea complexes

A: Benzyl thiourea (B.T.U.)

B: CuCl – B.T.U. complex

14. Cu(T.T.U.)Cl: 715(s), 755(m & b), 1520(w), 1560(s), 1610(s), 1620(v.w), 1660(w), 1680(w). (Fig.9B)

15. Cu(T.T.U.)$_3$I: 725(s), 1390(s), 1530(s), 1560(s), 1610(w), 1660(w), 1680(w).

16. B.T.U. : 705(s), 750(m & b), 1030(v.w), 1075(v.w), 1105(v.w), 1200(v.w), 1260(v.w), 1390(v.s), 1500(w), 1550(m), 1560(s), 1650(s), 1680(w). (Fig.10A)

17. Cu(B.T.U.)Cl: 700(s), 770(s), 850(w), 1035(v.w), 1050(v.w), 1200(v.w), 1240(v.w), 1410(s), 1520(v.w), 1550(m), 1560(s), 1650(s), 1660(v.w), 1680(v.w). (Fig.10B)

RESULTS AND DISCUSSION

Cuprous chloride forms 1:2 and 1:1 complexes with substituted thioureas. There is formation of 1:1 species with o-tolyl thiourea (brownish black), benzyl thiourea (brown) and allyl thiourea (yellowish white), 1:2 species are formed with diisopropyl thiourea (light yellow), naphthyl thiourea (dirty yellow) and s-diphenyl thiourea (light yellowish brown). The complexes are very stable at room temperature, soluble in acetone, very slightly soluble in alcohol but insoluble in water.

The composition of the complexes was also determined by performing potentiometric titrations using $Ag-Ag_2S$ as an indicator electrode. Both direct (substituted thiourea in the cell) and indirect titrations were performed, and in each case except A.T.U., a ratio of 1:2 was obtained from the curves (Fig.3). In the case of allyl thiourea a ratio of 1:1 was obtained from the inflexion points.

Cuprous iodide forms very stable tricoordinated complexes with diphenyl thiourea (yellow), naphthyl thiourea (brownish black), diisopropyl thiourea (dark amethyst), allyl thiourea (light yellow), and o-tolyl thiourea (dark brown). The complexes are crystalline, insoluble in water, sparingly soluble in alcohol but readily soluble in acetone and tetrahydrofuran.

The potentiometric titrations were also performed in case of cuprous iodide complex, both direct and reverse, gave a ratio of

1:3 (metal:ligand) in all these cases (typical curves are given in Fig.4).

The copper(I) chloride and copper(I) iodide complexes with substituted thioureas were found to be diamagnetic as expected from coordination compounds of copper(I).

The infra red spectra of substituted thioureas and their copper(I) complexes were studied in order to ascertain the nature of coordination in these complexes. These studies are based upon the existence of resonance structures for thiourea comprising of keto and enol forms, with 20-30% contribution of highly polar structures.[17] With the assumption that like thiourea, substituted thioureas also give canonical forms with equal contributions, coordination through sulphur should result in a decrease in double bond character of C-S and an increase in double bond character of C-N bond, whereas if coordination is through nitrogen then just the opposite effect is to be expected together with the reduction in N-H frequency. The latter remains unchanged if the coordination is through sulphur.[8-10]

An examination of the spectra of the substituted thioureas showed the presence of strong bands ca.1600cm^{-1} except in case of D.I.P.T.U. and D.P.T.U., the bands are assigned to NH_2 bending modes of the substituted ligands. D.I.P.T.U. and D.P.T.U. do not show any band in this region obviously due to the absence of NH_2 groups. On coordination, the position of the bands arising due to NH_2 bending modes remain almost unaltered. The strong band at 1630 cm^{-1} observed in A.T.U. may be assigned to C=C stretching and deformation vibrations of the allyl group. The band remainsuneffected on coordination.

The absorption bands observed ca.1550 cm^{-1} in the substituted thioureas are assigned to N-H deformation and C-N antisymmetric stretching vibrations. In case of A.T.U. complexes the band disappeared showing thereby the presence of coordinated nitrogen whereas in other cases the bands remain unshifted on coordination or there is an increase in frequency to the extent of 20 to 30 cm^{-1}.

TABLE -2:

NH deformation and CN antisymmetric stretching frequencies of substituted thioureas and their copper(I) complexes.

D.I.P.T.U.	D.P.T.U.	T.T.U.	N.T.U.	A.T.U.	B.T.U.
Ligands					
1520(s)	1560(s)	1520(w)	1620(w)	1540(s)	1550(m)
1550(s)		1540(m)			1560(s)
Copper(I) chloride complexes					
1520(s)	1580(s)	1520(w)	1520(w)	-	1550(m)
1560(s)		1560(s)			1580(s)
Copper(I) iodide complexes					
1540(m)	1570(s)	1530(s)	1540(s)	-	--
1560(s)		1560(s)			

(Vide Figures 5 to 10)

The strong bands at 1120 cm^{-1} and 1165 cm^{-1} in D.I.P.T.U. are assigned to isopropyl skeletal vibrations. The bands remain uneffected on coordination. The bands ca. 750 cm^{-1} in substituted thioureas are characterised by C-S stretching modes with small contribution of symmetric C-N stretching vibrations.[18] In all cases except that of A.T.U. there is a marked decrease in frequencies on coordination. A.T.U. on coordination shows an increase in frequency by 25 cm^{-1} and 35 cm^{-1} in copper(I) chloride and copper(I) iodide complexes, respectively. The decrease in frequencies in the coordinated products is attributed to the coordination through sulphur (Table 3). This behaviour is in conformity with the observations in 1500-1600 cm^{-1} region. The increase in frequencies in A.T.U. complexes indicate the strengthening of the double bond character of C=S and thus possibility of coordination through nitrogen.

T A B L E -3:

C-S stretching frequencies of substituted thioureas and their copper(I) complexes.

Ligands

D.I.P.T.U.	D.P.T.U.	T.T.U.	N.T.U.	A.T.U.	B.T.U.
750(s)	760(s)	760(s)	775(s)	740(s)	750-775([illegible])
Copper(I) chloride complexes					
745(s)	745(s)	715(s)	765(s)	765(s)	770(s)
Copper(I) iodide complexes					
740(s)	740(s)	725(s)	750(s)	775(s)	

(Vide Figures 5 to 10)

On the basis of i.r. studies, it may be concluded that in complexes with D.P.T.U., D.I.P.T.U., N.T.U., T.T.U. and B.T.U., there is coordination through sulphur whereas the possibility of coordination through nitrogen is not ruled out in case of A.T.U. complexes. The observed effects in infra red frequencies are more marked in cuprous iodide complexes which is an indication of comparatively strong bonding in these complexes.

The coordination of sulphur containing ligands with copper(I) compounds is well known and, in general such ligands and others which favour the formation of π bonds stabilises copper(I) state. In thiourea and substituted thioureas complexes, there is formation of $d_\pi - d_\pi$ bond due to availability of vacant d orbital in sulphur which also acts as an acceptor d orbital. In copper(I) chloride complexes, the formation of 1:1 and 1:2 species, and in the case of copper(I) iodide the formation of 1:3 species may be qualitatively explained on considering : (i) the possibility of minimising the excessive charge on Cu^+ by transferring it to d_π levels of the ligands which may also be directly related to the order of nucleophility of the substituted ligands: DIPTU > ATU > TTU > BTU > NTU > DPTU[19] (ii) the role of anions e.g., Cl^- and I^-. In copper(I) iodide complexes, due to the presence of highly polarised iodine atom in the vicinity of coordination sphere there is a possibility of drainage of electrons to more electronegative sulphur with the result that the deficiency of electrons created due to coordination to Cu^+ should be compensated by the electrons transferred from iodine. Consequently, the possibility of the transference of excessive charge on Cu^+ not only to $d\pi$ level of sulphur but also to $d\pi$ level of iodine cannot be ruled out. This charge distribution brings more stability to copper(I) iodide complexes than those of copper(I) chloride. Considering the latter, the electronegativity of chlorine is slightly higher than that of sulphur and obviously the charge distribution will not be so uniform.

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CHAPTER - III:

STUDIES ON MIXED LIGAND COMPLEXES OF COPPER(I)

Studies on Mixed Ligand Complexes of Copper(I).

The tendency of Cu^+ ion to form linear coordinate species is well known and this has been attributed to the small d-s separation in a small group of ions, e.g., Cu^+, Ag^+, Au^+ and Hg^{++} with d^{10} configurations.[1] A remarkable feat of linear coordination characteristics is the formation of lower complex species in d^{10} metal ions in general and copper(I) in particular. The coordination number of copper(I) in the complex species is frequently one or two and sometimes three, and only a few convincing examples are available for the tetracoordinate species, worth mentioning are those of cyanides, tertiary arsines and tertiary phosphines complexes. Although in these species, Cu^+ has initially a coordination number of two but by a polymerisation mechanism usually through a bridging, a tetracoordinate structure is obtained. In the chapters I and II of this thesis the complexes of copper(I) with heterocyclic amines and substituted thiourea have been described and the formations of mono-coordinated species with pyridine and related compounds, and di and tri coordinated species in substituted thioureas, have been explained on the basis of weak and strong π bonding capacities of the ligands, respectively. The thiourea and related compounds are highly polarised ligands having readily available d_π acceptor orbitals for $d_\pi - d_\pi$ bonding, whereas in heterocyclic amines due to weak acceptor properties the excessive electron cloud around the small positively charged Cu^+ ion may not be neutralised through back coordination, and hence the formation of only lower species is preferred.[2]

Based on the above mentioned information regarding the chemistry of copper(I) and combined with the fact that Cu(I) tries to achieve a maximum coordination four, it was planned to investigate the reactions of lower complex species of copper(I) with other ligands and initially examine the nature and composition of the mixed ligand complexes.

The work presented in the following pages consists of the syntheses of mixed ligand complexes formed by the interaction of heterocyclic amines such as pyridine, picolines, 2,6 lutidine, quinoline, isoquinoline, 2,2'dipyridyl and o-phenanthroline with tris(tu)copper(I)chloride and iodides. The studies have been supplemented with the determination of the compositions of the complexes by the conductometric and potentiometric titrations. Wherever possible spectrophotometric method has also been employed for determining their compositions.

The study of the infra red spectra was also utilized to determine the nature of the coordination bond in these complexes. The effects of substitution and addition have been discussed in the light of the observed changes in ca.1600 cm^{-1}(NH_2 bending, N - H deformation and C-N stretching vibrations of thiourea, ring CC,CN stretching vibrations in heterocyclic amines), and ca. 700 cm^{-1} (CH out of plane deformation vibrations in amines and C-S stretching vibrations in thiourea) regions.

EXPERIMENTAL

Preparation of the Complexes:

1. Tris(tu) copper(I) chloride: A concentrated solution of copper(I) chloride (2g) was prepared in concentrated KCl solution. The cuprous solution was mixed with an aqueous solution containing about 4g of thiourea. The resulting solution was warmed slightly with constant stirring and was then filtered. The filtrate was evaporated to dryness over a water bath. The product so obtained was washed several times with small aliquots of distilled water and was then dissolved in absolute alcohol. The insoluble portion was filtered out. The resulting solution was concentrated and then allowed to stand for about one hour when colourless crystals appeared. The crystals were separated and dried in a vacuum desiccator.

Tris(tu) copper(I) chloride. Colourless crystals, soluble in water and organic solvents.

Calc. for $C_3H_{12}N_6S_3$ CuCl: C-11.0, H-3.65, N-25.7, S-29.3, Cu-19.4, Cl-10.85. Found: C-10.7, H-3.6, N-25.5, S-29.1, Cu-19.5, Cl-10.80.

2. Tris(tu) copper(I) iodide: About 2g of copper(I) iodide was dissolved in 100 ml of acetone (containing about 5g of KI) and to it about 6g of thiourea was added. The resulting

solution was boiled for about 5 mts. over a water bath, filtered and the filtrate was evaporated to dryness. The light pink product so obtained was washed several times with small aliquots of water and alcohol and finally dissolved in acetone. The insoluble portion was filtered out. The resulting solution was concentrated and allowed to stand for 1-2 hours. The light pink crystals were separated and dried in vacuum desiccator.

Tris(tu) copper(I) iodide. Very light pink crystals, soluble in water and alcohol, highly soluble in acetone.
Calc. for $C_3H_{12}N_6S_3CuI$: C-8.6, H-2.9, N-20.1, S-22.9, Cu-15.2, I-30.3. Found: C-8.3, H-2.7, N-20.0, S-22.7, Cu-15.1, I-30.2.

3. Tris(tu) mono(py) copper(I) iodide: About 5g of tris(tu) copper(I) iodide was treated with about 50 ml. of pyridine (added in small volumes with constant mixing). To the resulting mixture about 100 ml. of acetone was added and the whole solution was refluxed over a water bath for about 3 hours, the refluxed solution was then evaporated slowly to dryness. The pink product so obtained was crystallised from acetone.

Tris(tu)mono(py)copper(I) iodide. Light pink crystals, m.p. 125°C, soluble in water and organic solvents.
Calc. for $C_8H_{17}N_7S_3$ CuI: C-19.3, H-3.4, S-19.3, N-19.7, Cu-12.8, I-25.5. Found: C-19.0, H-3.2, S-19.3, N-19.6, Cu-12.6, I-25.6.

The preparations of mixed complexes with 2,3 and 4 picolines, 2,6 lutidine, quinoline and isoquinoline were carried out by the same method as described in case of tris(tu)mono(py)copper(I) iodide.

The followings are the results of analysis and the properties of the complexes:

4. Tris(tu)mono(2pic) copper(I) iodide: Pink crystals, soluble in water and acetone, m.p. 120°C.
Calc. for $C_9H_{19}N_7S_3CuI$: C-21.1, H-3.7, N-19.2, S-18.8, Cu-12.4, I-24.8. Found: C-20.8, H-3.6, N-19.1, S-18.8, Cu-12.4, I-24.7.

5. Tris(tu)mono(3pic)copper(I) iodide: Light pink crystals, soluble in water and organic solvents, m.p. 122°C.
Calc. for $C_9H_{19}N_7S_3CuI$: C-21.1, H-3.7, N-19.2, S-18.8, Cu-12.4, I-24.8. Found: C-20.7, H-3.5, N-19.3, S-18.8, Cu-12.5, I-24.7.

6. Tris(tu)mono(4pic)copper(I)iodide: Pink crystals, soluble in water and organic solvents, m.p. 118°C.
Calc. for $C_9H_{19}N_7S_3CuI$: C-21.1, H-3.7, N-19.2, S-18.8, Cu-12.4, I-24.8. Found: C-20.8, H-3.6, N-19.3, S-18.7, Cu-12.4, I-24.7.

7. Tris(tu)mono(2,6L) copper(I) iodide: Light pink crystals, slightly soluble in water and soluble in organic solvents, m.p. 117°C.
Calc. for $C_{10}H_{21}N_7S_3CuI$: C-22.8, H-4.0, N-18.65, S-18.3, I-24.15, Cu-12.1. Found: C-22.1, H-3.8, N-18.6, S-18.3, I-24.1, Cu-12.2.

8. Tris(tu)mono(Q)copper(I) iodide: Dirty yellow product, slightly soluble in water, soluble in alcohol but highly soluble in acetone, m.p. 116°C.
Calc. for $C_{12}H_{19}N_7S_3CuI$: C-26.3, H-3.5, N-17.9, S-17.5, Cu-11.6, I-23.2. Found: N-17.6, S-17.3, Cu-11.7, I-23.0.

9. Tris(tu)mono(I.Q)copper(I) iodide: Pink crystals, slightly soluble in water but soluble in organic solvents, m.p. 118°C.
Calc. for $C_{12}H_{19}N_7S_3CuI$: C-26.3, H-3.5, N-17.9, S-17.5, Cu-11.6, I-23.2. Found: C-25.8, H-3.3, N-17.7, S-17.5, Cu-11.4, I-23.1.

Attempts to prepare 2,4-lutidine, acridine and piperidine mixed ligand complexes in sufficiently pure form proved unsuccessful.

10. Bis(tu)mono(dipy)copper(I)iodide: About 2g of 2,2'-dipyridyl was added to 200 ml. of acetone containing about 4.2g of tris(tu) copper(I) iodide. The resulting solution was refluxed for about half an hour and then evaporated slowly over a water bath. The pinkish product so obtained was washed several times with small aliquots of absolute alcohol and then dissolved in acetone and crystallised.

Bis(tu)mono(dipy)copper(I)iodide: Red crystals, insoluble in H_2O, soluble in acetone, m.p. 135°C.
Calc. for $C_{12}H_{16}N_6S_2CuI$: C-28.9, H-3.2, N-16.85, S-12.8, Cu-12.7, I-25.4. Found: C-28.6, H-3.1, N-16.7, S-12.8, Cu-12.6, I-25.4.

11. Bis(tu)mono(phOAs)copper(I): About 0.5g of phenyl arsonic acid (phOAs) was added to 100 ml. of 2.5% alcoholic solution of tris(tu)mono(py)copper(I)iodide. The whole mass was heated over a water bath for about 15 minutes, filtered and the filtrate was evaporated to dryness. The yellow product so obtained was washed several times with 80% ethanol and then dissolved in acetone and crystallised.

Bis(tu)mono(phOAs)copper(I): Lemon yellow crystals, soluble in acetone and alcohol but hydrolysed in presence of water.

Calc. for $C_8H_{14}O_3N_4S_2As$: C-26.5, H-3.4, N-13.4, S-15.4, Cu-15.25.
Found: N-13.2, S-15.5, Cu-14.8.

12. Bis(tu)mono(dipy)copper(I)iodide: It was obtained by the action of 2,2' dipyridyl on tris(tu)mono(py)copper(I)iodide. 100 ml. of 2.5% alcoholic solution of 2,2' dipyridyl was added to a solution of tris(tu)mono(py)copper(I) iodide (5g in 100 ml. of acetone). The resulting red coloured solution was concentrated by evaporating to half of its volume and then kept for crystallisation. After a few hours red crystals of the product appeared which were separated, dissolved in acetone and recrystallised.

Red crystals insoluble in water, and soluble in acetone, m.p. 126°C.

Calc. for $C_{12}H_6N_6S_2CuI$: N-16.8, S-12.8, Cu-12.7, I-25.5
Found: N-16.5, S-12.5, Cu-12.6, I-25.4.

13. Bis(tu)mono(dipy)copper(I)chloride: The complex was prepared by the procedure adopted in case of bis(tu)mono(dipy)copper(I) iodide, using tris(tu)copper(I) chloride as the starting material.

Bis(tu)mono(dipy)copper(I) chloride: Orange crystals, insoluble in water, soluble in acetone.
Calc. for $C_{12}H_{16}N_6S_2CuCl$: C-35.4, H-3.9, N-20.6, S-15.7, Cl-8.7 Cu-15.8. Found: C-35.6, H-3.85, N-20.4, S-15.8, Cl-8.8, Cu-15.7.

14.(a) Bis(tu)mono(o-phen)copper(I)iodide,(b) Bis(o-phen)mono(tu) copper(I) iodide and (c) Bis(o-phen)copper(I)iodide.

About 2g of o-phenanthroline was added to 200 ml. solution of tris(tu)copper(I)iodide in acetone (2g per 100 ml. of acetone). The resulting red coloured solution was heated over a water bath for a while and then allowed to stand for about half an hour. Black crystals appeared and settled at the bottom. The supernatant liquid was separated, diluted with about 20 ml. of distilled water, concentrated and allowed to stand for about one hour. Orange crystals appeared and deposited at the wall of the vessel, were separated from the residual liquid. The latter was concentrated by evaporating to half of its volume, diluted with about 25 ml. of water and kept for crystallisation. After 2-3 hours pink coloured needle shaped crystals appeared and were separated from the solution. The latter was kept for further crystallisation.

The black crystals, [Cu(o-phen)$_2$I] appearing first during the crystallisation process were washed with small aliquots of water and alcohol and then soaked with a filter paper and dried in vacuum desiccator.

The orange crystals, [Cu(tu)$_2$o-phen I] were washed with distilled water and alcohol, dissolved in acetone and recrystallised.

The pink crystals of [Cu(tu)o-phen$_2$ I] were dissolved in water, filtered and the filtrate was concentrated and kept for recrystallisation.

The whole process may be illustrated as follows:

Cu(tu)$_3$I + o-phen.
in acetone
$\downarrow$ I crystallisation
Black crystals (sol.in alcohol, acetone)
and insol. in water)
Cu(o-phen)$_2$I
$\downarrow$ II crystallisation
Orange crystals (sol.in acetone and insol.in water)
(Cu(tu)$_2$o-phen)I
$\downarrow$ III crystallisation
Needle shaped pink crystals(sol.in water, acetone)
and alcohol
[Cu(tu)o-phen$_2$] I

(a) Bis(tu)mono(o-phen)copper(I)iodide: Orange crystals, insoluble in water, soluble in alcohol and highly soluble in acetone, m.p. 230°C, diamagnetic.

Calc. for $C_{14}H_{16}N_6S_2CuI$: C-32.15, H-3.1, N-16.1, S-12.25, Cu-12.15, I-24.3, Found: C-33.2, H-3.8, N-16.1, S-12.2, Cu-12.1, I-24.1.

(b) Bis(o-phen)mono(tu)copper(I)iodide. Needle shaped pink crystals, soluble in water, acetone and alcohol, m.p.195°C; diamagnetic.

Calc. for $C_{25}H_{20}N_6S$ CuI: C-47.9, H-3.2, N-13.4, Cu-10.1, I-20.25, S-5.1. Found: C-46.3, H -3.5, N-13.2, Cu-10.0, I-20.1, S-5.2.

(c) Bis(o-phen)copper(I)iodide. Black fine crystals, insoluble in water and alcohol but soluble in acetone, m.p.320°C, diamagnetic.

Calc. for $C_{24}H_{16}N_4CuI$: C-53.3, H-2.9, N-10.2, Cu-11.5, I-23.05. Found: C-52.1, H-3.2, N-10.3, Cu-11.3, I-23.2.

C, H, N and S analyses were carried out by the Australian micro-analytical Service, and Indian Institute of Technology, Kanpur. Copper and halogens were estimated as described in the case of copper(I) heterocyclic amines complexes (chapter I).

Conductometric measurements:

Conductometric measurements were performed with a Philips Conductivity Bridge, model PR9500, using a dip type conductivity cell (cell const: 1.482).

The titrations were carried out by using solutions of various concentrations of pyridine, picolines (2,3 and 4), 2,6 lutidine, quinoline, isoquinoline, 2,2' dipyridyl, o-phenanthroline and phenylarsonic acid as titrants, and tris(tu) copper(I) chloride and iodides in the cell.

The data of conductivity titrations for pyridine, 3-picoline and quinoline are given in table 1 and the typical curves in Fig.1.

TABLE -1:

Conductometric titrations between heterocyclic amines and tris(tu)copper(I) iodide at 30^oC.

(10 ml. of $Cu(tu)_3 I$ ($5x10^{-2}M$) in the cell)		(10 ml. of $Cu(tu)_3 I$ ($5x10^{-2}M$) in the cell)	
Vol. of ($1x10^{-1}M$) pyridine in ml.	Conductance $X10^{-2}$ mhos.	Vol. of ($1x10^{-1}M$) 3 picoline in ml.	Conductance $X10^{-2}$ mhos.
0	2.083	0	1.41
1	1.960	1	2.272
2	1.886	3	2.083
4	1.754	5	1.787
8	1.673	7	1.787
10	1.66	9	1.787
12	1.646	10	1.785
15	1.6113	12	1.787
		15	1.787

(a) Bis(tu)mono(o-phen)copper(I)iodide: Orange crystals, insoluble in water, soluble in alcohol and highly soluble in acetone, m.p. 230°C, diamagnetic.

Calc. for $C_{14}H_{16}N_6S_2CuI$: C-32.15, H-3.1, N-16.1, S-12.25, Cu-12.15, I-24.3, Found: C-33.2, H-3.8, N-16.1, S-12.2, Cu-12.1, I-24.1.

(b) Bis(o-phen)mono(tu)copper(I)iodide. Needle shaped pink crystals, soluble in water, acetone and alcohol, m.p.195°C; diamagnetic.

Calc. for $C_{25}H_{20}N_6S$ CuI: C-47.9, H-3.2, N-13.4, Cu-10.1, I-20.25, S-5.1. Found: C-46.3, H -3.5, N-13.2, Cu-10.0, I-20.1, S-5.2.

(c) Bis(o-phen)copper(I)iodide. Black fine crystals, insoluble in water and alcohol but soluble in acetone, m.p. 320°C, diamagnetic.

Calc. for $C_{24}H_{16}N_4CuI$: C-53.3, H-2.9, N-10.2, Cu-11.5, I-23.05. Found: C-52.1, H-3.2, N-10.3, Cu-11.3, I-23.2.

C, H, N and S analyses were carried out by the Australian micro-analytical Service, and Indian Institute of Technology, Kanpur. Copper and halogens were estimated as described in the case of copper(I) heterocyclic amines complexes (chapter I).

Conductometric measurements:

Conductometric measurements were performed with a Philips Conductivity Bridge, model PR9500, using a dip type conductivity cell (cell const: 1.482).

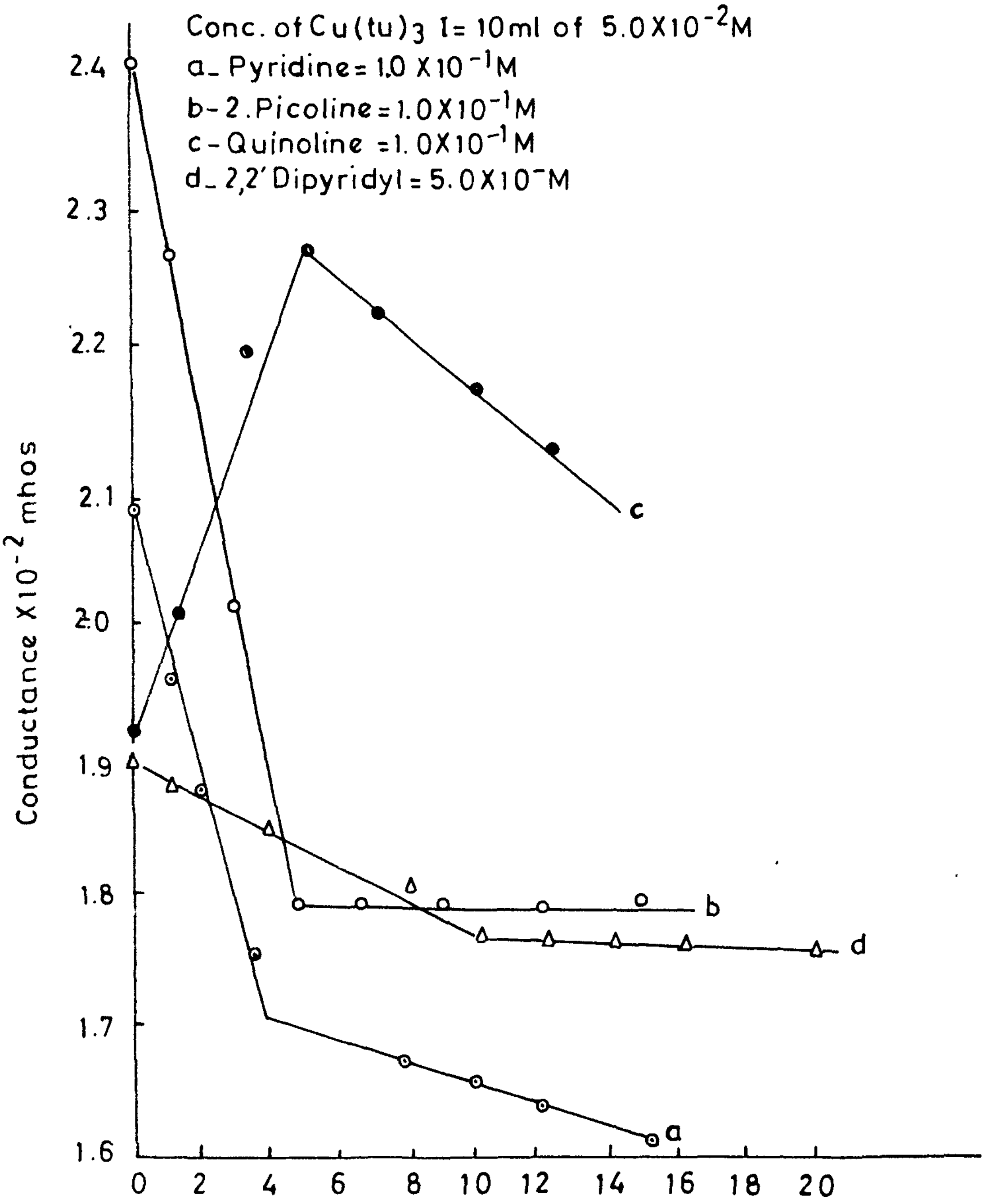


Fig. 1 Conductometric Titrations
(tris (tu)copper(I)iodide in the cell)

The titrations were carried out by using solutions of various concentrations of *pyridine*, *picolines* (2,3 and 4), 2,6 lutidine, quinoline, isoquinoline, 2,2' dipyridyl, o-phenanthroline and phenylarsonic acid as titrants, and tris(tu) copper(I) chloride and iodides in the cell.

The data of conductivity titrations for pyridine, 3-picoline and quinoline are given in table 1 and the typical curves in Fig.1.

TABLE -1:

Conductometric titrations between heterocyclic amines and tris(tu)copper(I) iodide at 30°C.

(10 ml. of $Cu(tu)_3I$ ($5x10^{-2}M$) in the cell)		(10 ml. of $Cu(tu)_3I$ ($5x10^{-2}M$) in the cell)	
Vol. of ($1x10^{-1}M$) pyridine in ml.	Conductance $X10^{-2}$ mhos.	Vol. of ($1x10^{-1}M$) 3 picoline in ml.	Conductance $X10^{-2}$ mhos.
0	2.083	0	1.41
1	1.960	1	2.272
2	1.886	3	2.083
4	1.754	5	1.787
8	1.673	7	1.787
10	1.66	9	1.787
12	1.646	10	1.785
16	1.6113	12	1.787
		15	1.787

10 ml. of $Cu(tu)_3I$ ($5x10^{-2}M$) in the cell

Vol. of($1x10^{-1}M$)quinoline in ml.	Conductance $X10^{-2}$mhos.
0	1.923
1	2.000
3	2.220
5	2.272
7	2.227
10	2.174
12	2.128
15	1.961
16	1.923
18	1.960

Spectrophotometric Studies:

Spectrophotometric measurements were performed in the visible range with a Bausch and Lomb Spectronic '20' colorimeter using 1 cm. diameter cuvette.

Applying spectrophotometric method to the complexes formed by the interaction of tris(tu) copper(I) chloride and iodides with o-phen. and dipy., the λ_{max} of the complexes were as follows:

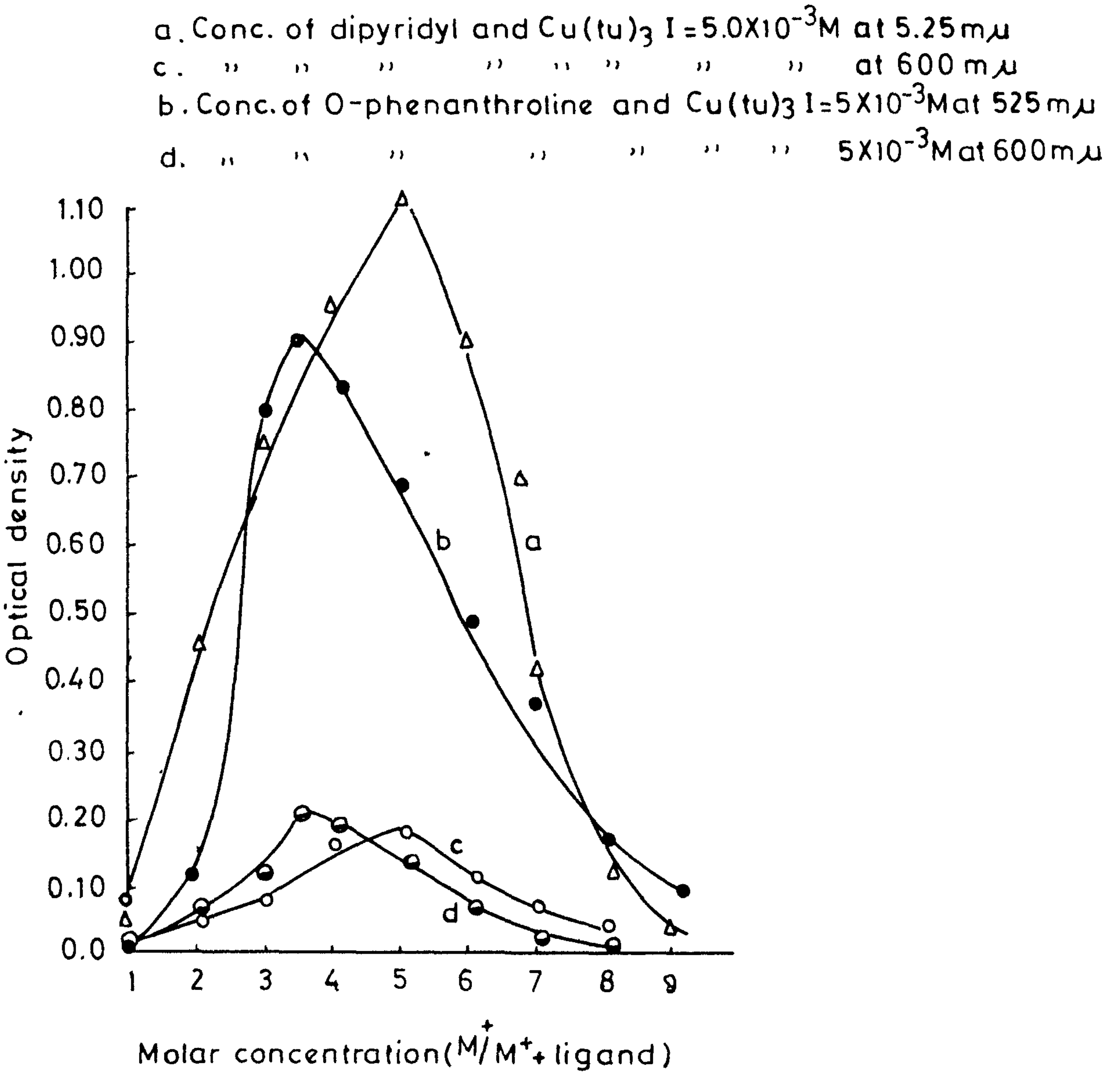


Fig. 2 Job's Method Of Continuous Variation

System $Cu(tu)_3 I$ and O-phenanthroline, and dipyridyl.

$Cu(tu)_3I$ + dipy.	525 m μ
$Cu(tu)_3I$ + o-phen.	525 m μ
$Cu(tu)_3Cl$ + dipy.	500 m μ
$Cu(tu)_3Cl$ + o-phen.	515 m μ

The composition of the complexes was determined by applying Job's method of continuous variation.[3] Typical curves for the systems: $Cu(tu)_3I$ + dipy and $Cu(tu)_3I$ + o-phen, at two different wave lengths e.g., 525 m μ and 600 m μ, are given in fig.2.

Potentiometric measurements:

Potentiometric measurements were carried out with a 'Kaycee' potentiometer type MG3 with a lamp and scale arrangement. Platinum and calomel were employed as indicator and reference electrodes, respectively.

Potentiometric titrations were carried out with several solutions containing: (i) 10 ml CuCl (9.75x10^{-1}M), (ii) 35 ml pyridine (1x10^{-1}M), (iii) 35 ml thiourea (1x10^{-1}), (iv) 22 ml dipyridyl (1x10^{-1}), (v) 10 ml CuCl (9.75x10^{-1}M) + 35 ml thiourea (1x10^{-1}M), (vi) 10 ml CuCl (9.75x10^{-1}M) + 35 ml pyridine (1x10^{-1}M), (vii) 10 ml CuCl (9.75x10^{-1}M) + 22 ml dipyridyl (1x10^{-1}M), (viii) 10 ml CuCl (9.75x10^{-1}M) + 35 ml pyridine (1x10^{-1}M) + 35 ml thiourea (1x10^{-1}M), (ix) 10 ml $Cu(tu)_3Cl$ (1x10^{-1}M), (x) 10 ml

$Cu(tu)_3Cl$ ($1x10^{-1}M$) + 35 ml pyridine ($1x10^{-1}M$), (xi) 10 ml $Cu(tu)_3Cl$ ($1x10^{-1}M$) + 22 ml dipyridyl ($1x10^{-1}M$),(xii) 10 ml CuI ($8.76x10^{-2}M$), (xiii) 10 ml CuI ($8.76x10^{-2}M$) + 35 ml pyridine ($1x10^{-1}M$), (xiv) 10 ml CuI ($8.76x10^{-2}M$) + 35 ml thiourea($1x10^{-1}M$), (xv) 10 ml CuI ($8.76x10^{-2}M$) + 22 ml dipyridyl ($1x10^{-1}M$), (xvi) 10 ml CuI ($8.76x10^{-2}M$) + 35 ml pyridine ($1x10^{-1}M$) + 35 ml thiourea ($1x10^{-1}M$), (xvii) 10 ml $Cu(tu)_3I$ ($1x10^{-1}M$), (xviii) 10 ml $Cu(tu)_3I$ ($1x10^{-1}M$) + 35 ml pyridine ($1x10^{-1}M$), (xix) 10 ml $Cu(tu)_3I$ ($1x10^{-1}M$) + 22 ml dipyridyl ($1x10^{-1}M$), (xx) 10 ml $Cu(tu)_3I$ ($1x10^{-1}M$) + 20 ml o-phen ($1x10^{-1}M$) + 6 ml KCl (1.0M), (xxi) 10 ml $Cu(tu)_3I$ ($1x10^{-1}M$) + 30 ml o-phen ($1x10^{-1}M$) + 12 ml KCl (1.0M), (xxii) 10 ml $Cu(tu)_3I$ ($1x10^{-1}M$) + 40 ml o-phen. ($1x10^{-1}M$) + 12 ml KCl (1.0M), (xxiii) 10 ml CuI($1x10^{-1}M$) + 30 ml o-phen. ($1x10^{-1}M$) + 8 ml KCl (1.0M), (xxiv) 10 ml CuI($1x10^{-1}M$) + 30 ml o-phen. ($1x10^{-1}M$) + 40 ml tu($1x10^{-1}M$) + 16 ml KCl(1.0M) and ,(xxv) 10 ml CuI ($1x10^{-1}M$) + 40 ml o-phen. ($1x10^{-1}M$) + 40 ml tu($1x10^{-1}M$) + 18 ml KCl (1.0M).

Standard $1x10^{-1}M$ nitric acid soln. was used as a titrant. A constant ionic strength was maintained in the solutions by the addition of unimolar potassium chloride.

The results of potentiometric titrations are summarised in table 2 and the curves are given in fig.3A to 3L.

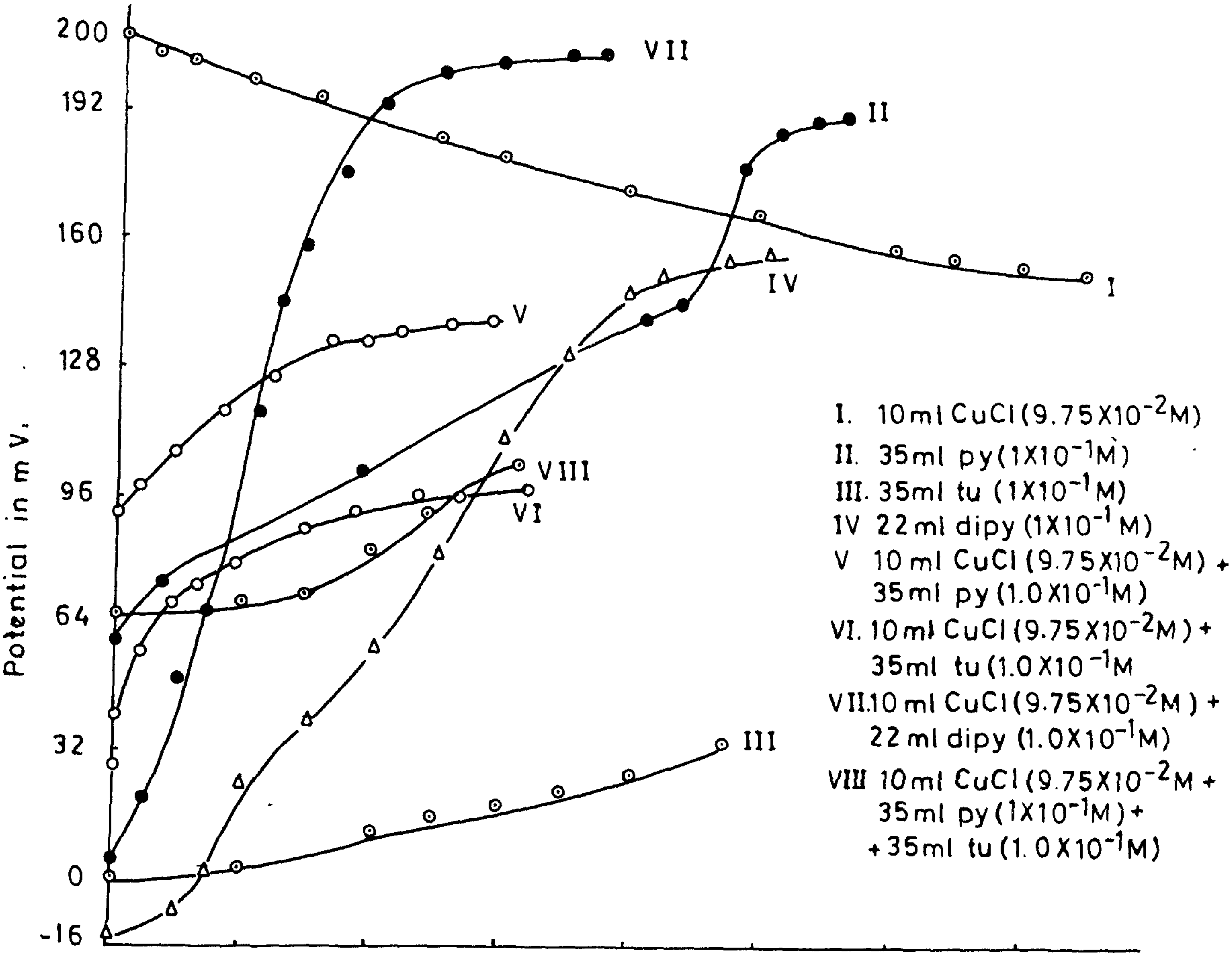


Fig. 3A Potentiometric Titrations

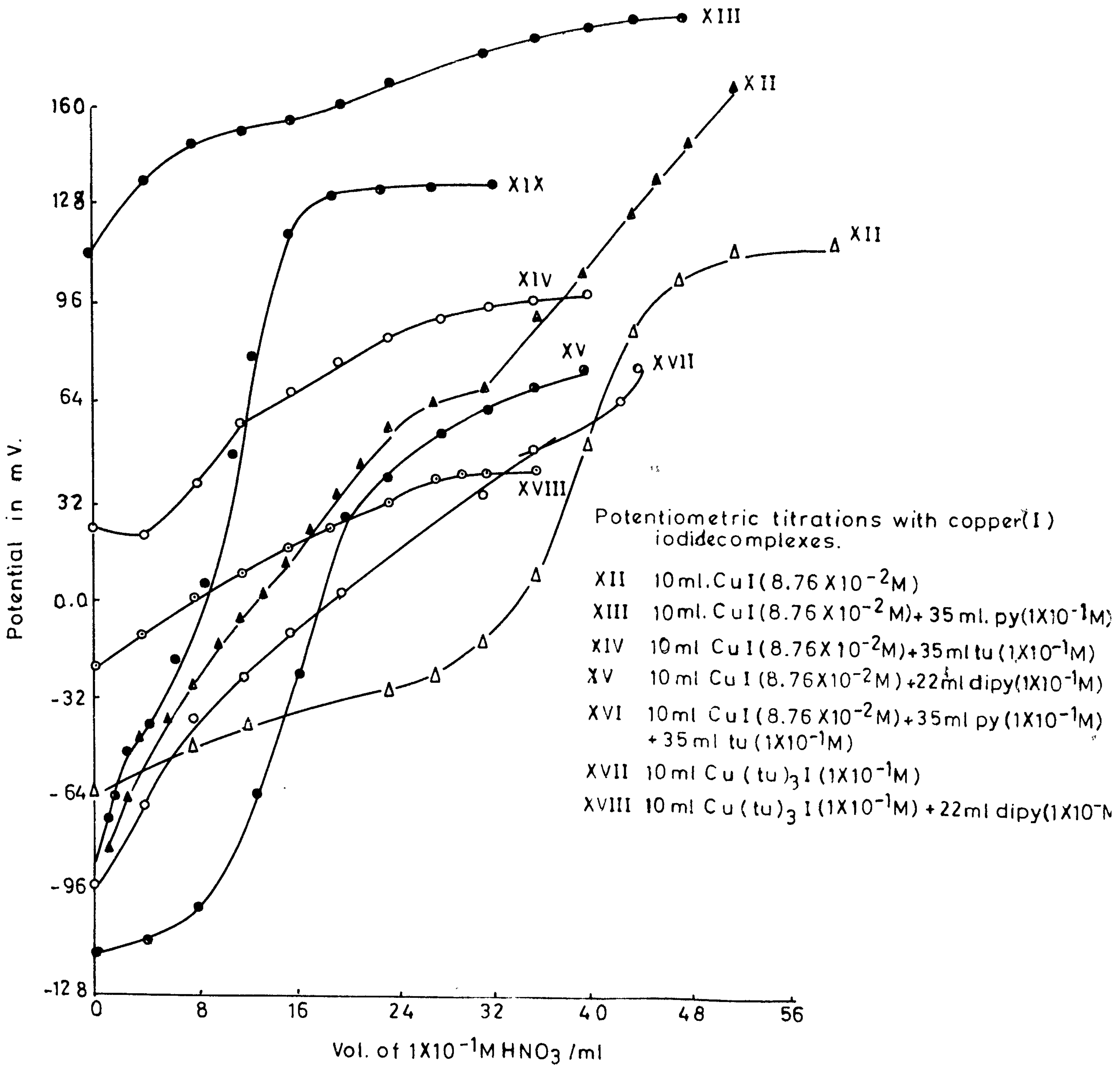


Fig. 3C Potentiometric Titrations

TABLE-2:

Summarised results of the potentiometric titrations for the systems: CuX + tu + am and $Cu(tu)_3X$ + am (X=Cl, I, am = amine) using HNO_3(0.1M) as a titrant.

S.No.	Concentration of the species present	Curve No.	Ionic strength
I.	10 ml CuCl (9.75×10^{-2}M)	3A(I)	2.0
II.	35 ml py (1×10^{-1}M)	3A(II)	-
III.	35 ml tu (1×10^{-1}M)	3A(III)	-
IV.	22 ml dipy (1×10^{-1}M)	3A(IV)	-
V.	I + II	3A(V)	0.44
VI.	I + III	3A(VI)	0.44
VII.	I + IV	3A(VII)	0.62
VIII.	I + II III	3A(VIII)	0.25
IX.	10 ml $Cu(tu)_3Cl$ (1×10^{-1}M)	3B(IX)	2.0
X.	IX + II	3B(X)	0.44
XI.	IX + IV	3B(XI)	0.62
XII.	10 ml CuI (8.76×10^{-2}M)	3B(XII)	-
XIII.	XII + II	3C(XIII)	0.44
XIV.	XII + III	3C(XIV)	0.44
XV.	XII + 11 ml. dipy (1×10^{-1}M)	3C(XV)	0.62
XVI.	XII + II + III	3C(XVI)	0.25
XVII.	10 ml $Cu(tu)_3I$ (1×10^{-1}M)	3C(XVII)	-
XVIII.	XVII + II	3C(XVIII)	0.44
XIX.	XVII + IV	3C(XIX)	0.62

(Contd.)

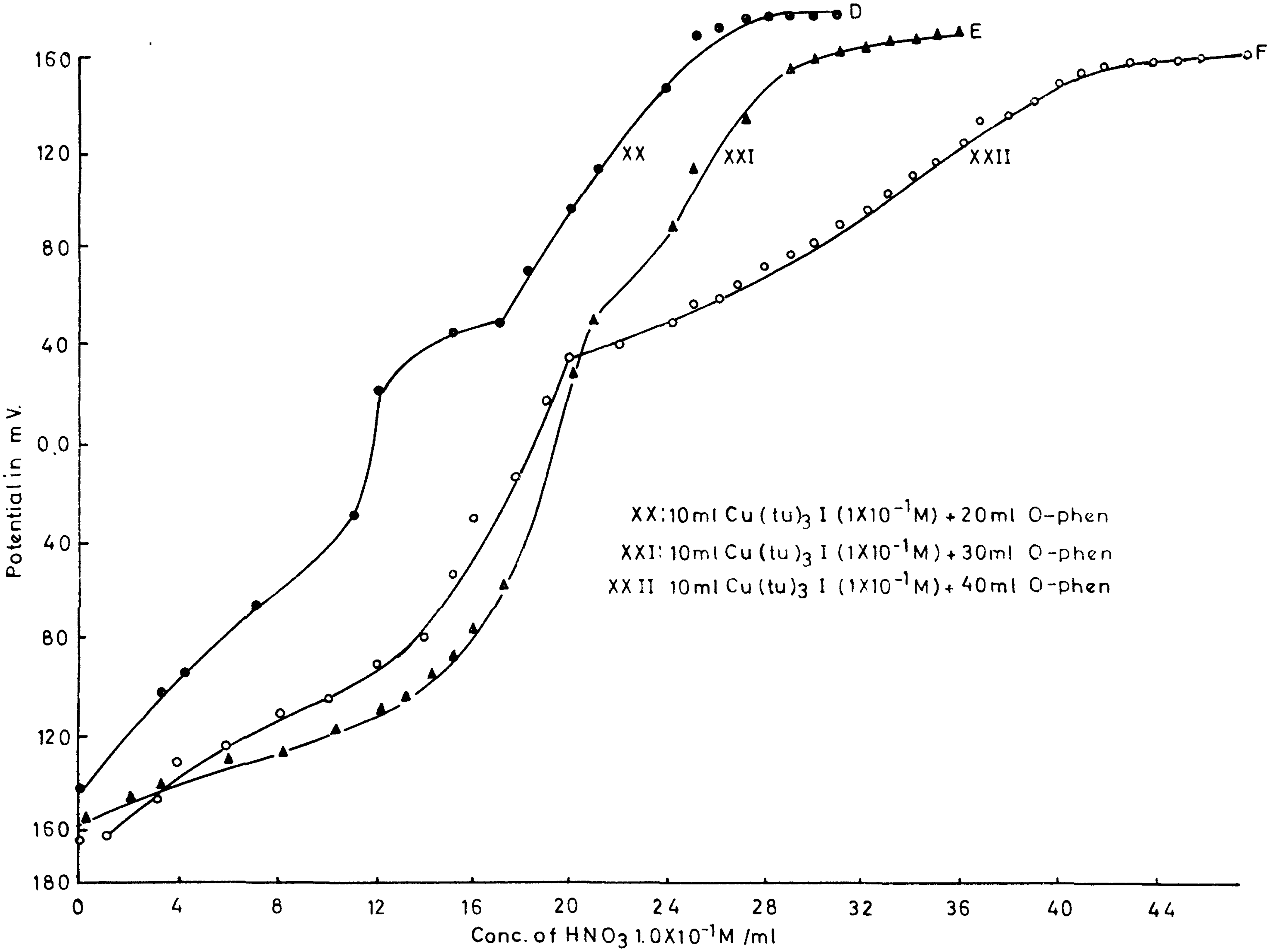


Fig.3D Potentiometric Titrations

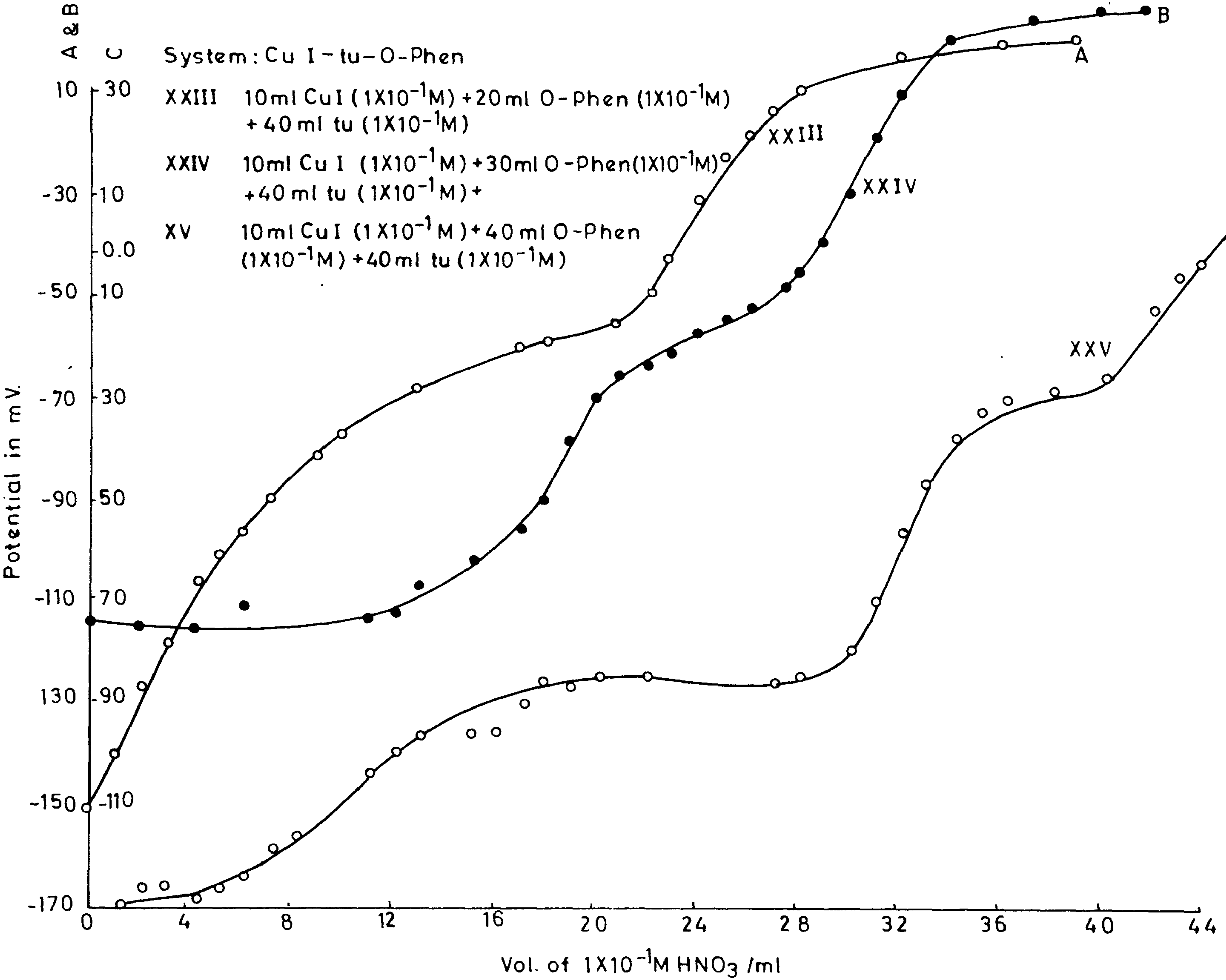


Fig. 3E Potentiometric Titrations

TABLE -2 (Contd.)

Summarised results of the potentiometric titrations for the systems: CuX+ tu + am and $Cu(tu)_3X$ + am (X = Cl, I; am = amine) using HNO_3 (0.1M) as a titrant.

S. No.	Concentration of the species present	Curve No.	Ionic strength
XX.	XVII + 20 ml o-phen ($1x10^{-1}M$)	3D(XX)	0.66
XXI.	XVII + 30 ml o-phen ($1x10^{-1}M$)	3D(XXI)	0.66
XXII.	10 ml $Cu(tu)_3I$ ($1x10^{-1}M$) + 40 ml o-phen ($1x10^{-1}M$)	3D(XXII)	0.66
XXIIA.	10 ml CuI ($1x10^{-1}M$)	-	-
XXIII.	XXIIA + 20 ml o-phen ($1x10^{-1}M$)	3E(XXIII)	0.66
XXIV.	XXIIA + 30 ml o-phen +40ml tu($1x10^{-1}M$)	3E(XXIV)	0.66
XXV.	XXIIA + 40 ml o-phen +40ml tu($1x10^{-1}M$)	3E(XXV)	0.66

TABLE -2: (Contd.)

Summarised results of the potentiometric titrations for the systems: CuX + tu + am and $Cu(tu)_3X$ + am (X=Cl, I; am = amine) using HNO_3(0.1M) as a titrant.

S.No.	Titrant value in ml. of 0.1M HNO_3	$\bar{n}$	Complex formed
I.	-	-	-
II.	35.0	-	-
III.	-	-	-
IV.	22.0	-	-
V.	12.5	2	$Cu(py)_2Cl$
VI.	3.6	3	$Cu(tu)_3Cl$
VII.	13.0	1	[Cu(dipy)] Cl
VIII.	14.4	3(tu) 2(py)	$Cu(tu)_3Cl$ + $Cu(py)_2Cl$
IX.	3.0 and 17.4	-	-
X.	25	1	$[Cu(tu)_3py]Cl$
XI.	11	1	$[Cu(tu)_3dipy]Cl$ or $[Cu(tu)_2dipy]Cl$ + tu
XII.	-	-	-
XIII.	26	1	Cu(py)I
XIV.	12	3	$Cu(tu)_3I$
XV.	14.2	1	Cu(dipy)I
XVI.	33.8	3(tu) 1(py)	$Cu(tu)_3I$ & Cu(py)I
XVII.	9.5	-	-

(Contd.)

TABLE -2: (Contd.)

S. No.	Titrant value in ml. of 0.1M HNO_3	$\bar{n}$	Complex formed
XVIII.	26.0	1	$[Cu(tu)_3py]I$
XIV.	11.0	1	$[Cu(tu)_3dipy]I$ or $[Cu(tu)_2dipy]I + tu$
XX.	11.0	1	$[Cu(tu)_3o\text{-}phen]I$ or $[Cu(tu)_2o\text{-}phen] + tu$
XXI.	18 & 27	2 1	$[Cu(tu)o\text{-}phen_2]I$ or $[Cu(o\text{-}phen)_2]I$ and $[Cu(tu)_2o\text{-}phen]I$
XXII.	20 &	2	$[Cu(tu)o\text{-}phen_2]I$ or $[Cu(o\text{-}phen)_2]I$
XXIIA.		-	-
XXIII.	10 & 22	2 1	$[Cu(o\text{-}phen)_2]$ and $[Cu(o\text{-}phen)]I$
XXIV.	20 & 27.8	2 1	$[Cu(tu)o\text{-}phen_2]I$ or $[Cu(o\text{-}phen)_2]I$ and $[Cu(tu)_2o\text{-}phen]I$
XXV.	18 & 32	2 1	$[Cu(tu)o\text{-}phen_2]I$ or $[Cu(o\text{-}phen)_2]I$ and $[Cu(tu)_2o\text{-}phen]I$

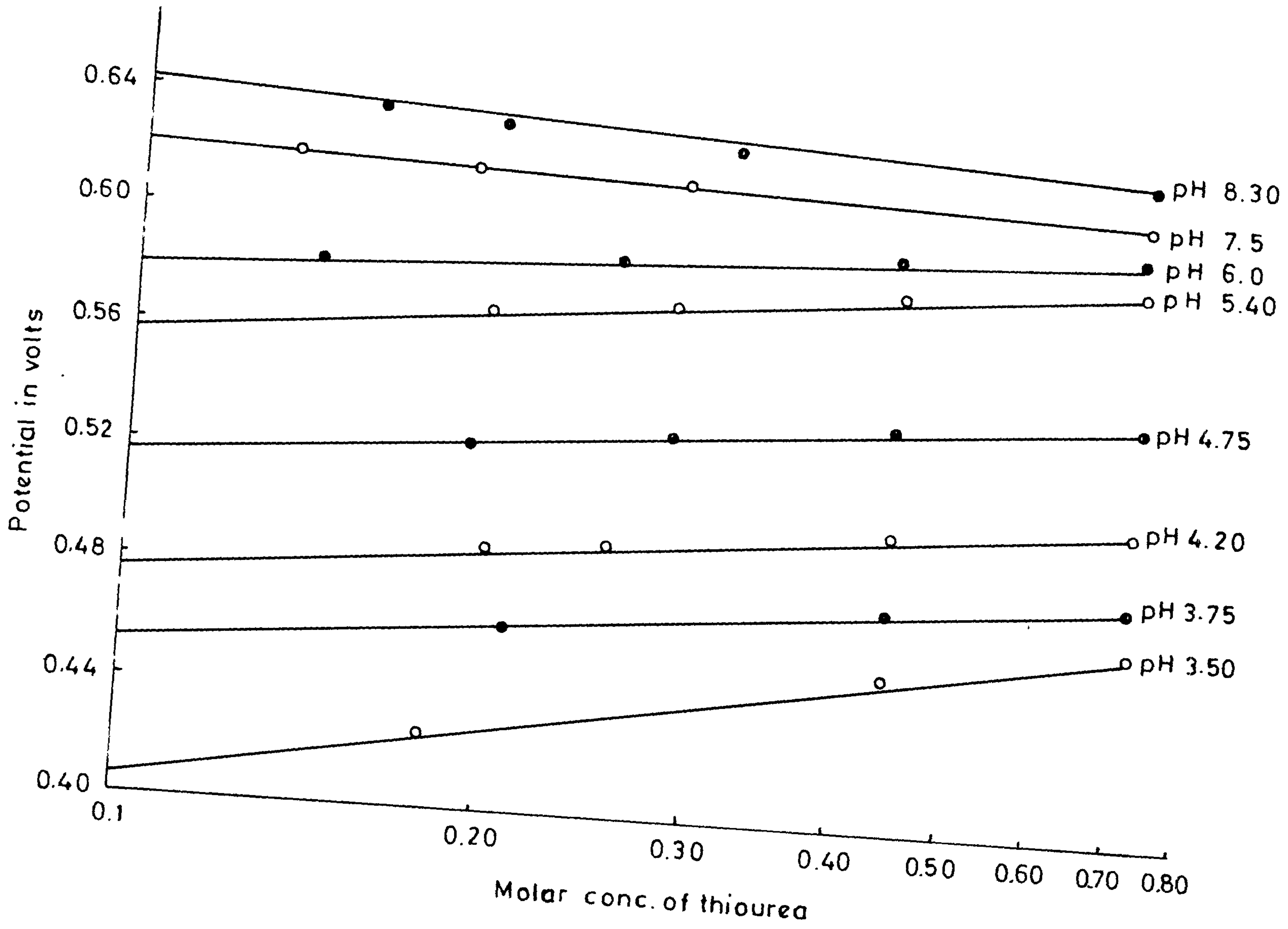


Fig. 4A Plot For Thiourea At Different pH Values
(Potential Vs. Log [tu])
(Logarithmic scale)

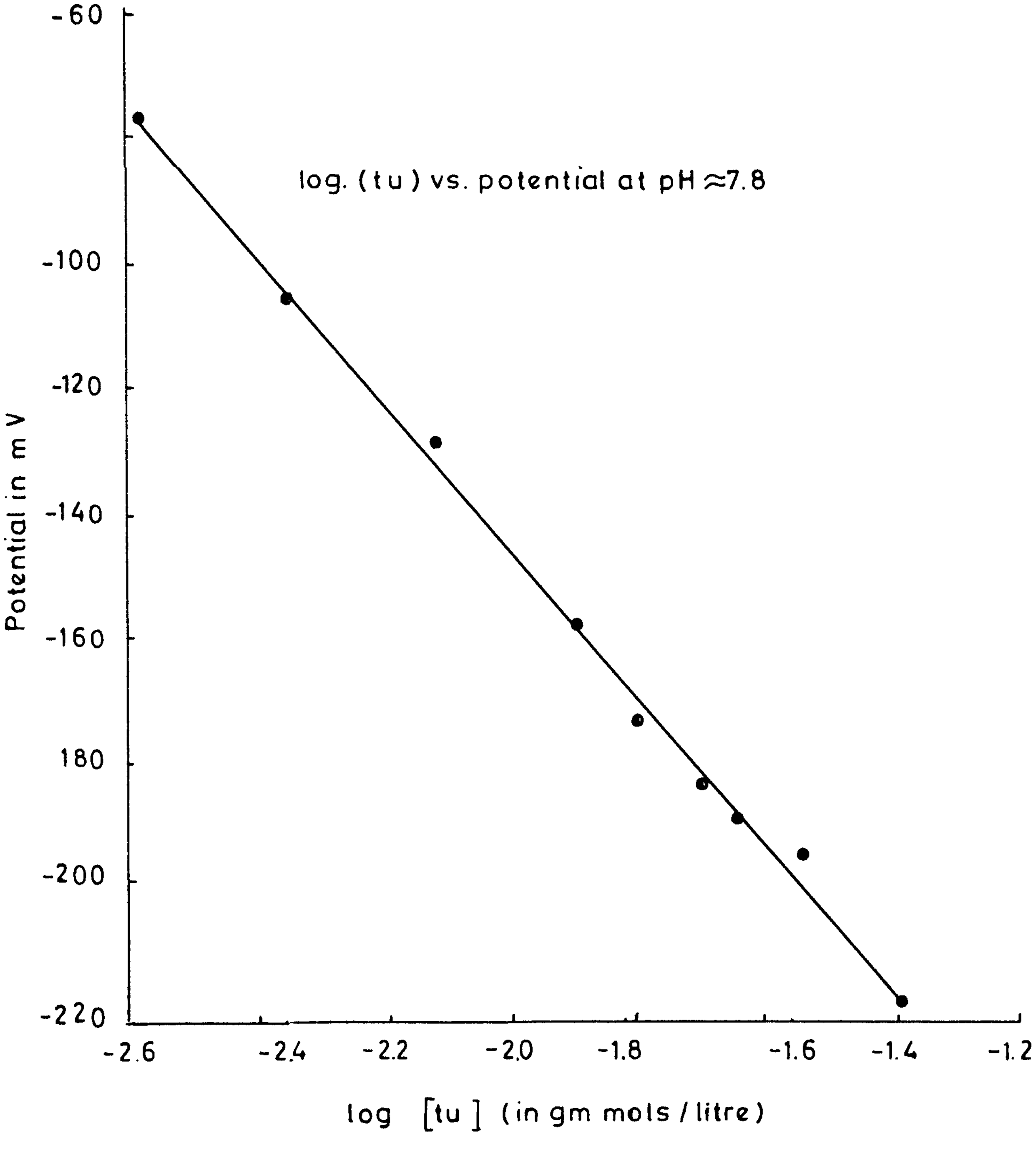


Fig. 4 B Calibration Curve

Test for the reversibility of Ag-Ag_2S indicator electrode in presence of thiourea and related compounds.

The plots of log S^{--} (thiourea in this case) against potential give straight lines (Fig.4A & 4B) in a wide pH range covering moderately acidic (pH ~3) to feebly basic solutions (pH ~8) indicating thereby the applicability of this electrode for the estimation of thiourea in this pH range, but not with solutions of higher pH (>8). In the present system, the pH of the solution varied in the range 6-8 and, therefore, the electrode could be used for determining the concentration of thiourea in the various substitution and addition reactions discussed here.

The influence of H^+ ions on the potential of this electrode may be seen from the following considerations:

For the electrode reaction,

$2Ag(s) + S^{--} \rightleftharpoons Ag_2S + 2e$, the usual equation,

$E = E^o + \frac{RT}{2F} \ln[S^{--}]$ —— (i) may be replaced by a relationship of the type,

$$E = E^o + \frac{RT}{2F} \ln \left[S^{--}\right] \left[H^+\right]^{-2\gamma} \quad —— (ii)$$

On plotting pH against E, for a fixed thiourea concentration (7.680g/litre), a straight line (Fig.4C) is obtained. Comparing equation (ii) with that of equation for a straight line $Y = mx + c$, we get $Y = E$, $c = E^o + 0.0295\ [S^{--}]$, $x = pH$ and $m = 0.059\gamma$ at 25°C.

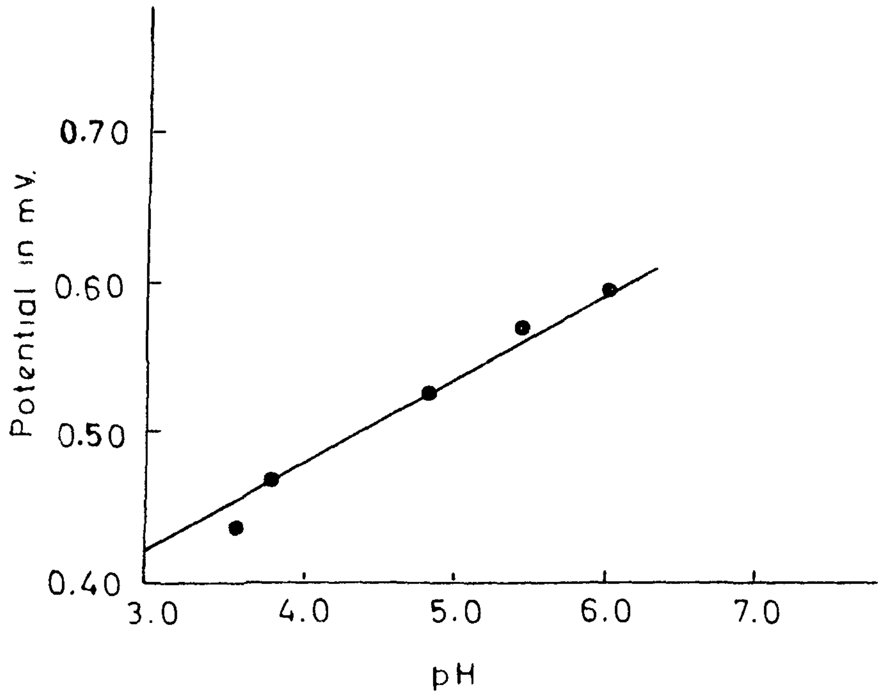


Fig 4c Plot of Potential Vs. pH (Ag-Ag_2S Electrode)

Now, from the slope of the curve in Fig.4 we have $m = .059$ giving a value of $\gamma = 1$. The equation (ii) then takes the form:

$$E = E^{0} + \frac{.059}{2} \log \frac{[S^{--}]}{[H^{+}]^{2}} \quad \text{———} \quad (iii)$$

or $$E = E^{0} + .0295 \log (S^{--}) + .059\, pH \text{ ——} \quad (iv)$$

The value of E^{0} obtained by equating the intercept of the straight line with $E^{0} + .0295 \log [S^{--}]$ comes out to be 0.236V. The values are found to agree with the values calculated from eqn.(iv) for the various thiourea concentrations.

TABLE-3:

Values of E^{0} obtained from the plots of pH and E and those calculated from equation (iv).

pH	E (in volt)	m	γ	E^{0} * (in volt)	E^{0} ** (in volt)
3.50	0.436	.059	1.0	0.236	0.236
3.75	0.466	"	1.0	"	"
4.20	0.492	"	1.0	"	"
4.75	0.525	"	1.0	"	"
5.40	0.565	"	1.0	"	"

* from the Fig.4C

** from the equation (iv)

The validity of the equation (iv) for the Ag-Ag_2S electrode may also be varified by another approach.

Since the plots of E against log [S^{--}] give straight line at a fixed pH (Fig.4A), the intercepts of the straight lines at various pH's (between 3.5 to 5.4) would give the value of E^o. The results are summarised in table 4.

T A B L E -4:

Values of E^o obtained from the plots of E and log [tu], and calculated from equation (iv).

log tu	E (in volt)	pH	m	E^{o*} (in volt)	E^{o**} (in volt)
0.3	0.426	3.5	0.0295	0.230	0.230
0.4	0.470	3.75	"	"	0.231
0.5	0.523	4.20	"	0.235	0.235
0.6	0.539	4.75	"	0.234	0.234
0.7	0.586	5.4	"	0.240	0.242
0.8	0.596	6.0	0.018	0.228	0.228

* calculated from the curve 4A
** calculated from the equation (iv)

The reversibility of the electrode was tested by measuring the potential of thiourea solutions of varying concentrations. From the concentration-potential curve, the concentration of known thiourea solution was checked (Fig.4B).

Kinetic measurements.

The reaction rate studies were carried out by measuring the e.m.f. of the solutions with time. The potential measurements were made with a Toshniwal potentiometer, type CL06 using Ag-Ag_2S and saturated calomel as indicator and reference electrodes, respectively. All the measurements were carried out at 20°C by immersing the solutions in a thermostatic water bath with temperature control of ± 0.5°C.

The Ag-Ag_2S electrode was prepared as described earlier (chapter II).

The potentiometric method applied to study the reaction kinetics of the interaction of tris(thiourea) copper(I) halides with heterocyclic amines, is based upon the utilization of Ag-Ag_2S electrode so as to give potential values (of the reaction mixtures) which are linear function of the concentration of thiourea. This linear relationship between potential and concentration exists in the concentration range used in the present system and the working pH. In the kinetic studies, an essential requirement for any physical measurement(in this case potential) is that the property (potential) should differ appreciably from reactants to products. In the present system, the general reaction may be represented as:-

$$M(tu)_3X + A \rightleftharpoons [M(tu)_3A]\ X$$

or

$$M(tu)_3X + 2A \rightleftharpoons [M(tu)_2A_2]\ X \quad \text{etc.}$$

and it is found that the potential is entirely dependent on the concentration of thiourea released during the course of reaction and independent of the concentration of reactants. Moreover, for thiourea solutions alone the equilibrium is achieved almost immediately, whereas for the system represented above the time for completion of the reaction is sufficient so as to carry out kinetics measurements accurately.

On the basis of the above formulations, the kinetic studies were carried out by using potential as a linear function of concentration.

The order of reaction in these studies was determined by adopting the procedures recommended by Frost and Pearson[4]. Firstly, concentration (c, $\log c$ and $\frac{1}{c}$) was plotted against time, t to determine the nature of reaction. Plots of time, t versus $\log \left(\frac{b-x}{a-x}\right)$, where a and b represent the initial concentrations of the reactants and x is the decrease in concentration of one of the reactants with t, were also tried for determining second order reaction. The first order kinetics was also studied by plotting $\frac{E_t}{E_\infty - E_t}$ versus t, where E and E_t are the potentials at equilibrium and at time, t, respectively.

The potentials of the several solutions were measured with time. Some of the typical compositions were: (i) 10 ml CuCl + 40 ml thiourea (1×10^{-1}M), (ii) 10 ml CuCl(9.5×10^{-2}M) + 40 ml thiourea(1×10^{-1}M) + 22 ml dipyridyl (1×10^{-1}M), (iii)

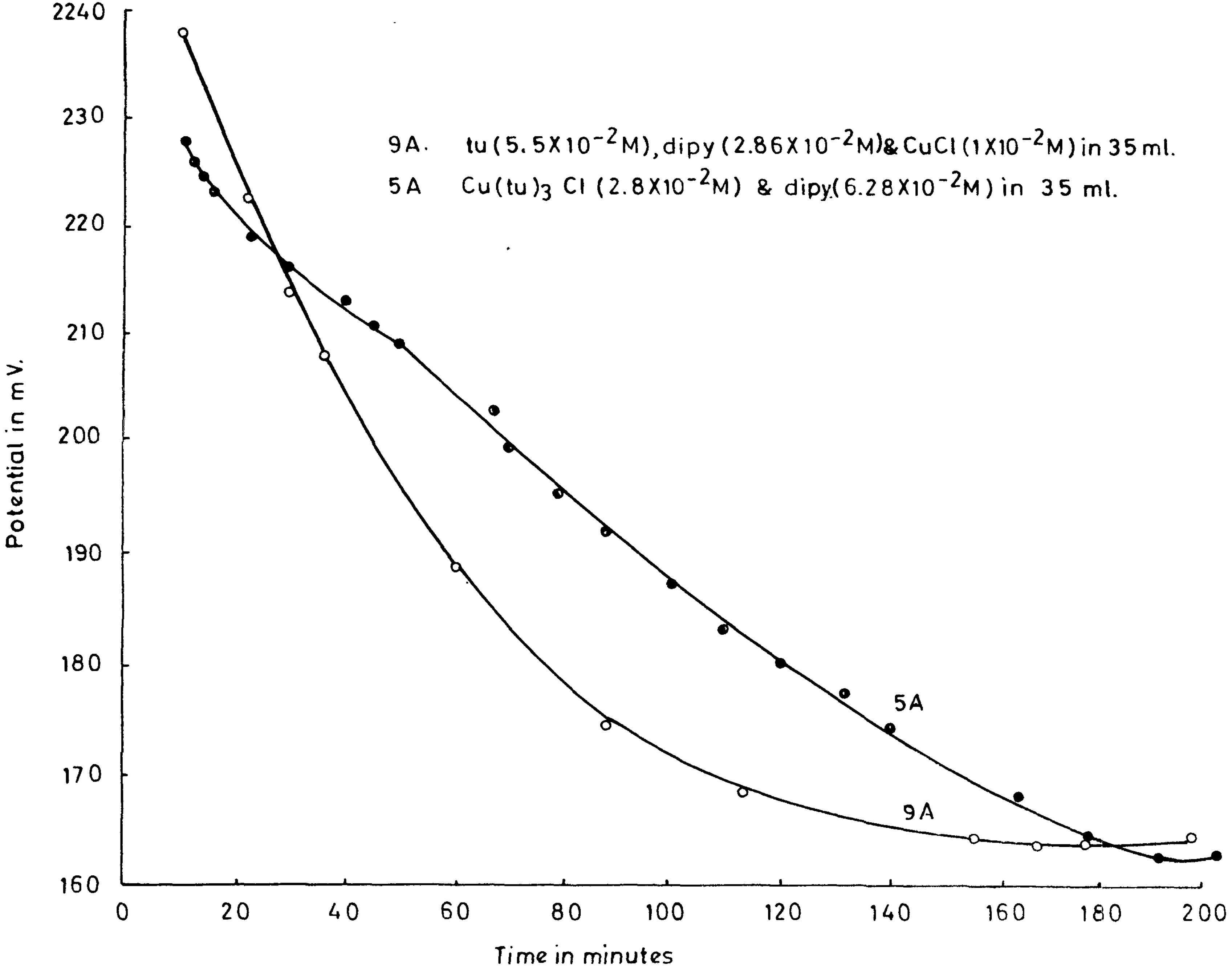


Fig. 5A & 9A Variation Of Potential With Time

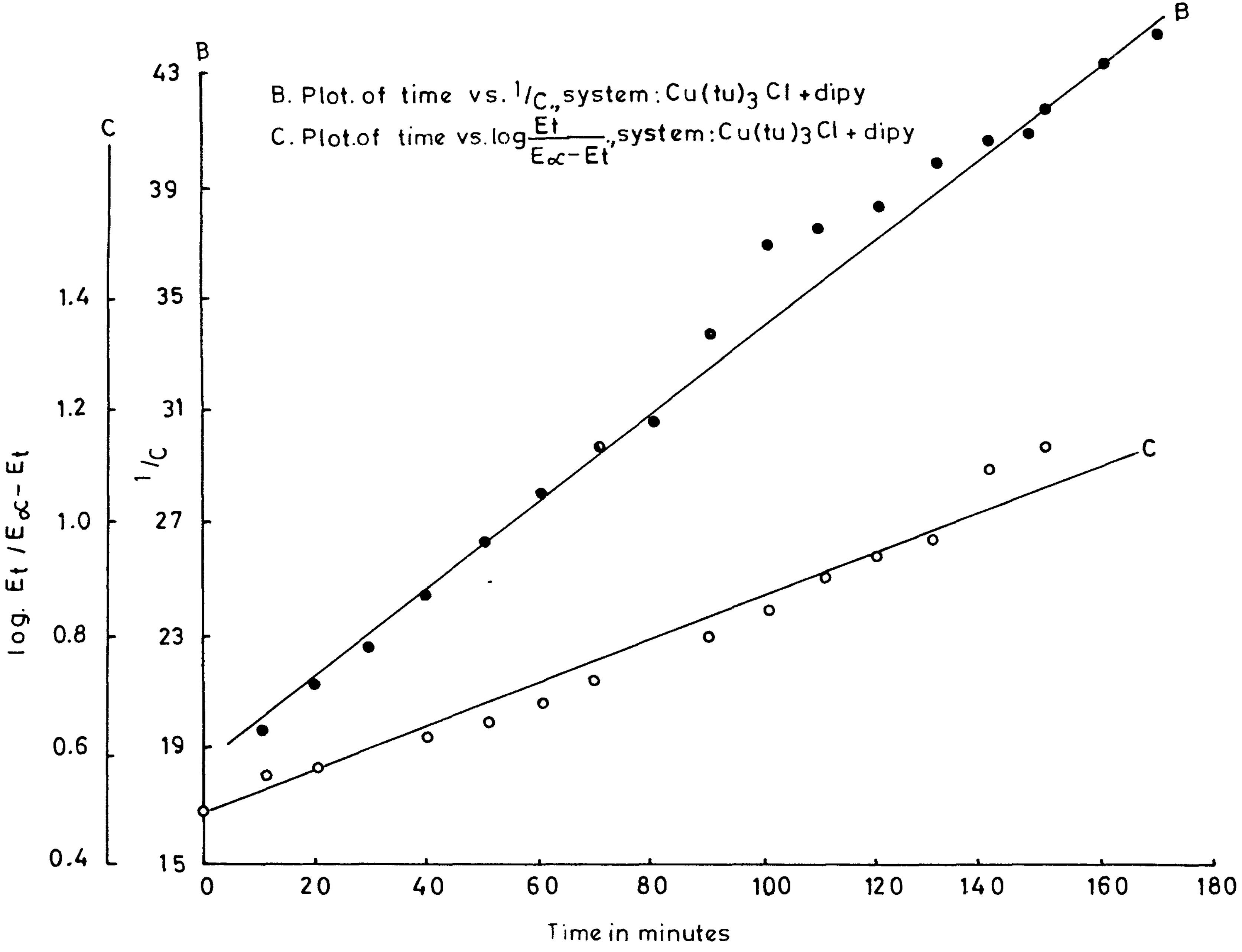


Fig. 5B & 5C

(Vide table 5)

4 ml CuCl(9.5×10^{-2}M) + 12 ml thiourea (1×10^{-1}M) + 12 ml phenyl arsonic acid (1×10^{-1}M), (iv) 10 ml $Cu(tu)_3Cl$ (1×10^{-1}M) + 22 ml dipyridyl (1×10^{-1}M), (v) 10 ml $Cu(tu)_3Cl$ (1×10^{-1}M) + 35 ml pyridine (1×10^{-1}M) and (vi) 10 ml $Cu(tu)_3I$ (1×10^{-1}M) + 22 ml dipyridyl (1×10^{-1}M).

A constant ionic strength of 0.2 was maintained in the solutions by the addition of unimolar potassium chloride solution.

The e.m.f. readings of the kinetic measurements are given in tables 5 to 9 and figures 5 to 9. The results of the reaction kinetics for the various systems are summarised in table 10.

TABLE -5:

Change in potential with time at the $Ag-Ag_2S$ electrode.
System: $Cu(tu)_3Cl$ + dipy.
10 ml (1×10^{-1}M) $Cu(tu)_3Cl$ + 22 ml (1×10^{-1}M) dipyridyl + 3.2 ml. (2M)KCl

E_∞ = 156 m.V., Temp. = 25°C

Time in minutes	Potential, E in m.V.	Conc., C (in moles)	$\frac{1}{C}$	$\log \frac{E_t}{E_\infty - E_t}$
0	230	0.066	15.15	0.4925
10	217	.051	19.61	.5512
20	213	.047	21.28	.5625
40	206	.041	24.39	.6149
50	202	.038	26.32	.6426
60	198	.0355	28.16	.6735
70	194	.0335	29.85	.7080
90	186	.0295	33.89	.7924
100	182	.027	37.04	.8451
110	178	.265	37.73	.9080
120	176	.026	38.46	.9445
130	174	.025	40.00	.9852
140	171	.0245	40.81	1.0569
150	170	.024	41.67	1.1461
160	166	.023	43.48	1.6021

(Vide Fig.5A to 5C)

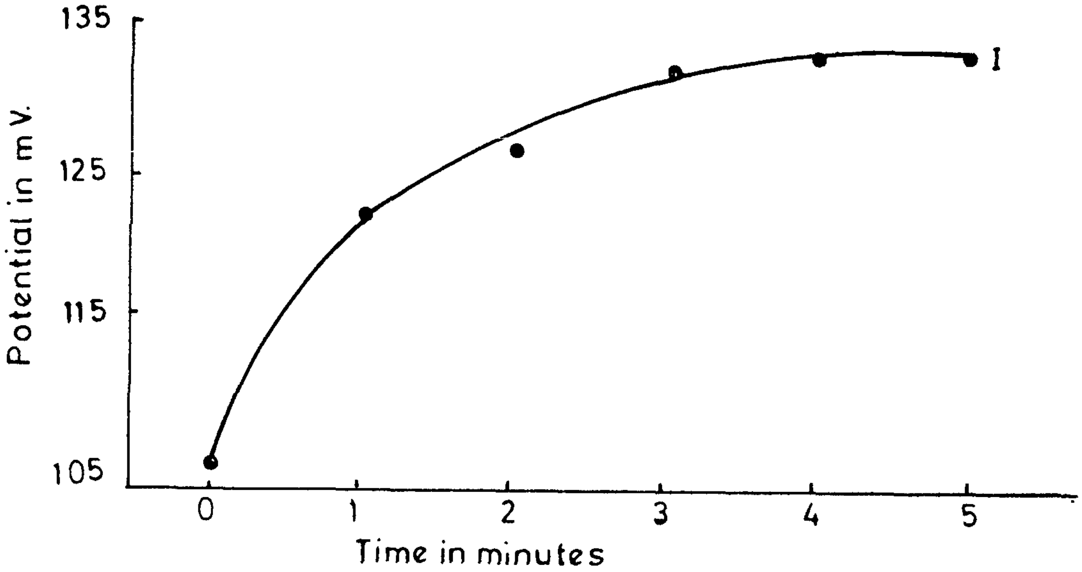


Fig. 7 Variation Of Potential With Time

(I) Cu $(tu)_3$ Cl (2.2×10^{-2}M) and py (7.70×10^{-2}M) in 45 ml

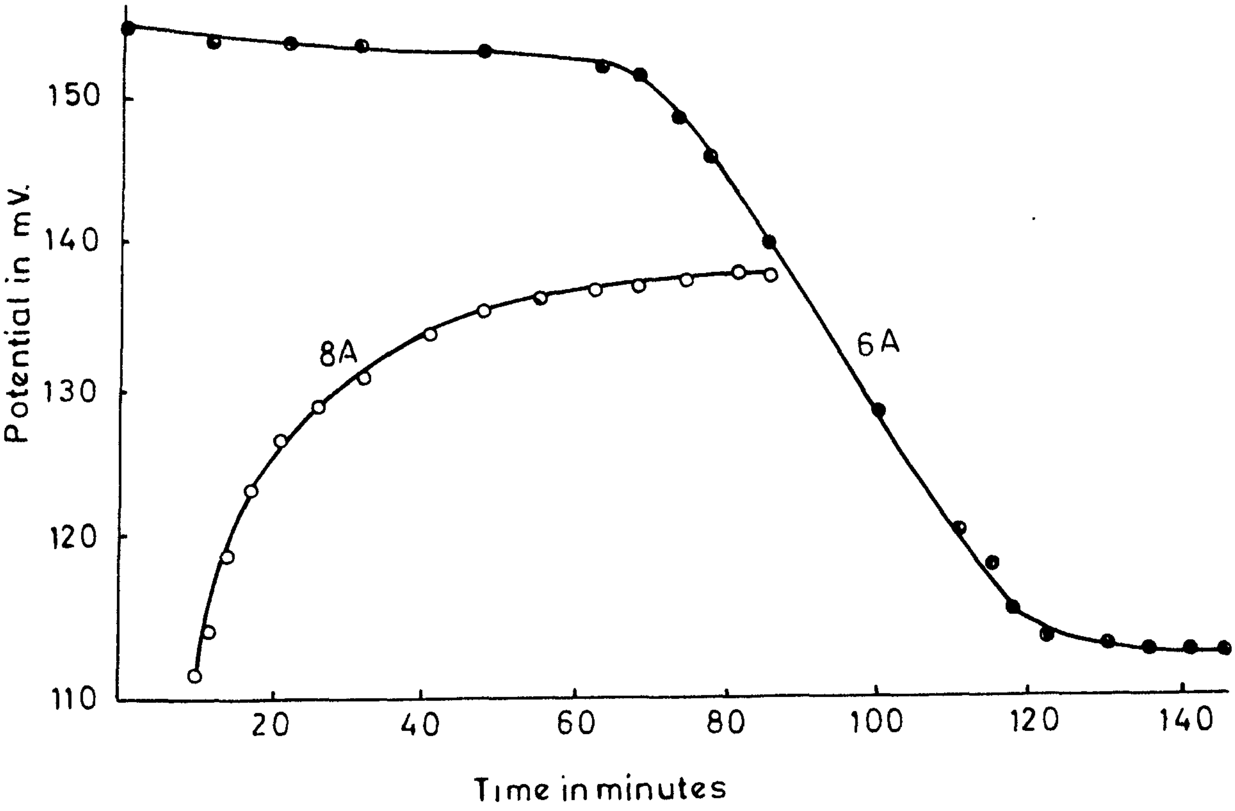


Fig. 6A & 8A Variation Of Potential With Time

6A– Cu $(tu)_3$ I (2.8×10^{-2} M) and dipy (6.28×10^{-2} M) in 35 ml

8A– (tu) (4.28×10^{-2}M), PhoAs (4.28×10^{-2}M) and CuCl (1.3×10^{-3}M) in 28 ml

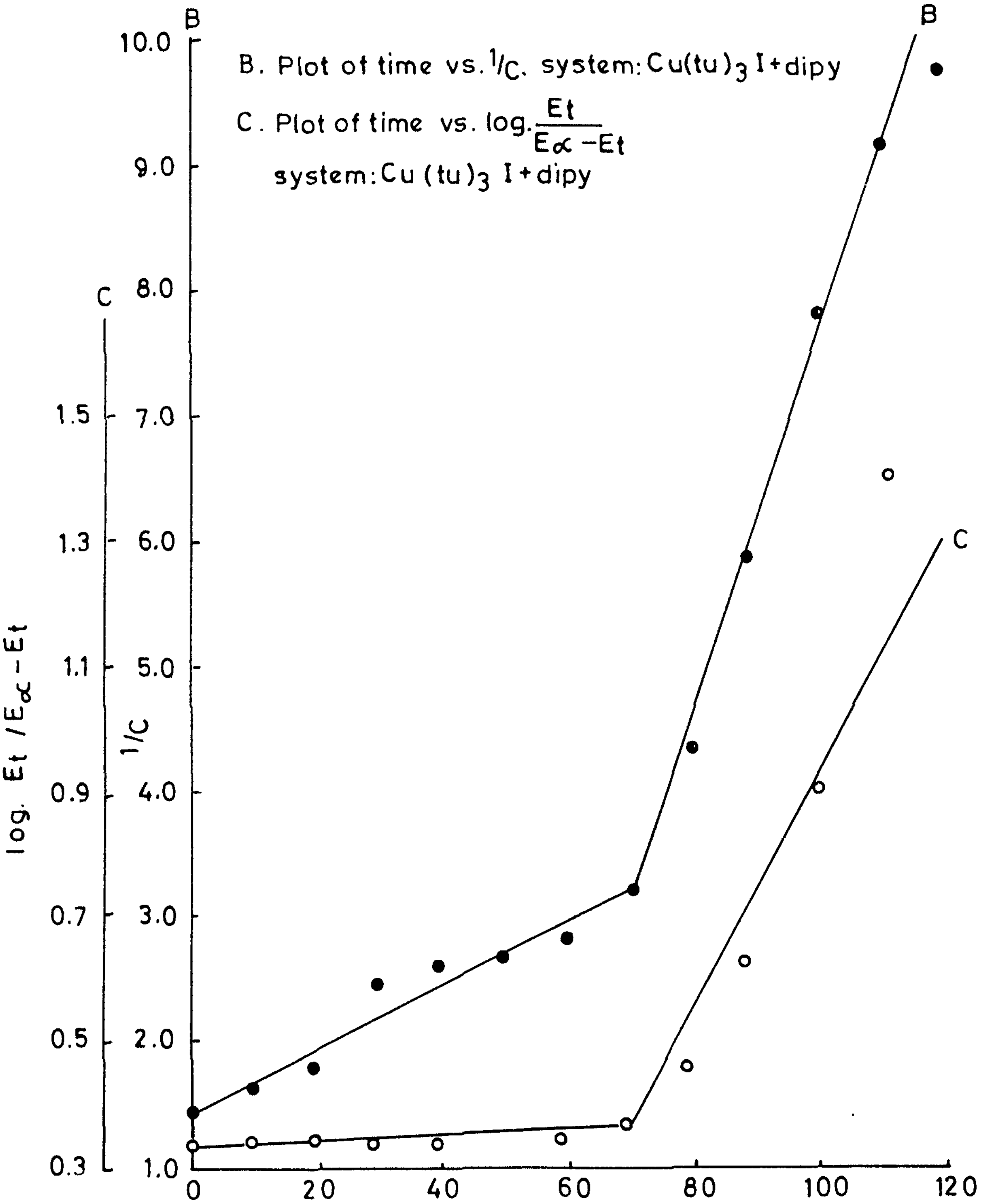


Fig. 6 B & 6 C

(Vide table 6)

TABLE -6:

Change in potential with time at the Ag-Ag_2S electrode,
System: $Cu(tu)_3I$ + dipy.

10 ml ($1x10^{-1}M$) $Cu(tu)_3I$ + 22 ml.($1x10^{-1}M$) dipyridyl + 3.2 ml. 2M KCl.

E_∞ = 200 m.V. Temp. = 25°C.

Time in minutes	Potential, E in m.V.	Conc., C (in moles)	$\frac{1}{C}$	$\log \frac{E_t}{E_\infty - E_t}$
0	339	0.68	1.47	0.3288
10	338	.60	1.66	.3302
20	337	.56	1.78	.3317
30	335	.40	2.5	.3347
40	332	.38	2.63	.3393
50	329	.374	2.67	.3440
60	324	.358	2.79	.3521
70	320	.312	3.2	.3775
80	275	.23	4.34	.4616
90	235	.156	6.4	.6307
100	205	.120	8.33	.9139
110	187	.108	9.2	1.4267
120	102	.102	9.8	-

(Vide Fig.6A to 6C)

TABLE -7:

Change in potential with time at the Ag-Ag_2S electrode.
System: $Cu(tu)_3Cl$ + py.

Conc.of $Cu(tu)_3Cl$ = $2.2x10^{-2}M$
" " pyridine = $7.7x10^{-2}M$
E_∞ = 133 m.V. Temp.= 25°C

Time in minutes	Potential E, in m.V.	Conc., C (in moles)
0	119	0.0205
10	1195	.0206
20	120	.02075
30	120	.02076
40	122	.0208

(Vide

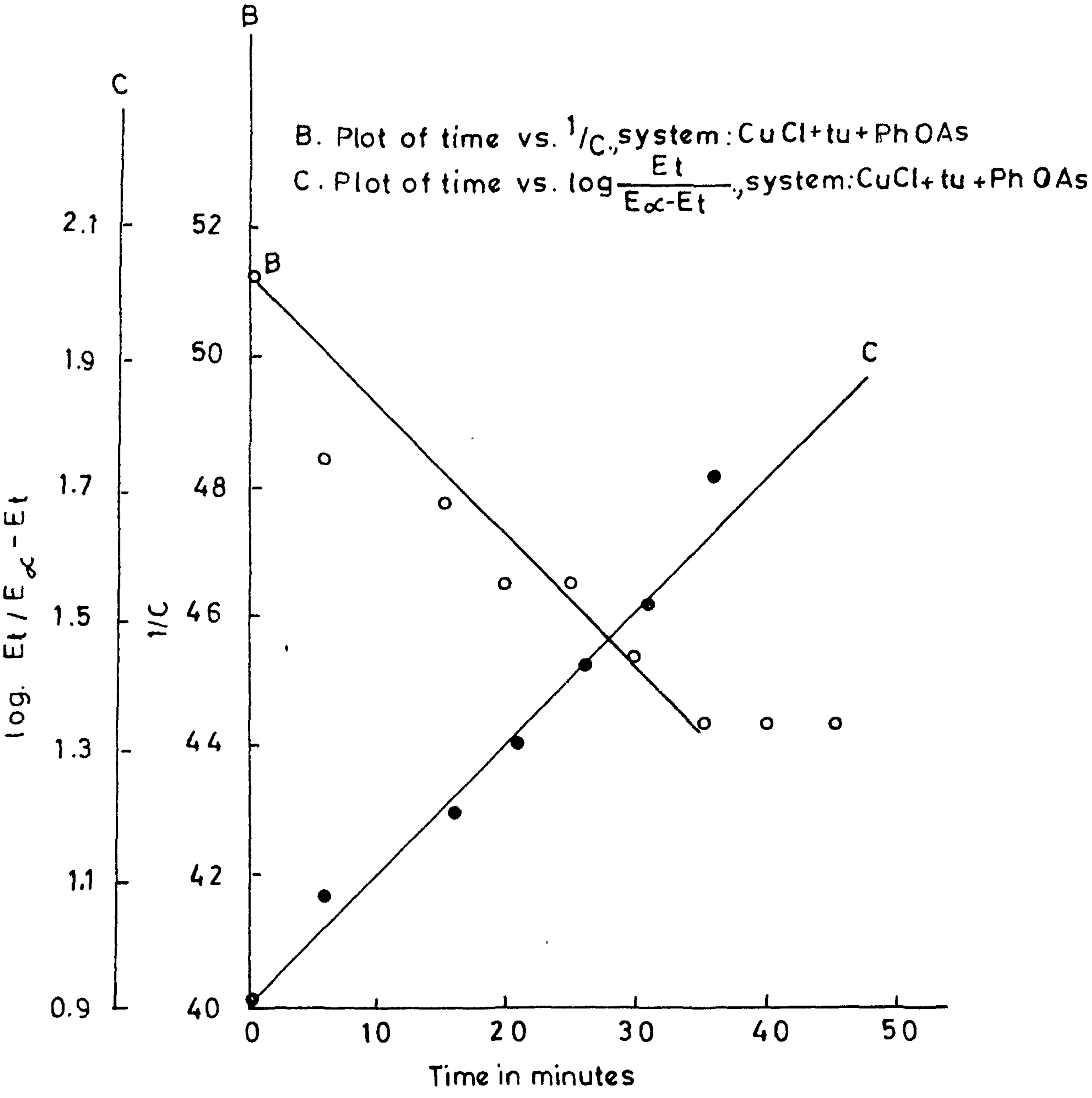


Fig. 8 B & 8C

(Vide table 8)

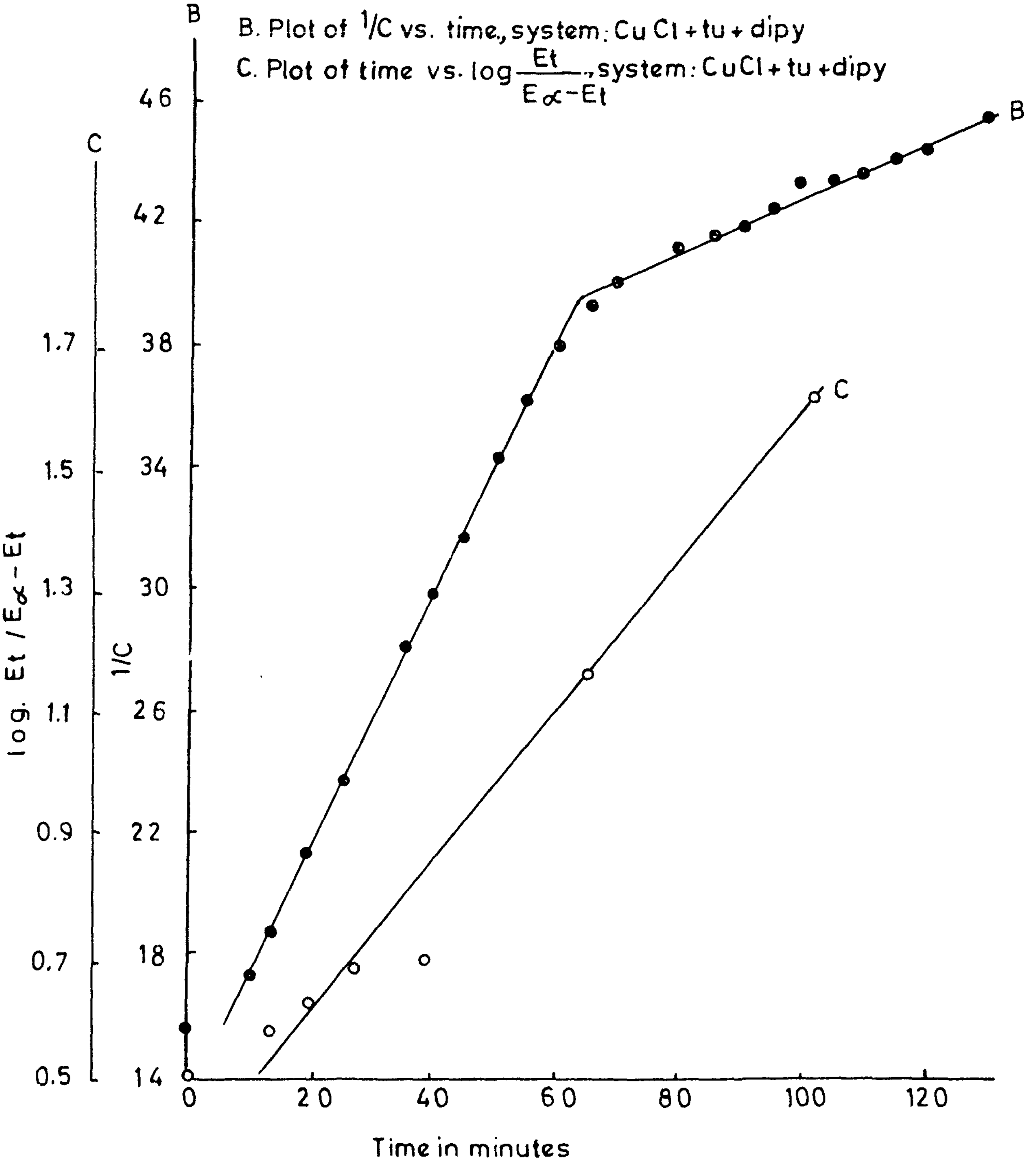


Fig. 9 B & 9C

(Vide table 9)

TABLE -8:

Change in potential with time at the Ag-Ag_2S electrode.

System: CuCl + phenyl arsonic acid + thiourea.

12 ml ($1x10^{-1}$M) phenyl arsonic acid + 4 ml ($9.18x10^{-2}$M) CuCl + 12 ml ($1x10^{-1}$M) thiourea.

E_∞ = 138 m.V. Temp. = 25°C

Time in minutes	Potential, E in m.V.	Conc., C (in moles)	$\frac{1}{C}$	$\log \frac{E_t}{E_\infty - E_t}$
0	122	0.0195	51.2	0.9031
5	126	.0205	48.3	1.059
15	128.6	.021	47.6	1.185
20	130.4	.0215	46.5	1.2957
25	132	0.0215	46.5	1.4216
30	133	.022	45.45	1.5218
35	134.4	.0225	444	1.7134
40	136	.0225	44.4	2.1335
45	136.5	.0225	44.4	1.2729
60	137	.023	43.48	-

(Vide Fig.8A to 8C)

TABLE -9:

Change in potential with time at the Ag-Ag_2S electrode.

System: CuCl + thiourea + dipy.

10 ml($9.51x10^{-2}$M) CuCl + 40 ml ($1x10^{-1}$M) thiourea + 22 ml ($1x10^{-1}$M) dipyridyl.

E_∞ = 161 m.V. Temp. = 25°C.

Time in minutes	Potential, E in m.V.	Conc., C (in moles)	$\frac{1}{C}$	$\log \frac{E_t}{E_\infty - E_t}$
0	236	-	-	0.5037
12	220	0.54	18.52	.5790
20	212	.047	21.28	.6273
26	206	.040	25.00	.6704
38	204	.039	25.64	.6864
65	174	.0255	39.22	1.1613
78	172	.025	40.0	1.2355
103	166	.0225	44.44	1.6180
130	162	.022	45.45	-

(Vide Fig.9A to 9C)

T A B L E -10:

Summarised results of the kinetic measurements for copper(I) complexes.

S. No.	Original concentration of the species present (ionic strength =2)	Curve No.	Time required for completion of the reaction e.g., time at constant potential (in secs.)	Concentration of the species present after the completion of the reaction
1.	$Cu(tu)_3$ Cl(2.2×10^{-2}M) and py(7.7×10^{-2}M) in 45 ml.	7A	fast	tu(1.85×10^{-2}M) in 46 ml
2.	tu(5.5×10^{-2}M) dipy(2.86×10^{-2}M) and CuCl(1.1×10^{-2}M) in 77 ml	9A	145	tu(2.25×10^{-2}M) in 77 ml
3.	$Cu(tu)_3Cl$(2.8×10^{-2}M) and dipyridyl (6.28×10^{-2}M) in 35 ml	5A	200	tu(2.3×10^{-2}M) in 35 ml
4.	$Cu(tu)_3$ I (2.8×10^{-2}M) and dipyridyl (6.28×10^{-2}M) in 35 ml.	6A	135	tu(2.75×10^{-2}M) in 35 ml
5.	tu(4.28×10^{-2}M), phOAs (4.28×10^{-2}M) and CuCl(1.3×10^{-3}M) in 28 ml.	8A	60	tu(1.9×10^{-2}M) in 28 ml.

(Contd.)

TABLE -10i(Contd.)

S.No.	Concentration of species consumed during the reaction	Complex species formed	Order of the reaction	Rate constant in mole/sec.	Mode of the reaction
1.	tu(4.75×10^{-2}M) in 45 ml	$[Cu(tu)_2py_2]^+$	-	-	$Cu(tu)_3^+ \rightleftharpoons Cu(tu)_2^+ + tu \xrightarrow[fast]{2py} [Cu(tu)_2py_2]^+$
2.	tu(3.25×10^{-2}M) in 77 ml	$[Cu(tu)_2dipy]Cl$	2nd	6.6×10^{-3}	$CuCl + tu \xrightarrow[fast]{} [Cu(tu)_3]Cl \xrightarrow{dipy} [Cu(tu)dipy]Cl \xrightarrow{slow} [Cu(tu)_2dipy]Cl + tu$
3.	tu(6.1×10^{-2}M) in 35 ml	$[Cu(tu)_2dipy]Cl$	2nd	2.5×10^{-3}	$[Cu(tu)_3]Cl + dipy \xrightarrow{fast} [Cu(tu)_3dipy]Cl \xrightarrow{slow} [Cu(tu)_2dipy]Cl + tu$
4.	tu(5.6×10^{-2}) in 35 ml	$[Cu(tu)_2dipy]I$	2nd	2.5×10^{-3}	$Cu(tu)_3^+ \xrightarrow[slow]{+H_2O} [Cu(tu)_3H_2O]^+ \xrightarrow[dipy]{fast} [Cu(tu)_3dipy]^+ \xrightarrow[slow]{} [Cu(tu)_2dipy]^+$
5.	tu(2.38×10^{-2}M) in 28 ml	$[Cu(tu)_2phOAs]$	2nd	3.2×10^{-3}	$Cu^+ + 3tu \xrightarrow{fast} Cu(tu)_3^+ \overset{slow}{\rightleftarrows} [Cu(tu)_2]^+ + tu \xrightarrow[fast]{phOAs} [Cu(tu)_2\ phOAs]$

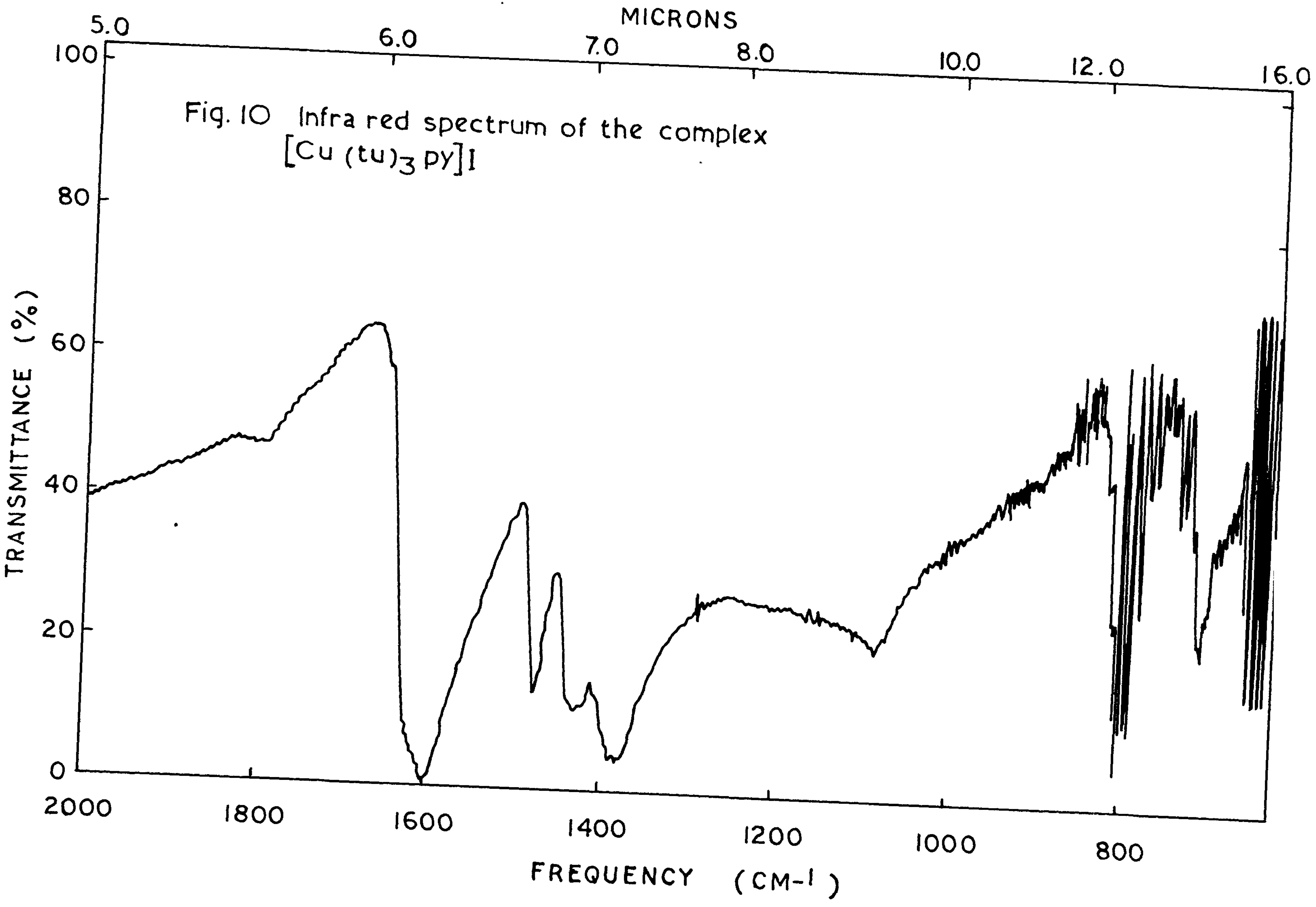


Fig. 10 Infra red spectrum of the complex $[Cu(tu)_3py]I$

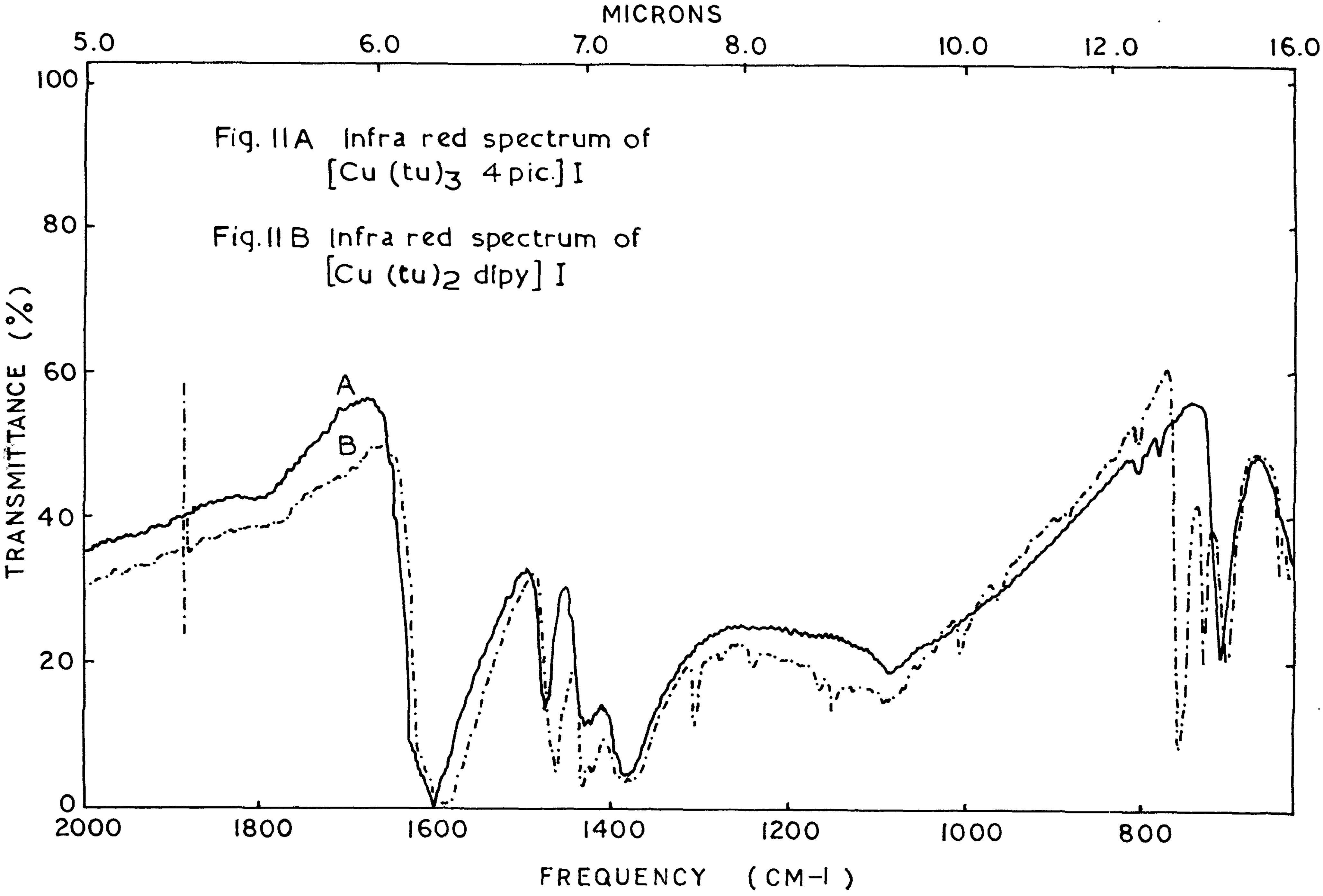


Fig. 11A Infra red spectrum of [Cu $(tu)_3$ 4 pic.] I

Fig. 11B Infra red spectrum of [Cu $(tu)_2$ dipy] I

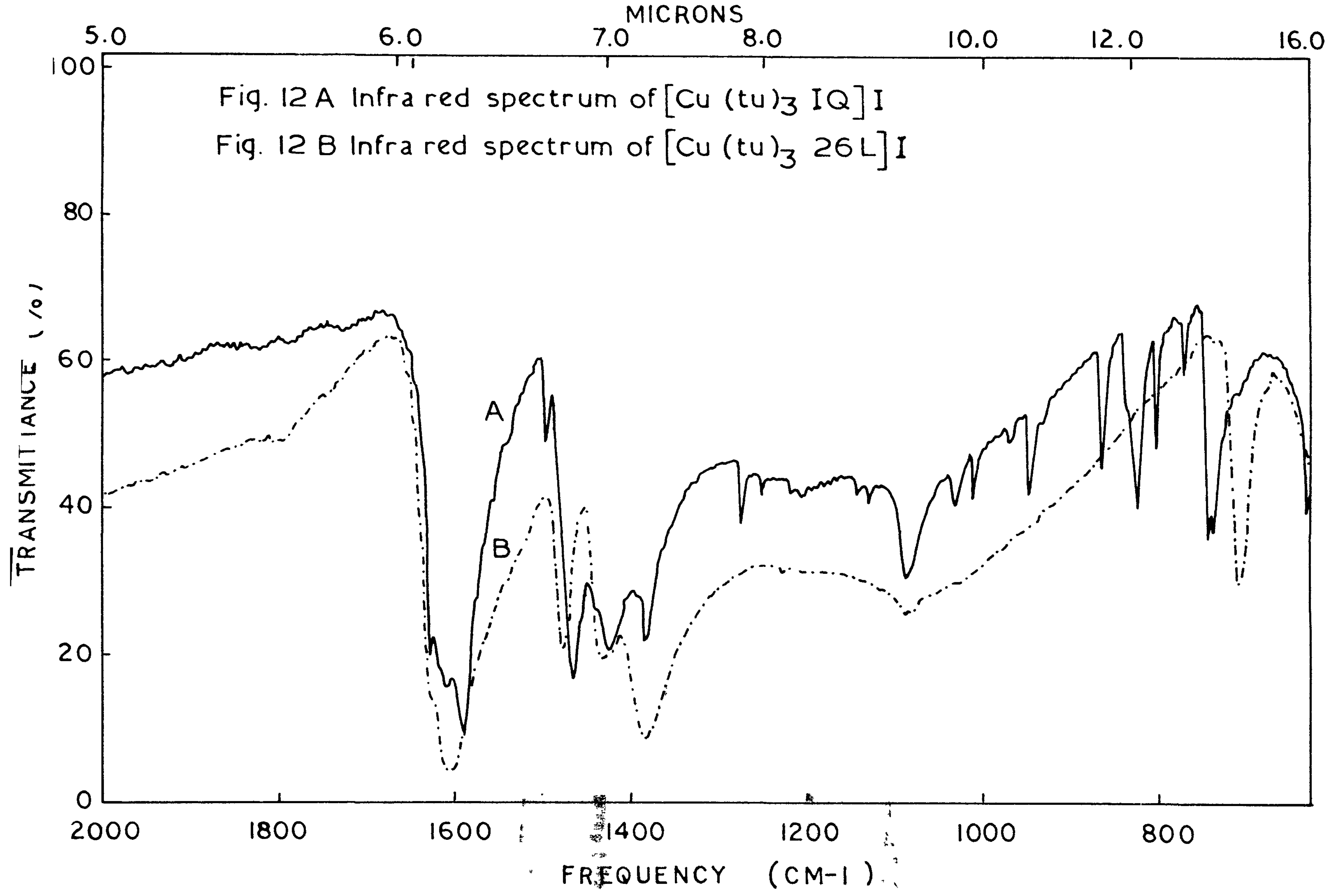


Fig. 12 A Infra red spectrum of $[Cu(tu)_3 IQ]I$

Fig. 12 B Infra red spectrum of $[Cu(tu)_3 26L]I$

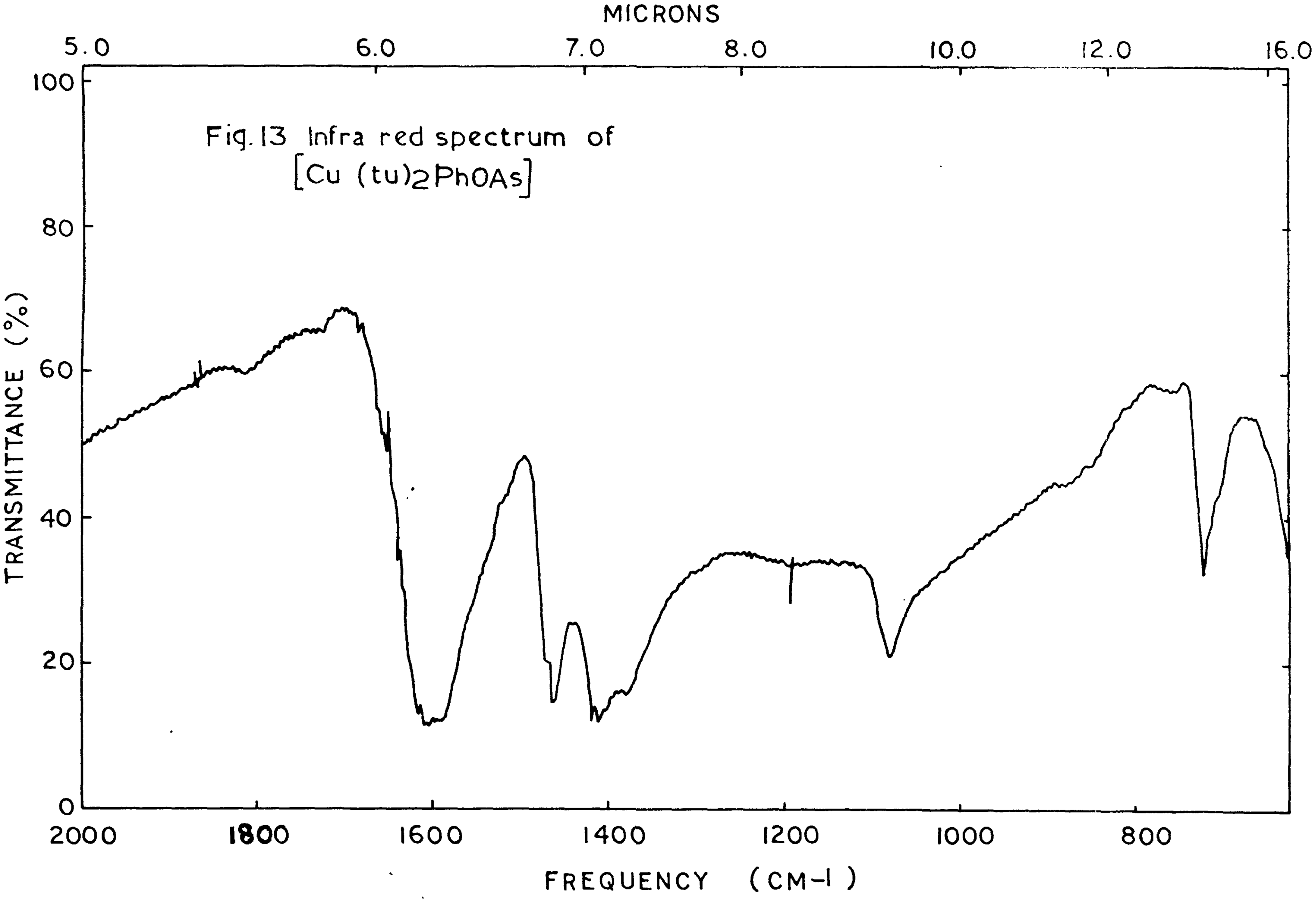


Fig. 13 Infra red spectrum of
$[Cu(tu)_2PhOAs]$

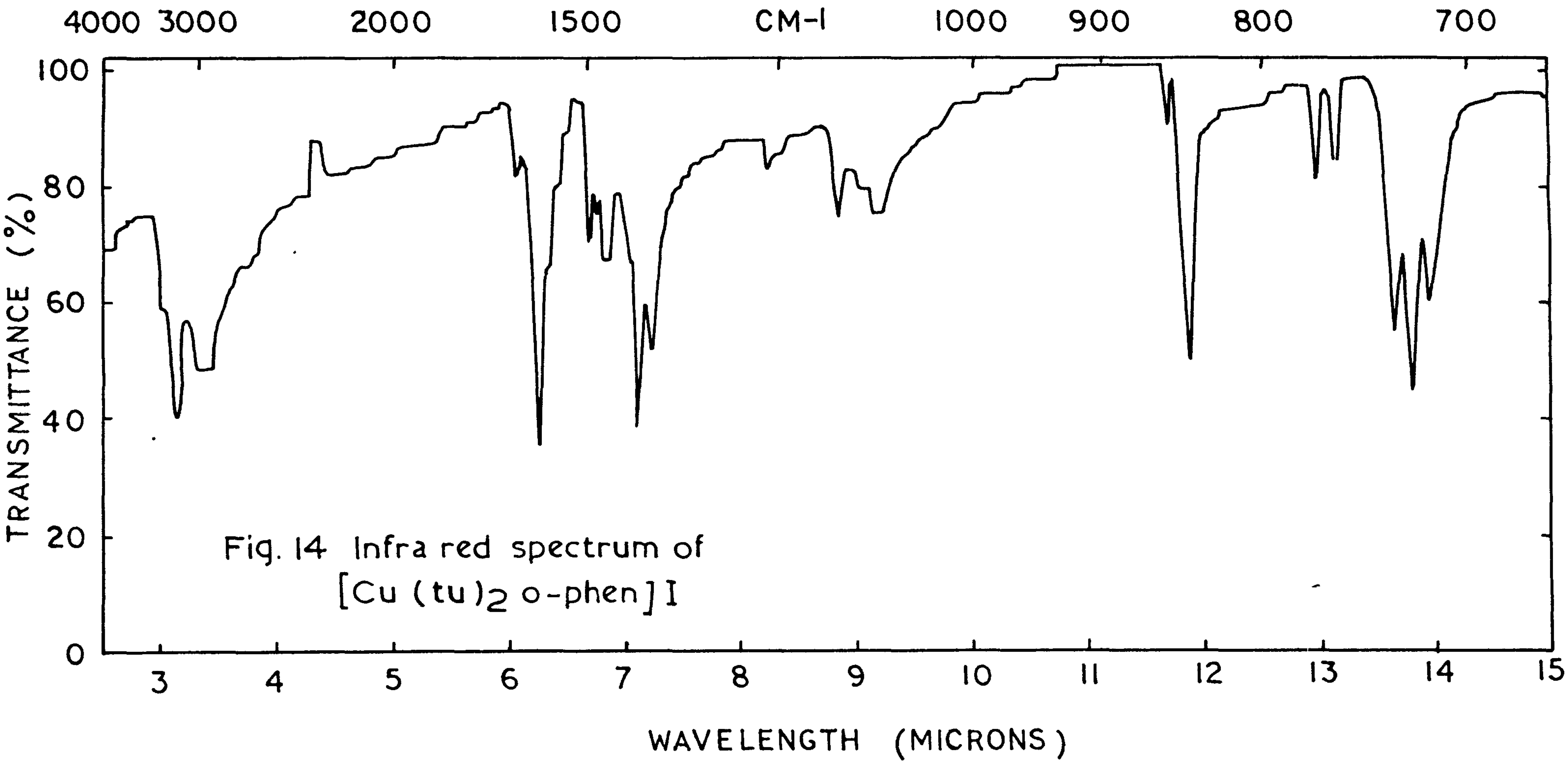


Fig. 14 Infra red spectrum of $[Cu(tu)_2\text{o-phen}]I$

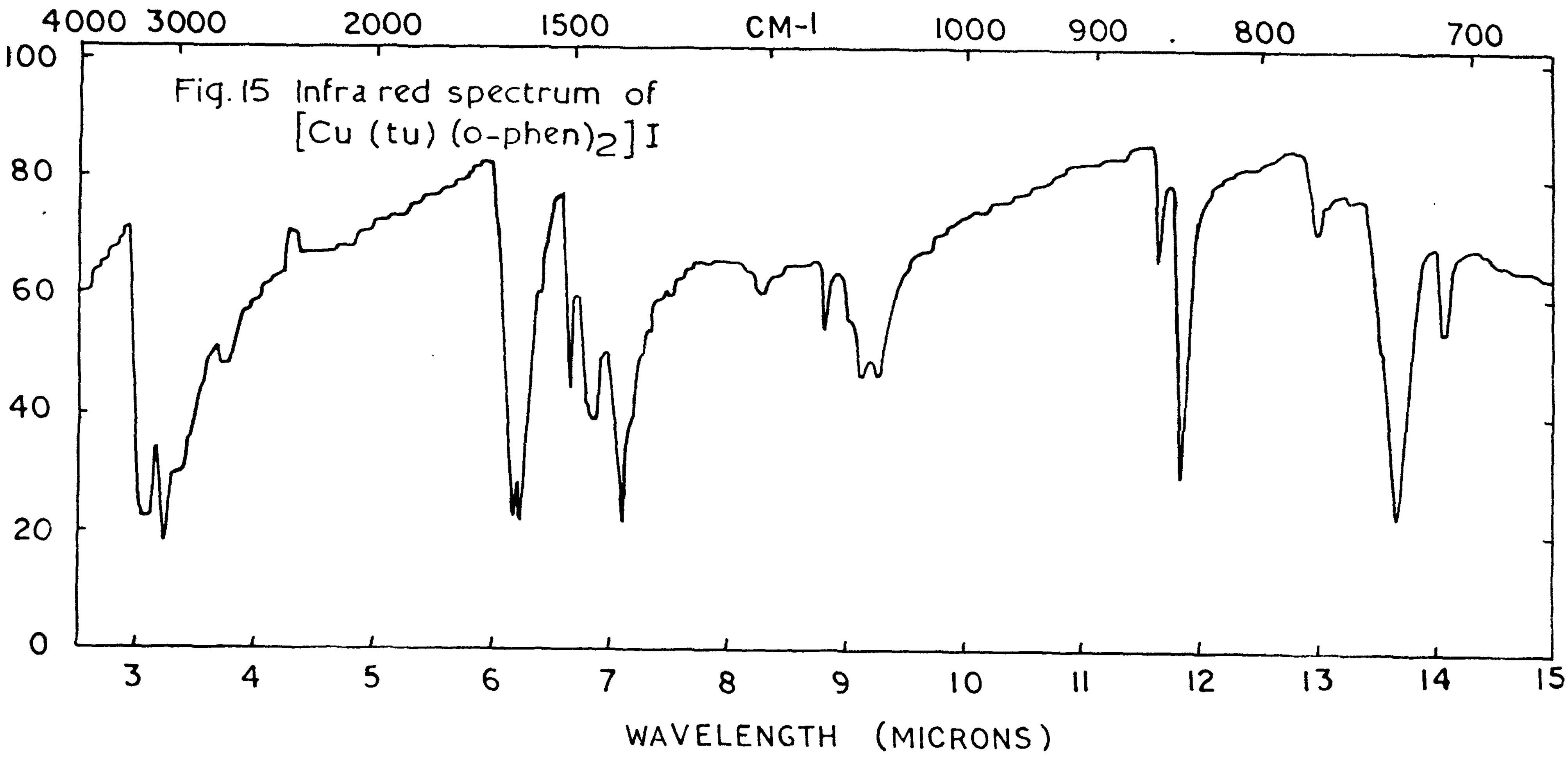


Fig. 15 Infra red spectrum of $[Cu(tu)(o\text{-}phen)_2]I$

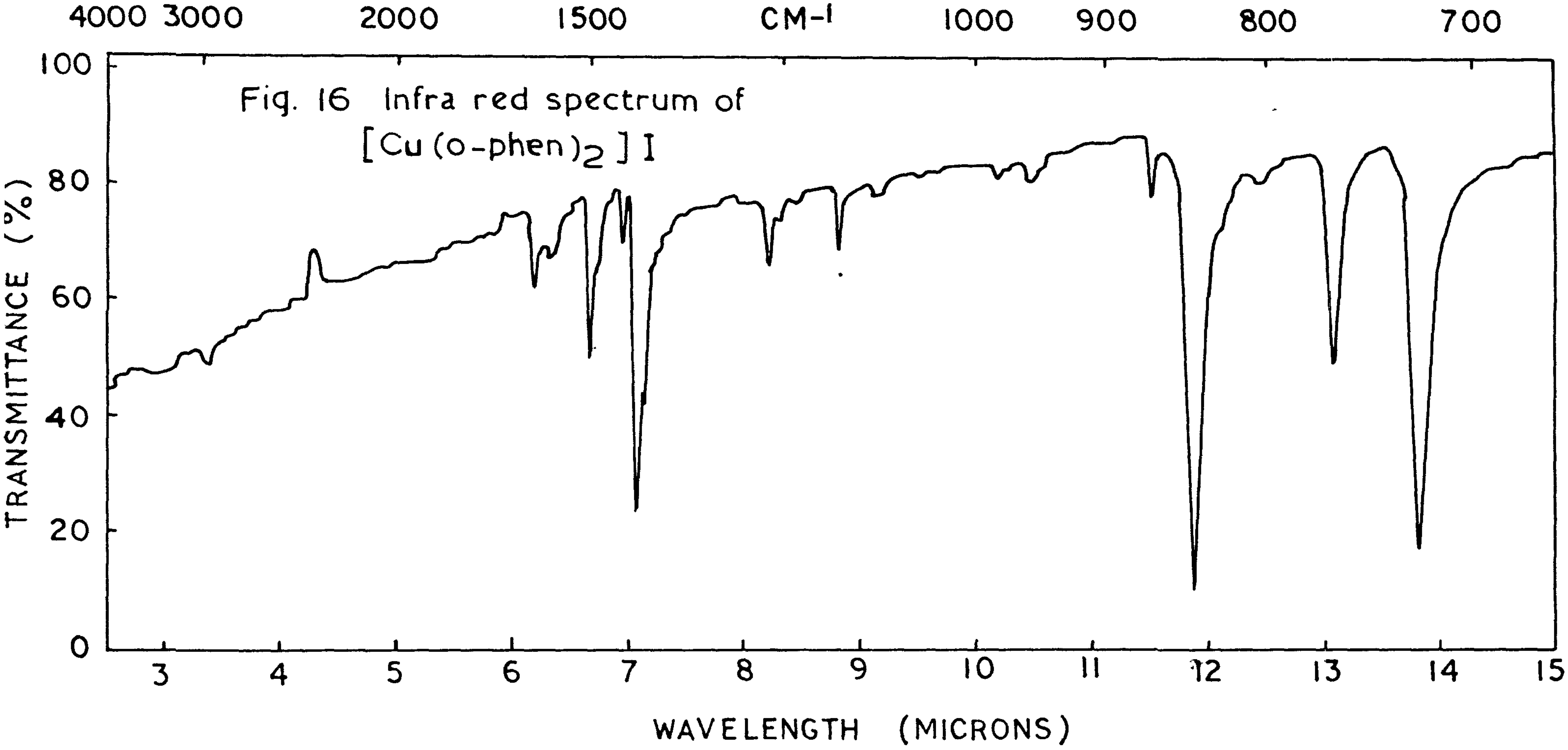


Fig. 16 Infra red spectrum of
$[Cu(o\text{-}phen)_2]I$

Infra red spectra of copper(I)complexes:

The infra red spectra of the mixed ligand complexes of copper(I) were taken with a Perkin Elmer 237 recording spectrometer, in the region 6 to 15 μ , employing the standard KBr technique using spectral grade KBr.

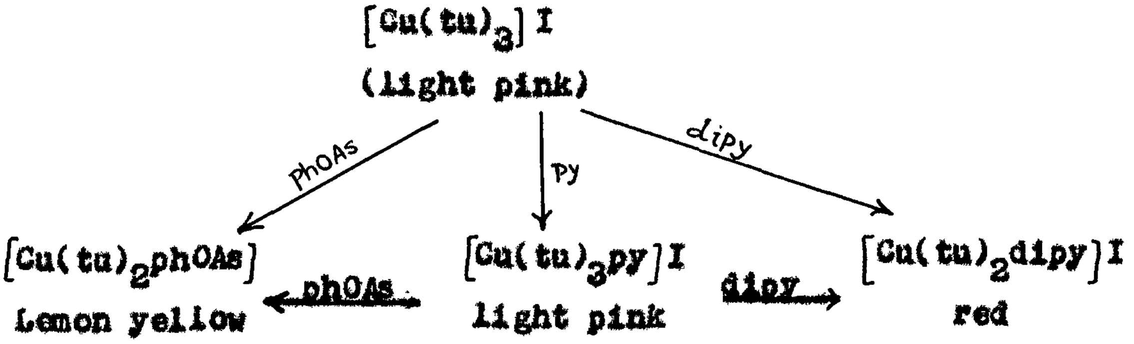
The position of the various bands in the i.r. spectra of the complexes is given below:

1. $[Cu(tu)_3py]I$: 1600(v.s), 1475(s), 1430(m&b), 1370(m), 1080(m), too many bands around 12 and 16 μ including a strong band at 710 cm^{-1}. (fig.10)
2. $[Cu(tu)_3\ 4pic]I$: 1600(s), 1480(s), 1440(w), 1380(m&b), 1080(w), 800(w), 730(w), 710(s) (fig.11A).
3. $[Cu(tu)_3\ I.Q.]I$: 1590(s), 1495(m), 1465(s), 1425(s), 1380(m), 1380(m), 1275(m),1080(m), 1030(m), 1010(m), 945(s) , 860(s), 830(v.s), 800(s), 770(m), 710(m&b), (fig.12A).
4. $[Cu\ phOAs(tu)_2]$: 1600(m&b), 1460(s), 1410(m), 1080(m),730(s). (fig.13).
5. $[Cu\ (tu)_3\ 2,6L]I$: 1605(v.s), 1480(s), 1430(m), 1380(s), 1080(w&b), 710(s). (fig.12B)
6. $[Cu\ (tu)_2dipy]I$: 1600(s&b), 1470(s), 1380(m), 1310(m), 1160(w), 760(v.s), 730(s), 705(s). (fig.11B)
7. $[Cu\ (tu)_2o\text{-}phen]I$: 1650(m), 1600(s), 1500(m), 1460(m), 1410(s), 1380(m), 1220(w), 1130(m), 1080(m&b), 855(m), 840(s), 770(s), 765(m), 735(m), 725(s), 715(m). (fig.14)
8. $[Cu\ (tu)(o\text{-}phen)_2]I$: 1620(s), 1600(s), 1500(s), 1460(m), 1410(s), 1215(w), 1130(m), 1080(w), 1070(w), 860(m), 845(v.s), 770(m), 735(s), 710(m). (fig.15)
9. $[Cu\ (o\text{-}phen)_2]I$: 1640(m), 1600(s), 1440(m), 1410(s), 1225(m), 1135(m), 1030(w), 980(w), 955(w), 870(m), 840(v.s), 765(s), 725(v.s). (fig.16)

RESULT AND DISCUSSION

Copper(I) formed mixed ligand complexes of the type: $[Cu(tu)_3py]I$ (light pink), $[Cu(tu)_3 2\ pic]I$ (pink), $[Cu(tu)_3\ 3pic]I$ (light pink), $[Cu(tu)_3\ 4\ pic]I$ (pink), $[Cu(tu)_3\ 2,6L]I$ (light pink), $[Cu(tu)_3\ Q]I$ (dirty yellow), $[Cu(tu)_3\ I.\ Q]I$ (pink), $[Cu(tu)_2dipy]I$ (red), $[Cu(tu)_2\ (phOAs)]$(lemon yellow), $[Cu(tu)_2dipy]Cl$ (orange), $[Cu(tu)_2\ (o\text{-}phen)]I$ (orange) and $[Cu(tu)o\text{-}phen_2]I$ (pink),. The complexes are very stable and except those of 2,2'-dipyridyl and o-phenanthroline all the complexes are soluble in water as well as organic solvents. Magnetic susceptibility measurements carried out at 30°C indicate that all the complexes were diamagnetic.

Copper(I) iodide forms 1:1 complexes with heterocyclic amines, also, with thiourea a 1:3 complex is formed. In the formation of mixed nitrogen and sulphur ligated complexes, a maximum coordination number of four is achieved. The replacement of thiourea and pyridine molecules by dipyridyl and phenyl arsonic acid, as shown in the following scheme supported the tetracoordinate structure for the complexes.



The evidence for the formation of tetracoordinate species in these reactions is further obtained by considering the results from the potentiometric measurements. Potentiometric titrations performed with various mixtures: (CuCl + tu + py), (CuCl + tu + dipy), (CuI + tu + dipy), ($Cu(tu)_3Cl$ + py), ($Cu(tu)_3I$ + py), ($Cu(tu)_3Cl$ + dipy) and ($Cu(tu)_3I$ + py), using 0.1M HNO_3 as a titrant, indicate a combining ratio of 1:1 for $Cu(tu)_3$ Cl and py, $Cu(tu)_3Cl$ and dipy, $Cu(tu)_3$ I and py, and $Cu(tu)_3$ I and dipy, respectively (fig.3A,3B and 3C). The results are summarised in table 2.

The formation of 1:1 complex, $[Cu(tu)_3py]X$, by the interaction of $[Cu(tu)_3]X$ (X = Cl,I) and pyridine results in attaining maximum coordination number of four for the copper(I). The copper atom in the central group $[Cu(tu)_3]^+$ is capable of accepting at least one pyridine molecule as the resulting charge accumulation of Cu^+ will be minimised by transferring it to the vacant d level of the ligand.

For the system, $[Cu(tu)_3]X$-dipy, the results of potentiometric titrations (fig.3B,3C and table 2) lead to the formation of 1:1 mixed ligand complex having a coordination number of five which is unusual for copper(I). However, the following mechanism,

$$Cu(tu)_3^+ + H_2O \longrightarrow [Cu(tu)_3H_2O]^+ \xrightarrow{dipy} [Cu(tu)_2dipy]^+ + tu$$

would explain the formation of the complex, $[Cu(tu)_2dipy]^+$, and such a mechanism is substantiated by the isolation of the red crystalline complex, $[Cu(tu)_2dipy]I$, as described above.

The study of the reaction between tris(thiourea) copper(I) iodide and o-phenanthroline is interesting in the respect that there are evidences for the formation of pentacoordinate $Cu(tu)(o\text{-}phen)_2\,I$, and tetracoordinate $Cu(tu)_2o\text{-}phen\,I$ and $Cu(o\text{-}phen)_2\,I$. The tetracoordinate and pentacoordinate complexes are isolated and fully characterised. The mechanism of the reaction in such a case may follow the path:

$$\underset{I}{[Cu(tu)_3]I} \xrightarrow{+\,o\text{-}phen} \underset{II}{[Cu(tu)_2\ o\text{-}phen]\,I} \xrightarrow{+\,o\text{-}phen}$$

$$\underset{III}{[Cu(tu)(o\text{-}phen)_2]I} \rightleftharpoons \underset{IV}{[Cu(o\text{-}phen)_2]I} + tu$$

The fact that the complex species II, III and IV have been isolated from the reaction mixture containing the complex, $[\mathrm{Cu(tu)_3}]\mathrm{I}$, and o-phenanthroline and the species are fully characterised by the chemical analysis supports the above mechanism (see preparation of the complexes).

The potentiometric measurements were made by carrying out titrations with mixtures containing (a) CuI-tu-o-phen (b) $\mathrm{Cu(tu)_3I}$ -o-phen, using 0.1M $\mathrm{HNO_3}$ as a titrant. From the potentiometric curves (fig.3D and 3E), ratios of 1:1 and 1:2 are obtained for $\mathrm{Cu(tu)_3I}$ and o-phenanthroline, respectively. This indicates the formation of species II, III and possibly IV, also. The results of potentiometry thus justified the above mechanism.

Using Job's method of continuous variation, the spectrophotometric studies on the interaction of $[\mathrm{Cu(tu)_3}]\mathrm{I}$ with dipyridyl and o-phenanthroline indicate the combination of two ligand molecules with one central group (fig.2b and 2d) in case of o-phenanthroline and one ligand molecule with one central group (fig.2a and 2c) for dipyridyl.

In dipyridyl complex, the reaction may be explained on considering the following path:

$$\mathrm{Cu(tu)_3}{}^{+} + \mathrm{H_2O} \longrightarrow [\mathrm{Cu(tu)_3H_2O}]^{+}$$

$$[\mathrm{Cu(tu)_3H_2O}]^{+} + \mathrm{dipy} \longrightarrow [\mathrm{Cu(tu)_3dipy}]^{+} + \mathrm{H_2O}$$

$$[\mathrm{Cu(tu)_3dipy}]^{+} \longrightarrow [\mathrm{Cu(tu)_2dipy}]^{+} + \mathrm{tu}$$

The species, $[Cu(tu)_2dipy]^+$, has been isolated and characterised, therefore supporting the above mechanism.

For o-phenanthroline complex, the formation of 1:2 complex species supports the results derived from potentiometric titration method.

The interaction of heterocyclic amine and tris(thiourea) copper(I) iodide was also studied by conductometric method. Taking alcoholic solution of the complex, $[Cu(tu)_3]I$, in the cell, conductometric titrations were performed using amines as titrants. From the conductometric titration curves (fig. 1) a ratio of 1:1 is obtained in all the cases indicating thereby the formation of the complex species, $[Cu(tu)_3py]I$, $[Cu(tu)_3\ 2pic]I$, $[Cu(tu)_3Q]I$, $[Cu(tu)_2dipy]I$ etc. The results are in conformity with those of chemical analysis and potentiometry.

The mechanism of reactions of tricoordinate copper(I) thiourea complexes with heterocyclic amines has been studied by e.m.f. measurements using Ag-Ag_2S as an indicator electrode. The order of reaction has been found out by observing the change in potential with time, the results are summarised in table 10.

The reaction of pyridine with tris(tu) copper(I) chloride was found to be fast one and equilibrium is attained almost immediately. The reaction seems to proceed by the following mechanism:

$$Cu(tu)_3^+ \rightleftharpoons Cu(tu)_2^+ + tu \xrightarrow[fast]{2py} [Cutu_2py_2]^+$$

involving an increase in the concentration of thiourea at the completion of the reaction (fig.7). The formation of the complex, $[Cutu_2py_2]Cl$, by the substitution of pyridine and subsequent elimination of thiourea is to be expected due to higher nucleophilic order of pyridine[5] (tu: 0.4, py: 5.3) and the tendency of copper(I) to achieve its maximum stable coordination number.

The mechanism of the substitution of tris(tu) copper(I) chloride with dipyridyl has been studied by carrying out kinetic studies with mixtures of CuCl + tu + dipy and $Cu(tu)_3Cl$ + dipy. On the basis of potentiometric studies, the formation of the complex, $[Cu(tu)_2dipy]Cl$, is revealed. In both cases the reaction is of second order, first order with respect to each of the reactants, $Cutu_3$ Cl and dipy (fig.5A to 5C 9A to 9C, table 5 & 9). The mechanism of substitution in this case appears to be associative involving the formation of trigonal bipyramidal or square pyramid intermediates.

$$[Cutu_3]Cl + dipy \xrightarrow{fast} [Cutu_3dipy]Cl \xrightarrow{slow} [Cu(tu)_2dipy]\ Cl + tu$$

The associative mechanism described above is further supported on considering the gradual decrease in thiourea concentration with time.

Potentiometric studies carried out on the reaction of 2,2' dipyridyl with tris (tu) copper(I) iodide indicate the formation of mixed ligand complex, $[Cu(tu)_2dipy]I$. Unlike chloride complex, the iodide complex shows an interesting behaviour, in the initial stages it shows a zero order reaction and after about fifty minutes the reaction proceeds with a second order dependent (first order with respect to the reactants) (fig. 6A, to 6C, table 6). On the basis of this unique behaviour, the formation of aquo complex, $[Cu(tu)_3 H_2O]^+$, in the initial stages is suggested followed by the formation of an intermediate pentacoordinate species, the latter subsequently dissociates in $[Cu(tu)_2dipy]^+$.

$$Cu(tu)_3{}^+ + H_2O \xrightarrow{slow} [Cu(tu)_3 H_2O]^+$$

$$[Cu(tu)_3 H_2O]^+ + dipy \xrightarrow{fast} [Cu(tu)_3dipy]^+ + H_2O$$

$$[Cu(tu)_3dipy]^+ \xrightarrow{slow} [Cu(tu)_2dipy]^+ + tu$$

An interesting aspect of the substitution in tri-coordinate copper(I) complex is the study of the substitution reaction of phenyl arsonic acid with tris(thiourea) copper(I) chloride. Potentiometric studies carried out with the mixtures of copper(I) chloride, thiourea and phenyl arsonic acid indicate the presence of only two thiourea molecules after the completion of the reaction. The formation of mixed ligand complex, $[Cu\ (tu)_2\ phOAs]$, can be represented by the following reaction mechanism which follows a second order rate law (fig.8A to 8C).

$$\begin{tikzcd} Cu^{+} + tu \arrow[r, "fast"] & Cu(tu)_3^{+} + \arrow[r, shift left, "slow"] & Cu(tu)_2^{+} + tu \arrow[l, shift left] \arrow[d] \\ & & {[Cu(tu)_2phOAs]} \arrow[from=1-3, to=2-3, phantom] \end{tikzcd}$$

$$[Cu(tu)_2phOAs] \xleftarrow[fast]{phOAs}$$

The above mechanism is supported by the observed increase in thiourea concentration with time indicating the slow dissociation of the complex into thiourea and lower coordination species, and ultimate substitution by strong π bonding tertiary arsine. The complex, $[Cu(tu)_2phOAs]$, is isolated by the reaction of tris(tu) copper(I) iodide with phenyl arsonic acid.

The rate law studies carried out with mixtures of CuI+tu+o-phen and $Cu(tu)_3I$ + o-phen have not proved successful. The e.m.f. measurements carried out, using $Ag-Ag_2S$ as an indicator electrode, showed no appreciable change in potential with time indicating thereby immediate attainment of the equilibrium by the substitution of thiourea molecules by highly nucleophilic and strong π bonding o-phenanthroline molecules.

$$Cu(tu)_3I + \text{o-phen} \longrightarrow \underset{\text{II}}{[Cu(tu)_2(\text{o-phen})]I} \xrightleftharpoons[\text{o-phen}]{}$$

$$\underset{\text{III}}{[Cu(tu)\text{o-phen}_2]^{+}} \rightleftharpoons \underset{\text{IV}}{[Cu(\text{o-phen})_2]^{+}}$$

The fact that species II, III and IV are obtained from the reaction mixture ($Cu(tu)_3I$ + o-phen) supports the above view point.

The infra red spectra of the mixed ligand complexes were studied keeping in view the changes occurring on coordination in the spectra of heterocyclic amines and thiourea complexes of copper(I). As expected the spectra of these complexes are marked by a large number of bands and therefore it was not found plausible to give a definite assignment to every band. The following regions were found to be of interest with regard to the bonding in these complexes.

Ca.1600 to 1000 cm^{-1}: This region is specified by four strong bands namely ca.1600 cm^{-1}, ca.1475 cm^{-1}, ca.1370 cm^{-1} and 1085 cm^{-1} and are assigned to the composite bands of NH_2 bending, N-H deformation and C-N stretching vibrations in thiourea.[6,7,8] The bands at ca.1600 and ca.1400 cm^{-1} may also be assigned to ring CC, CN stretching vibrations of heterocyclic amines.[9]

Although it is difficult to assign a particular band specifically either to coordinated thiourea or coordinated amine, however, the spectra are marked by two distinct changes (i) the bands assigned to NH_2 bending (ca.1600 cm^{-1}), N-H deformation and C-N antisymmetric stretchings(ca. 1475 cm^{-1}), and N-C-N stretchings(ca. 1085 cm^{-1}) in thiourea remain almost unaltered on coordination (ii) the bands in coordinated amines due to CC, CN stretching vibrations (1439, 1485, 1584, 1600, 1636 cm^{-1} in pyridine) are greatly reduced in number, a behaviour which was also observed in Cu(i)-heterocyclic amine complexes (chapter I). The results are summarised in table 11.

TABLE -11:

Infra red frequencies of coordinated thiourea and coordinated heterocyclic amines in the region 1600 to 1000 cm^{-1}.

Complex	Fig. No.	Position of bands
$[Cu(tu)_3py]I$	10	1600(v.s), 1475(s), 1430(m&b), 1370(m), 1080(m)
$[Cu(tu)_3 2,6L]I$	12B	1605(v.s), 1480(s), 1430(m), 1380(s), 1080(w&b)
$[Cu(tu)_3 I.Q]I$	12A	1590(s), 1495(m), 1465(s), 1425(s), 1380(m), 1275(m), 1080(m).
$[Cu(tu)_2 dipy]I$	11B	1600(s&b), 1470(s), 1380(m), 1310(m)
$[Cu(tu)_3 4pic]I$	11A	1600(s), 1480(s), 1380(s&b), 1080(w)
$[Cu(tu)_2 o\text{-}phen]I$	14	1650(w), 1600(s), 1500(m), 1460(m), 1410(s), 1380(m), 1220(w), 1130(m), 1080(m&b).
$[Cu(tu)_{o}\text{-}phen_2]I$	15	1620(s), 1600(s), 1500(s), 1460(m), 1410(s), 1215(m), 1130(w), 1080(w), 1070(w).
$[Cu(o\text{-}phen)_2]I$	16	1640(s), 1500(s), 1440(m), 1410(s)

An interesting behaviour is met with while comparing the spectra of o-phenanthroline complexes, the strong band ca.1600 cm^{-1} assigned to NH_2 bending modes is absent in the complex, $[Cu(o\text{-}phen)_2]I$, whereas the position of the other is more or less the same, for example, the CH in plane deformation vibrational band appeared in o-phenanthroline at 1130 cm^{-1} remains unaltered in the complexes.

Ca. 600-800 cm^{-1}: The spectra in this region are marked by a number of bands which are assigned to CH out of plane deformation vibrations of amines[9] (702, 744, 810 cm^{-1} in py) and C-S stretching modes of thiourea[6,8] (730 cm^{-1} in tu). The strong band appearing at ca.710 cm^{-1} in the complexes corresponds to C-S stretching vibrations of thiourea which lowers on coordination through sulphur. The complexities in the spectra in this region may be due to the splitting of CH out of plane deformation vibrational bands. The latter occur due to the coordination with heterocyclic nitrogen and the strong polarisation effect in the coordination sphere by the large iodine atom (the behaviour is not observed in $[Cu(tu)_2phOAs]$ complex).

The coordination chemistry of copper(I) is unique in the sense that the complexes formed are usually of lower coordination number ($n < 4$). These complexes are formed with ligands having π bonding capacities ($p_\pi - d_\pi$ or $d_\pi - d_\pi$ bonds).

However, there is always a tendency of complexes with lower coordination number to achieve the stable coordination maximum either by bridging through ligand atoms or by the addition of another more reactive group. The present studies on the substitution and addition in the tris(tu) copper(I)X (X=Cl,I) may be grouped in the latter category. The reactions of tri-coordinated copper(I) thiourea complexes were studied with ligands of varying π bonding capacities, which follow the order[2]: py $<$ tu $<$ dipy $<$ o-phen $<$ tertiary arsine.

In tricoordinated copper(I) complexes there is likelihood of the addition of a ligand to give tetracoordinated species. Moreover, there is also a possibility of the replacement of a relatively weak π bonding ligand (e.g. thiourea) by ligands with strong π bonding capacities e.g., o-phen, dipy, tertiary arsine etc. In the present reaction mechanism studies, pyridine is found to enter in the coordination sphere of $Cu(tu)_3^+$ to form a tetracoordinate $[Cu(tu)_3py]^+$. The reaction proceeds with a faster rate and the equilibrium is reached within a very short time, but with a potential nucleophile like dipyridyl the substitution reaction proceeds with an associative mechanism involving the formation of a pentacoordinated intermediate, the latter converts into tetrahedral $[Cutu_2dipy]^+$. The second order rate in these reactions and gradual decrease in thiourea concentration lead to an associative mechanism.

Another aspect of this reaction is the replacement of thiourea by dipyridyl molecules giving the final product, $[Cu(tu)_2dipy]^+$, as inferred from the spectrophotometric studies (fig.2).

In case of o-phenanthroline, a pentacoordinated intermediate, $[Cu(tu)\ o\text{-}phen_2]^+$, together with $[Cu(o\text{-}phen_2)]^+$, have been isolated and characterised, moreover, spectrophotometric studies give evidence for a 1:2 complex.

The substitution reaction of phenyl arsonic acid with tricoordinated copper(I) thiourea complex seems to proceed with a dissociative mechanism involving the dissociation of the tricoordinated complex into lower complex species and subsequent addition of arsine ligand. The gradual increase of thiourea with time and the second order dependent lead to a dissociative mechanism involving the formation of the complex, $[Cu(tu)_2\ phOAs]$.

A comparative study of the entering group effect based upon the rate constant values of the reactions give the reactivities of the various ligands in the order: Py $<$ dipy $<$ phOAs $<$ o-phen.

A comparison of the reactivities of dipyridyl in the substitution reactions of $[Cu(tu)_3]X$, X=Cl, I give higher values for chloride than iodide complex. This may be attributed to the greater stability of the iodide complex, $[Cu(tu)_3]I$, than that of the corresponding chloride complex.

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CHAPTER - IV:

STUDIES ON THE INTERACTION OF COPPER(I) HALIDES WITH 2, MERCAPTOBENZTHIAZOLE

Studies On The Interaction of Copper(I) Halides With 2,Mercaptobenzthiazole.

Like thiourea, 2 mercaptobenzthiazole is a thiocarbonyl derivative existing in two canonical forms, e.g., thioketo and thioenol. The former containing C-SH linked to a tertiary nitrogen and sulphur, and the latter having C=S group linked to imino nitrogen and sulphur. Infra red spectral studies indicated the presence of - N - C = S group in the solid compound[1] although, according to Flett[2] during reactions with metal ions, the reagent behaves as if in the enolic form. The presence of - N - C = S in the compound makes it a potential coordinating ligand as is obvious from a large number of references available in the literature regarding its interactions with a large number of metals, viz., Cd, Bi, Hg(II), Ni, Zn, Tl(I), Pt metals[3-8] etc. It has also been recommended as an analytical reagent for a reasonable number of metals. A glance on the available chemical literature indicates the absence of references on the reaction of this compound with lower valence ions. Although extensive work on the reactions of 2,mercaptobenzthiazole with copper(II) has been done[9,10] nothing so far has been reported on corresponding reactions with copper(I) ions.

The present work describes the interaction of copper(I) salts with 2, mercaptobenzthiazole. The bright yellow product so formed has been studied by various physico-chemical methods and its structure discussed on the basis of infra red spectral studies. The possibility of using this compound for the gravimetric estimation of Cu^+ has also been explored.

EXPERIMENTAL

Preparation of Copper(I)-2, Mercaptobenzthiazole Complex.

To a warm aqueous solution of cuprous chloride in concentrated KCl (containing a few drops of dil. HCl), a concentrated soln., of 2, mercaptobenzthiazole in absolute alcohol was added in excess. The whole mixture was warmed over a water bath with continuous stirring for about 15 mts to accelerate precipitation. The yellow precipitate so obtained was transferred on a medium porosity sintered glass crucible and washed with hot water (to remove KCl) and then with small aliquots of absolute alcohol (to remove excess of the reagent) several times, and finally dried with ether. The dried yellow product was then dissolved in a large volume of acetone, warmed slightly and filtered. The filtrate was kept for crystallisation. After about 24 hours, bright yellow crystals of the product appeared.

Bright yellow coloured complexes with copper(I) bromide and iodides were prepared by the similar procedure.

Analytical Data:

Mono (mercaptobenzthiazole) copper(I) complex: Bright yellow crystals(flakes), m.p. 160°C., Calc. for $C_7H_4NS_2Cu$: C-36.6, H-1.7, N-6.1, S-27.88, Cu-27.7. Found: C-37.0, H-1.7, N-6.1, S-28.1, Cu-27.7.

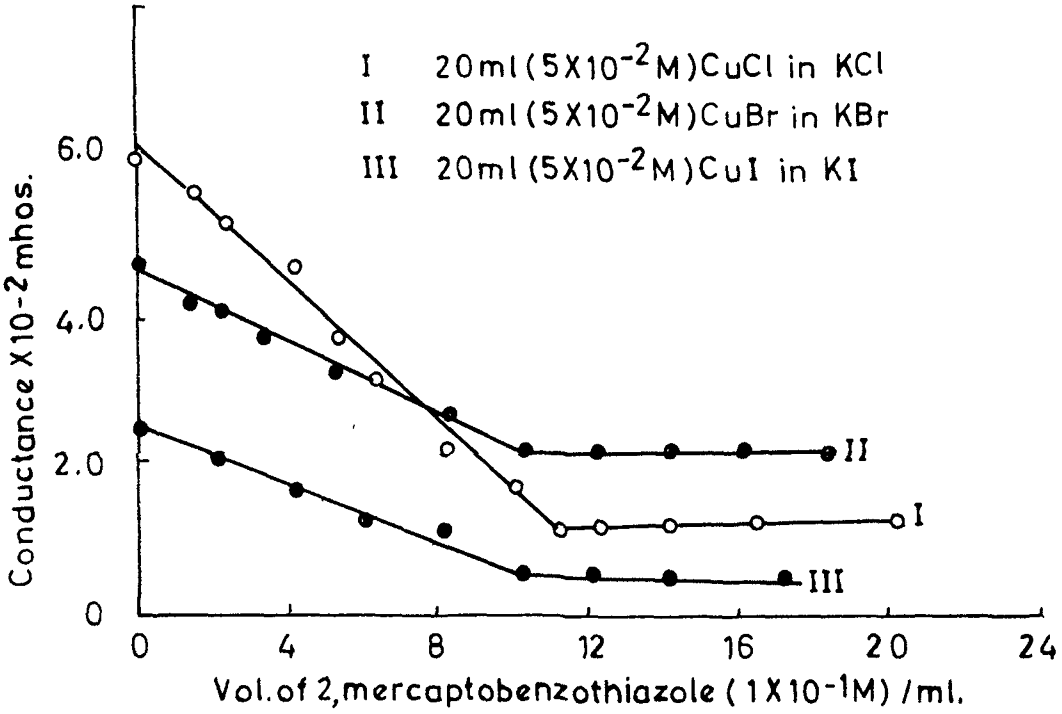


Fig. 1 Direct Conductometric Titrations
System: Copper (I) Halide - 2, Mercaptobenzothiazole

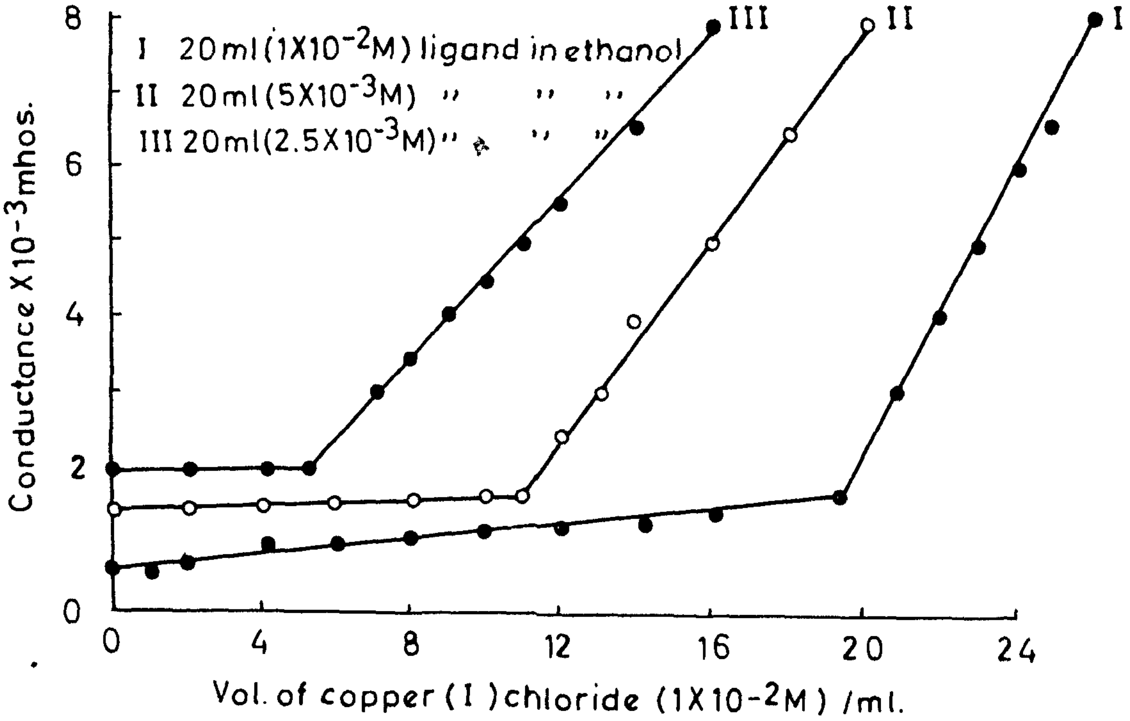


Fig. 2 Reverse Conductometric Titrations

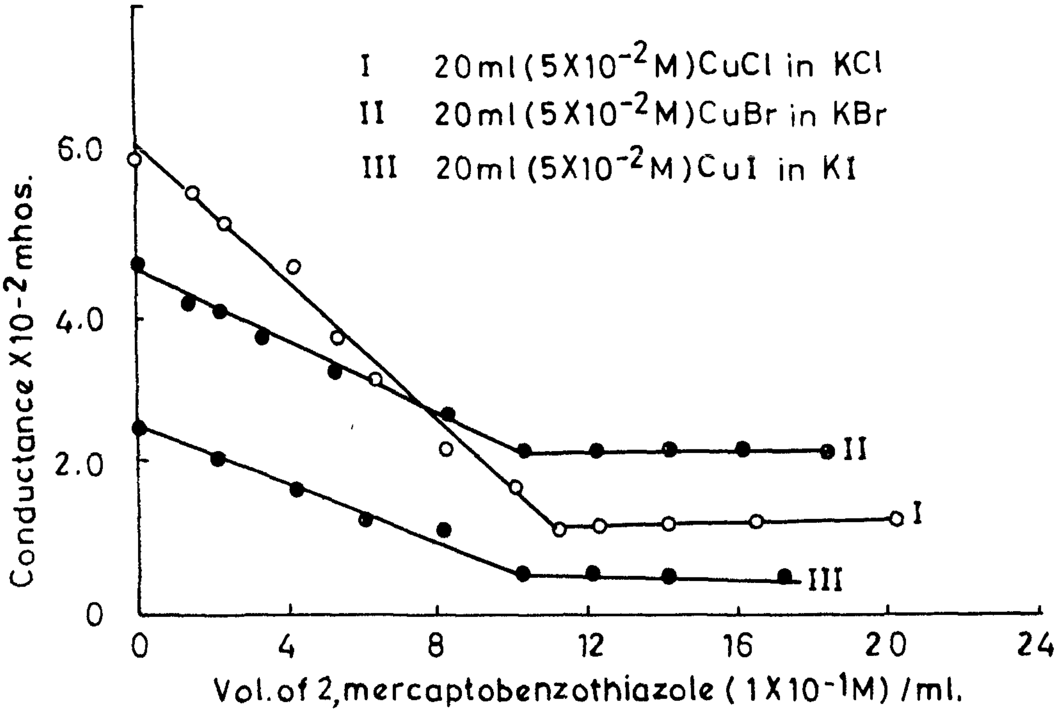


Fig. 1 Direct Conductometric Titrations
System: Copper (I) Halide - 2, Mercaptobenzothiazole

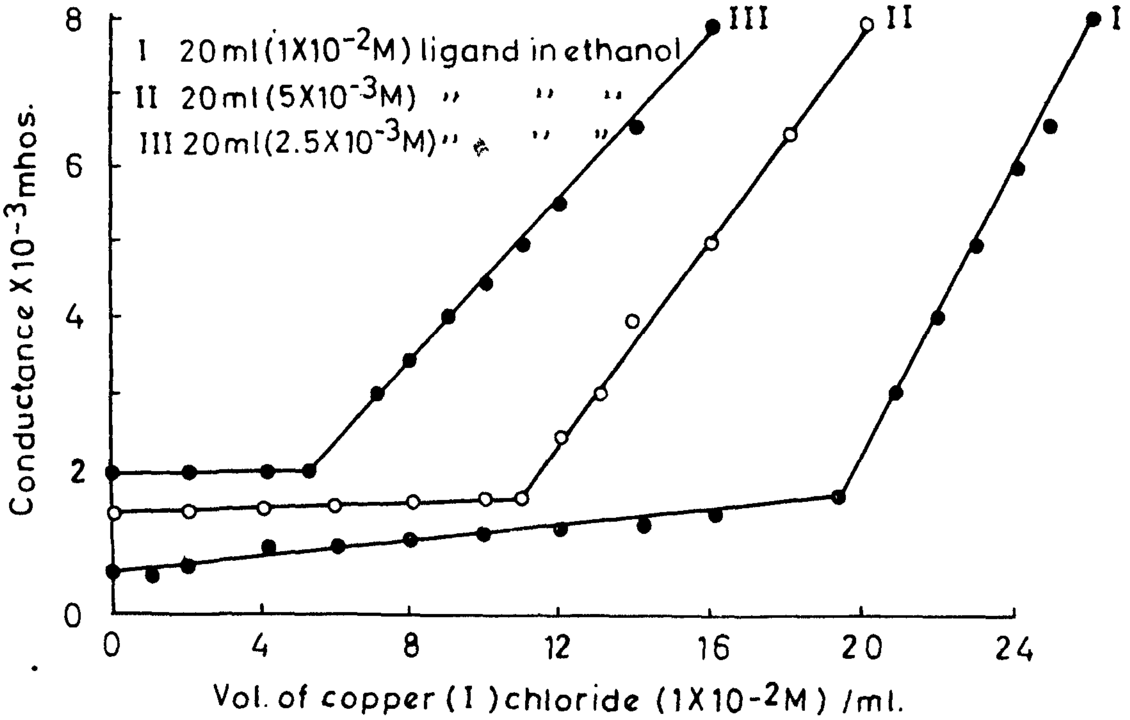


Fig. 2 Reverse Conductometric Titrations

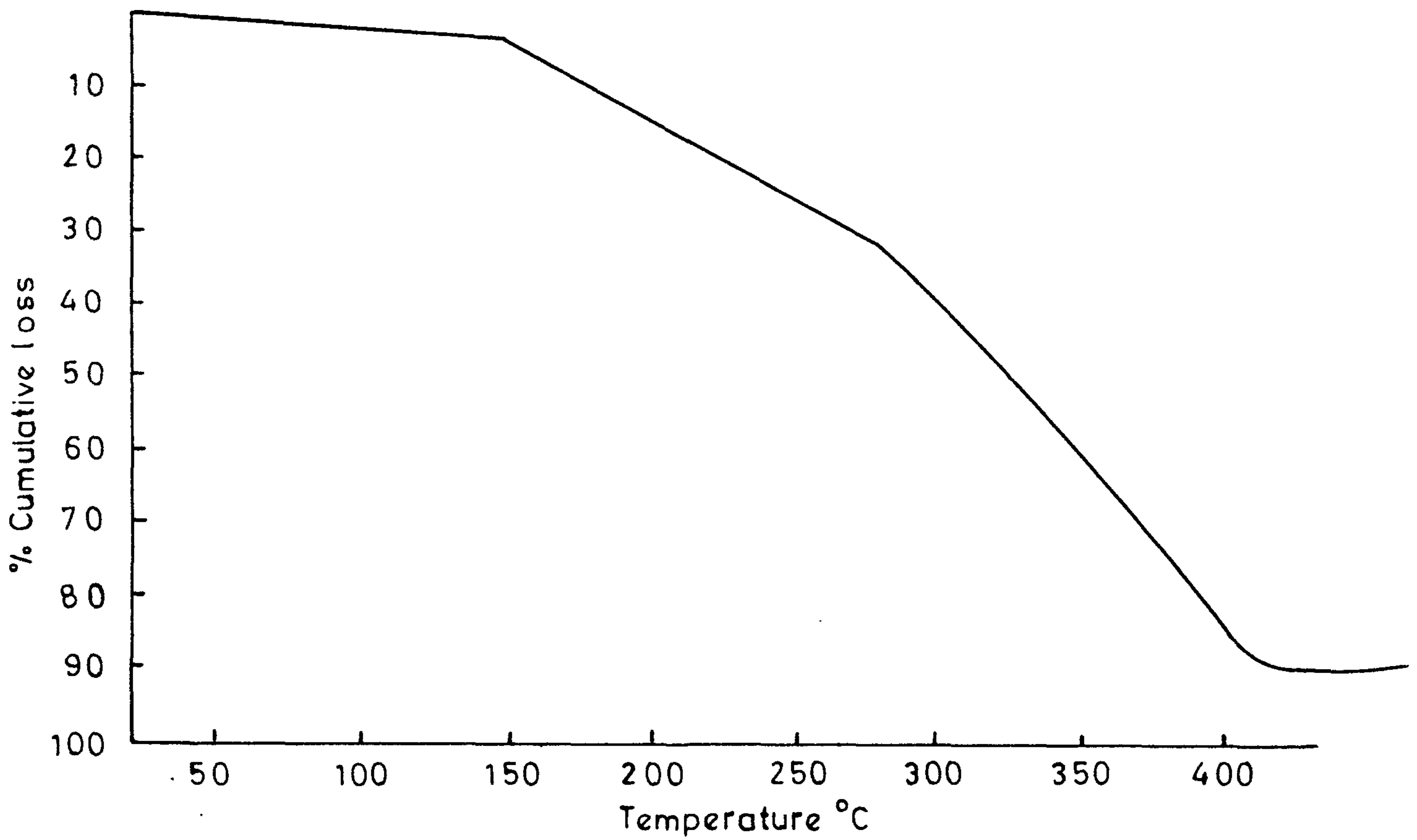


Fig. 3. Pyrolysis Curve Of
Cu(I)-2, Mercaptobenzothiozole Complex

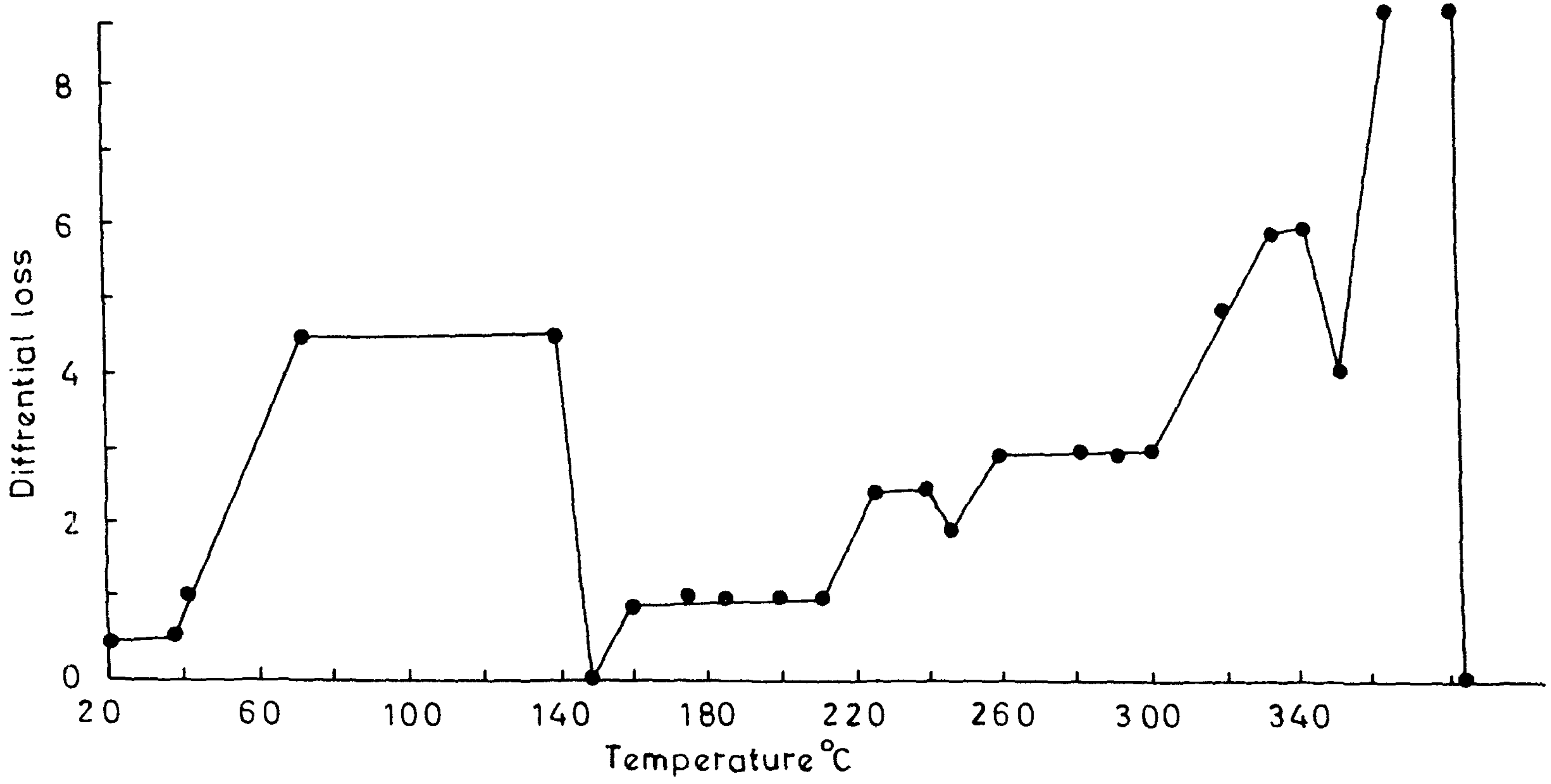


Fig. 4 Diffrential Loss Curve
Cu(I)-2, Mercaptobenzothiozole Complex

C,H,N and S were analysed by the Australian Microanalytical Service, University of Melbourne, Australia. Copper was estimated iodometrically.

Conductometric Titrations:

The conductometric measurements were made with a Philips conductivity bridge (Type PR 9500) using a dip type conductivity cell (cell const. · 1.52).

Both direct(CuCl in the cell) and reverse titrations were performed using varying concentrations of the reagents (Fig.1 and 2). From the breaks in the conductance curves, a ratio of 1:1 is obtained in direct as well as reverse titrations. The specific conductivity of the complex(in 10^{-3}M acetone)was measured at 15°C. The calculated value of the molar conductivity for the complex was found to be 22 cm^2/ohm.

Thermogravimetric Analysis:

Thermogravimetric analysis of the complex was carried out with a Stantont thermogravimetric balance (type STM), with a maximum range of 1400°C and heating range of 3°C/minute. The pyrolysis curve (Fig.3) showning the cumulative loss in weight with increasing temperature, and the differential loss curve (Fig.4) were plotted.

Thermogravimetric analysis of the complex showed that there was no loss of weight upto 150°C, above this temperature

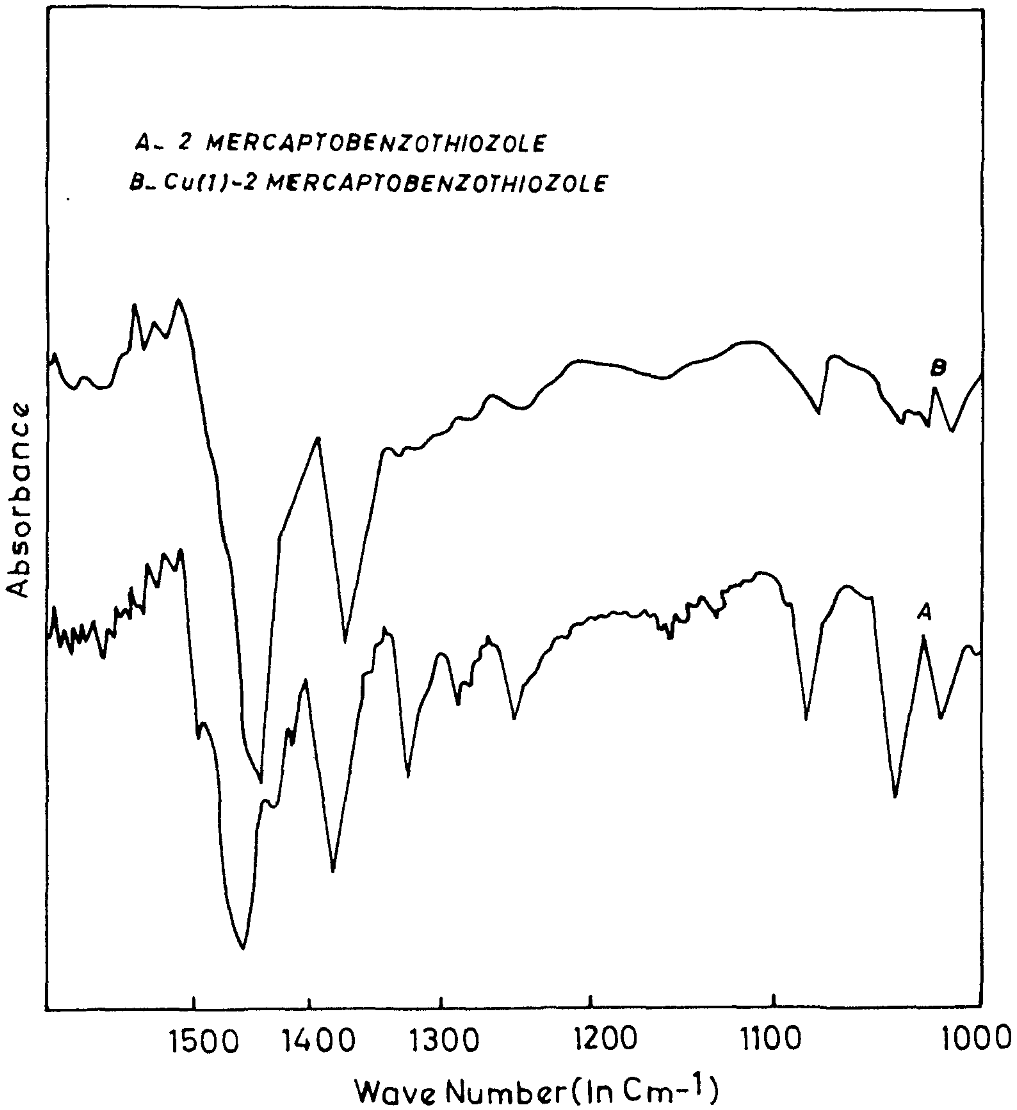


Fig.5 Infra Red Spectra Of 2, Mercaptobenzothiozole And its Complex

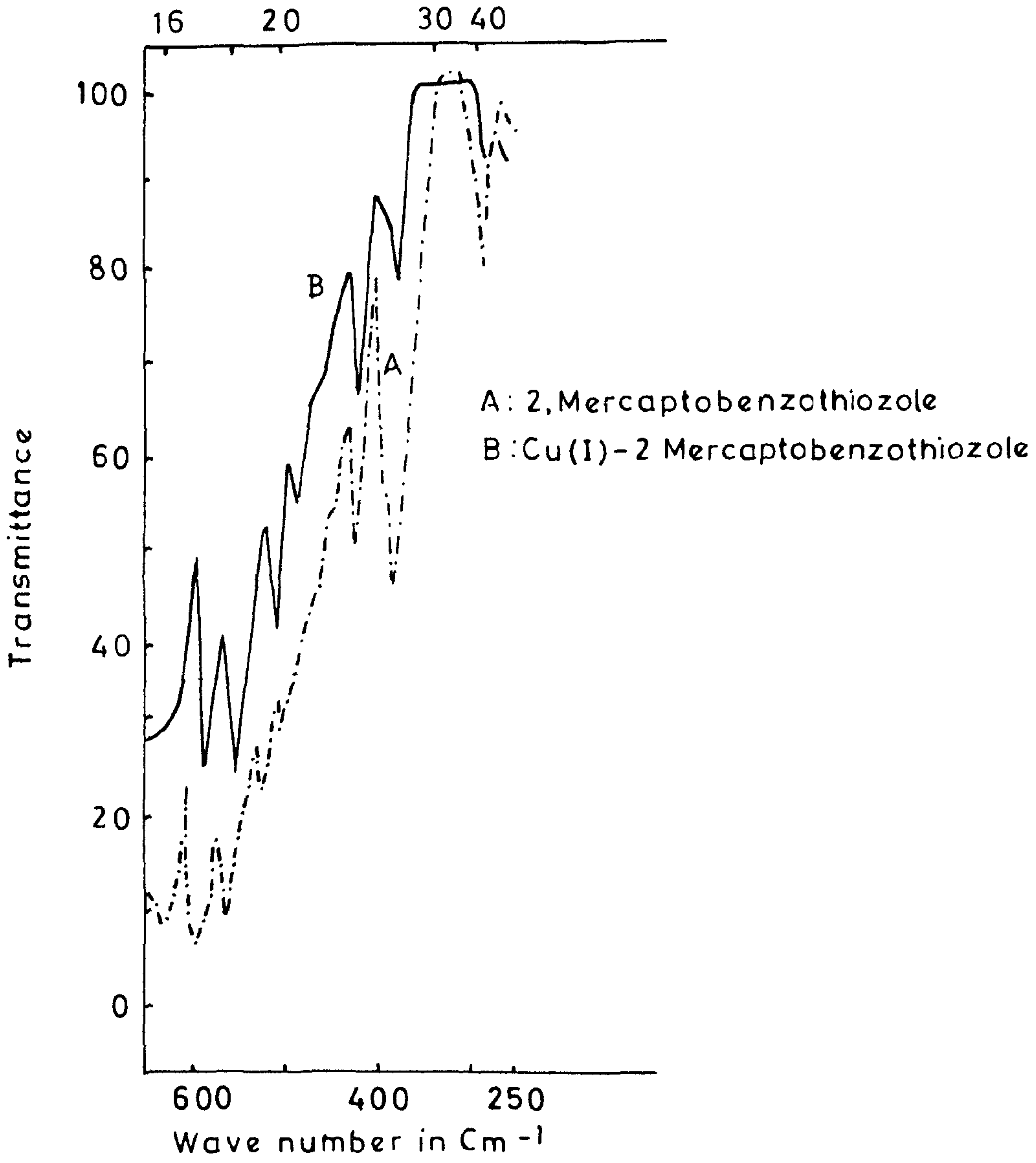


Fig. 6 Infra Red Spectra

there was rapid loss in weight and at about 400°C, a brownish black residue, probably of cuprous oxide was left.

Infra red spectra:

The infra red spectra (in the range: 2.5 to 16 μ) of the complex and reagent, were obtained with a Beckman IR-5 spectrophotometer, using KBr technique, for the far infra red region, a Beckman IR-7 spectrophotometer, was employed, using CsI prism and nujol as mulling agent.

The details of the spectra of 2, mercaptobenzthiazole and its copper(I) complex are as follows:

2-mercaptobenzthiazole: 280(s), 380(v.s), 420(s), 500(m), 520(m), 560(m), 590(m), 620(b), 650(m), 745(m), 845(m), 1010(m), 1030(s), 1080(s), 1120(w), 1240(s), 1270(m), 1330(s), 1440(v.s), 1500(s), 1590(s), 3100(m). (Fig.5A,6A)

Cu(I) mercaptobenzthiazole : 280(s), 380(s), 420(v.s),490(m), 510(m), 560(s), 580(v.s), 670(m), 755(s), 1020(m), 1040(m&b), 1070(m), 1120(w), 1245(m), 1280(m), 1450(m), 1480(v.s),1600(s), 2850(w), 2950(w).(Fig.5B,6B)

Magnetic Susceptibility Measurements: Magnetic susceptibility measurements were performed at 36°C with a Gouy magnetic balance, with temperature control adjustment. The complex was found to be diamagnetic.

2,Mercaptobensthiazole as an analytical reagent:

Due to the insoluble nature of copper(I)-2, mercaptobensthiazole complex and its stability to a considerable high temperature (150°C) it was thought worthwhile to study the use of 2, mercaptobensthiazole as a gravimetric reagent for Cu(I).

PROCEDURE:

To a warm solution of copper(I) chloride in KCl contained in a beaker, a few drops of conc. HCl were added and with the subsequent addition of the reagent, 2, mercaptobenziazole (1% in ethanol) with constant shaking. The yellow precipitate so obtained was allowed to settle, a few drops of the reagent were added to the supernatant liquid to ensure complete precipitation. The whole mass was then warmed over a water bath for about one hour, cooled and then kept at room temperature for about one more hour to coarsen the size of the precipitates. The precipitate was then transferred carefully to a previously weighed medium size sintered crucible and filtered on a Buchner funnel. Some of the precipitates adhered to the wall of the beaker were removed by treating with small volumes of absolute alcohol and transferring them to the crucible with the help of a glass rod. The precipitate was washed several times with small aliquots of hot water and then alcohol. The crucible was then kept in a hot air oven maintained at 110°C for about 1 hr. and then weighed.

Solutions of copper(I) chloride, bromide and iodides of varying concentrations were used and copper contents were determined by the procedure described above. The results of the analysis are summarised in table 1.

TABLE - 1:

Gravimetric data of the estimated values of copper by the thiocyanate and 2,mercaptobenzthiazole methods.

pH of the solution: ~2

Weight of copper (determined by thiocyanate method) (in m,gm.)	Weight of copper (determined by the present method) (in m,gm.)
86.40	86.00
76.90	76.30
52.80	52.30
26.40	26.50
17.20	17.30
6.90	6.80
3.60	3.50
3.40	3.45
2.60	2.60
2.10	2.10

The effect of pH was studied in the range 1.0 to 5.0. The results indicate that precipitation may be effectively carried out in the pH range 2-3.5. However, unbuffered solutions having ordinarily a pH of about 2 gave sufficiently reliable results in the concentration range recommended above. The results are given in table 2.

TABLE -2:

Effect of pH on the estimation of copper by 2,mercapto-benzthiazole method.

Weight of copper (by thiocyanate method)=22.10 mgm.

pH	Weight of copper (by the present method) (in m.gm.)
4.9	22.01
4.5	22.02
4.2	22.01
3.8	22.0
3.5	22.0
3.1	22.0
2.8	22.12
2.5	22.11
2.0	22.10
1.5	22.31
1.0	22.40

RESULTS AND DISCUSSION

Copper(I) ions form 1:1 bright yellow complex with 2, mercaptobenzthiazole. The complex is insoluble in water and alcohol but slightly soluble in acetone.

The conductometric titrations (both direct and reverse) carried out to determine the composition also gave a ratio of 1:1 for the complex (Fig.1 and 2). The molar conductivity of the complex (for approx.$1x10^{-3}$M acetone) was 22 cm^2/ohm at 15°C indicating the non-ionic character of the complex.

The pyrolysis curve (Fig.3) showing the cumulative loss in weight with increasing temperature, indicated no loss in weight on heating upto 150°C showing thereby the stability of the complex upto this temperature.

The quantitative analysis carried out to investigate the possibility of 2, mercaptobenzthiazole as a gravimetric reagent for copper(I) indicates the possible use of this reagent for determining copper in the concentration range of 2-85 m.gm. with an error of less than 0.1%. The pH range found for the reliable estimations was 2 to 3.5. Though the reagent is of limited applicability, however, it could be recommended for the rapid determination of copper(I) ions which are susceptible to quick oxidation.

The infra red spectrum of 2-mercaptobenzthiazole shows a strong peak at 1500 cm^{-1} which is assigned to N-C=S stretching vibrations resulting from the coupling of C-N stretching and NH deformation vibrations. This indicates the presence of unconjugated thioketo form.[1] The band shifted to the lower frequency (1480 cm^{-1}) in the complex. The bands at 1440 and 1330 cm^{-1} in the ligand are assigned to N-C = S symmetric and antisymmetric stretching vibrations with a major contribution from NH deformation modes.[11] The spectrum of the complex does not show any of these bands indicating thereby the removal of a proton on coordination. The displacement of imino proton is further confirmed by the absence of a band ca. 3000 cm^{-1} which is observed at 3100 cm^{-1} (strong) in the ligand (NH stretching vibrations). It is difficult to make any specific assignments to the bands appearing at 1080, 1030 and 1010 cm^{-1}. However, it may be correctly assumed to assign these bands as a result of delocalised C = S stretching vibrations (due to coupling effect of N - C = S unit). All the bands are shifted to lower frequencies on complexation, also there is marked decrease in their intensities. This may be due to the greater charge localisation in sulphur on complexation than that in uncoordinated thioketo form.

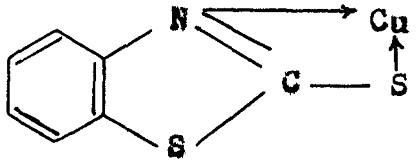
On the basis of infra red studies, the structure of the complex may be represented in the following forms:

i) a 4-ring structure resulting by the coordination of Cu(I) through nitrogen and sulphur.

ii) a simple salt like structure in which H is replaced by Cu(I).

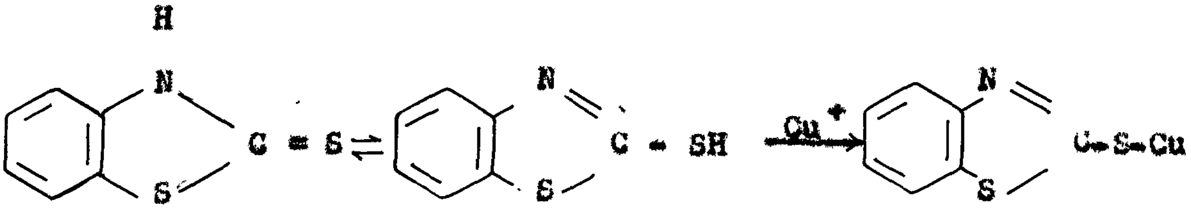
iii) a polymeric structure through S bridge in which Cu(I) tends to achieve its maximum coordination number.

The formation of the chelate with 4 ring structure (A) is not very probable because of its high strain, although there are reported cases of stable 4 ring structure, e.g., titrazoline 5-thione complexes.[12] An indirect evidence for the improbability of 4 ring structure is the absence of Cu - N peak in the far infra red spectrum of the complex which would otherwise be present at ca.240 cm^{-1}.



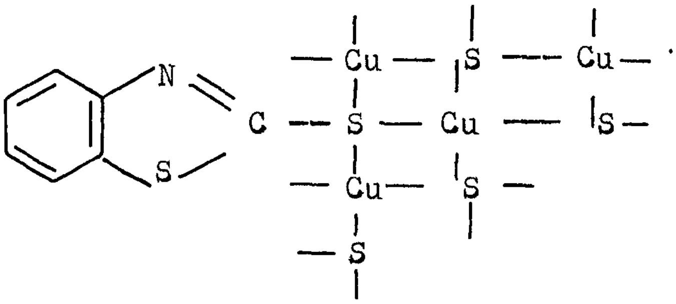
A

According to Flett[2] who gave the clear interpretation on the infra red spectrum of 2, mercaptobenzthiazole, it would be more correct to assume that the reagent itself may be present as thioketo form (I) and may react with metal ions as the thioenol form (*II*), through dissociation of an SH-proton to form a salt (*B*). A copper(*I*) compound of this type, however, likely to be ionic. Therefore, the possibility of such a structure is excluded due to the fact that the complex had extremely low solubility and poor conductivity.



I II B

The nearly insoluble nature of the complex, extremely low conductivity (22 cm^2/ohm for $1x10^{-3}M$ acetone) and absence of Cu-N band in the far infra red spectrum of the complex, therefore, support the view regarding a polymeric structure (*C*) through S bridging in which Cu^+ tends to achieve its maximum coordination number. The formation of polymeric species in Cu^+ in which the latter acquires its maximum coordination number through polymerisation is not uncommon.[13]



With the available experimental evidence, out of the three possible structures, the evidence for polymeric structure although not conclusive but is most convincing.

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CHAPTER - V:

COORDINATION COMPOUNDS OF RARE EARTHS WITH SOME SUBSTITUTED THIOUREA.

Coordination Compounds Of Rare Earths With Some Substituted Thioureas.

The coordination chemistry of rare earth metals is of relatively recent origin. Most of the work cited in literature has been carried out during the course of the last two decades. A survey of the literature concerning the complexes of lanthanides reveals that most of the work is concerned with oxygen and nitrogen ligated complexes;[1-10] and a very few references are available on lanthanide complexes with sulphur containing ligands.[11-12] This is perhaps due to the presence of high charge on rare earth metal ion which could be stabilised only by highly electronegative atoms e.g., fluorine, nitrogen and oxygen. These anion transfer the charge by way of σ type coordinate bond and also have the capacity to donate more charge by way of a π donor bond involving another pair of electrons. Sulphur, on the other hand, is less electronegative having weak σ donor but strong π acceptor properties which make it more suitable for reaction with lower valence ions such as copper(I), Ag(I) etc.

The work described in this part concerns with the studies on the complexes of rare earths with some substituted thioureas.

EXPERIMENTAL:

Chemical: Spectroscopically pure oxides of rare earths were obtained from Jhonson and Matthey (London). The chlorides were prepared by dissolving the oxides in Analytical grade HCl(B.D.H.). Naphthyl thiourea (Light product), allyl thiourea, diphenyl thiourea and diisopropyl thiourea were all B.D.H. products and were recrystallised from acetone before use.

Preparation of the Complexes:

To an aqueous solution of rare earth chloride (about 1%) in an Erlenmyer flask was added an excess of 2% substituted thiourea solution in acetone. The resulting solution was then warmed slightly over a water bath to dissolve any precipitating agent (substituted thiourea) and refluxed for about one hour. The refluxed solution was then evaporated to dryness over a water bath. The dried product was extracted with about 10 ml. of water and heated for about half an hour, filtered and the filtrate was concentrated and kept for crystallisation. After 24-36 hours, the crystals of the complex appeared, the latter were separated from the main liquor, dissolved in water and recrystallised.

Analytical Data*

1. Tetrakis (diisopropyl thiourea) gadolinium(iii) chloride. $Gd(DIPTU)_4Cl_3$. Colorless crystals, highly soluble in water but slightly soluble in alcohol. Calc. for $C_{28}H_{64}N_8S_4$ $GdCl_3$: C-37.1, H-7.1, N-12.3, S-14.05. Found: C-36.4, H-7.7, N-12.5, S-14.1.

2. Bis(o-tolyl thiourea) gadolinium(iii) chloride. $Gd(TTU)_2Cl_3$. Light pink crystals, highly soluble in water but slightly soluble in alcohol. Calc. for $C_{16}H_{20}N_4S_2GdCl_3$: C-32.2, H-3.2, N-9.4, S-10.7. Found: C-31.1, H-2.9, N-9.3, S-10.7.

3. Bis(allyl thiourea) gadolinium(iii) chloride. $Gd(ATU)_2Cl_3$. Light yellow crystals, soluble in water and alcohol. Calc. for $C_8H_{16}N_4S_2GdCl_3$: C-19.4, H-3.2, N-11.3, S-12.9. Found: C-18.6, H-3.3, N-11.3, S-12.8.

4. Mono(diphenyl thiourea) gadolinium(iii) chloride. $Gd(DPTU)Cl_3$. Light pink crystals, soluble in water sparingly soluble in alcohol. Calc. for $C_{13}H_{12}N_2S$ $GdCl_3$: C-31.7, H-2.4, N-5.7, S-6.5, Gd-32.0, Cl-21.25. Found: C-30.8, H-2.5, N-5.8, S-6.5, Gd-31.8, Cl-21.3.

5. Tetrakis (diphenyl thiourea) dysprosium(iii) chloride. $Dy(DPTU)_4Cl_3$. Light yellow crystals, soluble in water but slightly soluble in alcohol. Calc. for $C_{52}H_{48}N_8S_4DyCl_3$: C-52.8, H-4.1, N-9.4, S-10.8. Found: C-54.3, H-4.3, N-9.2, S-10.7.

6. Hexa(o-tolyl thiourea) dysprosium(iii) chloride.

$Dy(TTU)_6Cl_3$. Light yellow crystals soluble in water, slightly soluble in alcohol. Calc. for $C_{48}H_{60}N_{12}S_6DyCl_3$: C-45.6, H-4.7, N-13.2, S-15.1. Found: C-46.1, H-5.1, N-13.4, S-15.4.

7. Bis(allyl thiourea) dysprosium(iii) chloride.

$Dy(ATU)_2Cl_3$. Light yellow crystals, highly soluble in water but slightly soluble in alcohol. Calc. for $C_8H_{16}N_4S_2DyCl_3$: C-19.2, H-3.2, N-11.2, S-12.8 Found: C-19.7, N-11.1, S-12.8, H-3.1.

8. Bis(naphthyl thiourea) dysprosium(iii) chloride.

$Dy(NTU)_2Cl_3$. Yellow crystals, soluble in water and alcohol. Calc. for $C_{22}H_{20}N_4S_2$: C-39.2, H-3.0, N-8.3, S-9.5. Found: C-39.8, H-3.1, N-8.3, S-9.6.

9. Bis(naphthyl thiourea) erbium(iii) chloride.

$Er(NTU)_2Cl_3$. Buff coloured product, soluble in water but slightly soluble in alcohol. Calc. for $C_{22}H_{20}N_4S_2ErCl_3$: C-38.8, H-2.9, N-8.2, S-9.4. Found: C-38.4, H-2.6, N-8.1, S-9.5.

10. Bis(allyl thiourea) erbium(iii) chloride.

$Er(ATU)_2Cl_3$. Amethyst crystals, highly soluble in water but very slightly soluble in alcohol. Calc. for $C_8H_{16}N_4S_2ErCl_3$: C-19.0, H-3.2, N-11.1, S-12.6. Found: C-18.6, H-3.5, N-10.9, S-12.6.

11. Mono(diphenyl thiourea) erbium(iii) chloride.

$Er(DPTU)Cl_3$. Buff coloured product, soluble in water but slightly soluble in alcohol. Calc. for $C_{13}H_{12}N_2S\ ErCl_3$: C-31.2, H-2.4, N-5.6, S-6.5. Found: C-30.8, H-2.5, N-5.6, S-6.5.

12. Bis(allyl thiourea) samarium(iii) chloride.

Sm(ATU)$_2$Cl$_3$. Light pink crystals, highly soluble in water but slightly soluble in alcohol. Calc. for $C_8H_{16}N_4S_2$ SmCl$_3$: C-19.6, H-3.2, N-11.4, S-13.1. Found: C-20.0, H-3.5, N-11.5, S-12.8.

13. Mono(diisopyropyl thiourea) samarium(iii) chloride.

Sm(DIPTU)Cl$_3$. Light yellow crystals, highly soluble in water but slightly soluble in alcohol. Calc. for $C_7H_{16}N_2S$ SmCl$_3$: C-20.1, H-5.6, N-7.2, S-8.2. Found: C-20.1, H-5.7, N-7.1, S-8.1.

14. Bis(naphthyl thiourea) samarium(iii) chloride.

Sm(NTU)Cl$_3$. Light yellow crystals, soluble in water but sparingly soluble in alcohol. Calc. for $C_{22}H_{20}N_4S_2$ SmCl$_3$: C-40.0, H-3.3, N-8.5, S-9.7. Found: C-38.8, H-3.1, N-8.3, S-9.6.

*
Abbreviations used:

diisopropyl thiourea-DIPTU, s-diphenylthiourea-DPTU, naphthyl thiourea -NTU, allyl thiourea - ATU, o-tolyl thiourea -TTU. C,H,N and S analyses were carried out by the Australian Microanalytical Service, Melbourne.

Infra red spectral data:

The infra red spectra of the complexes were recorded with a Perkin Elmer Infracord (model 521), using KBr pallets, and in the wavelength range of 5 to 15 μ. The details of

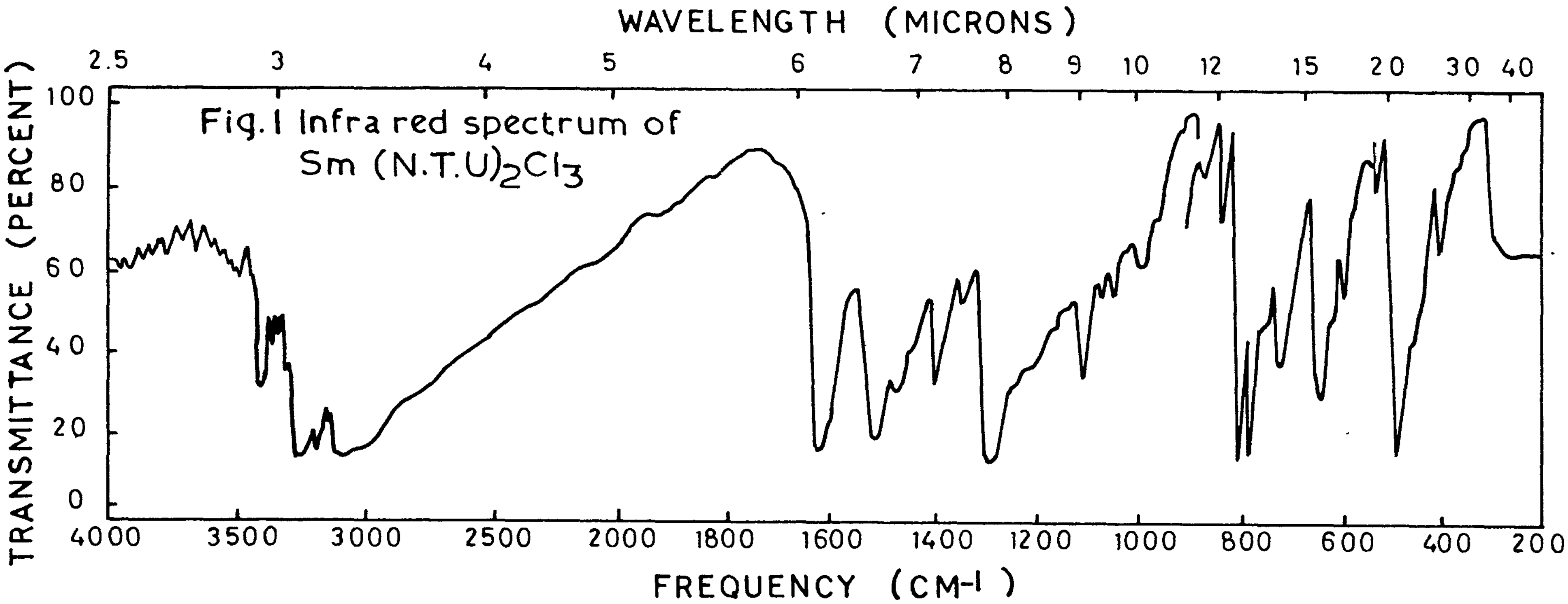


Fig. 1 Infra red spectrum of $Sm(N.T.U)_2Cl_3$

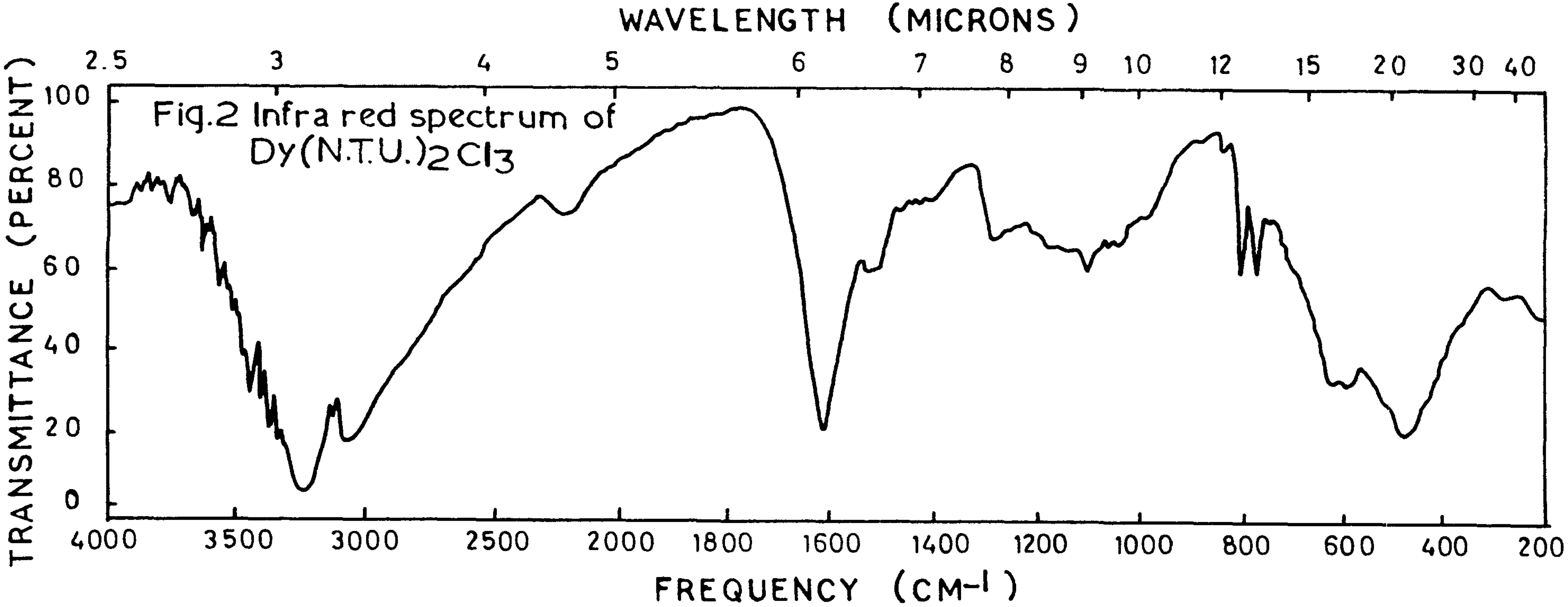
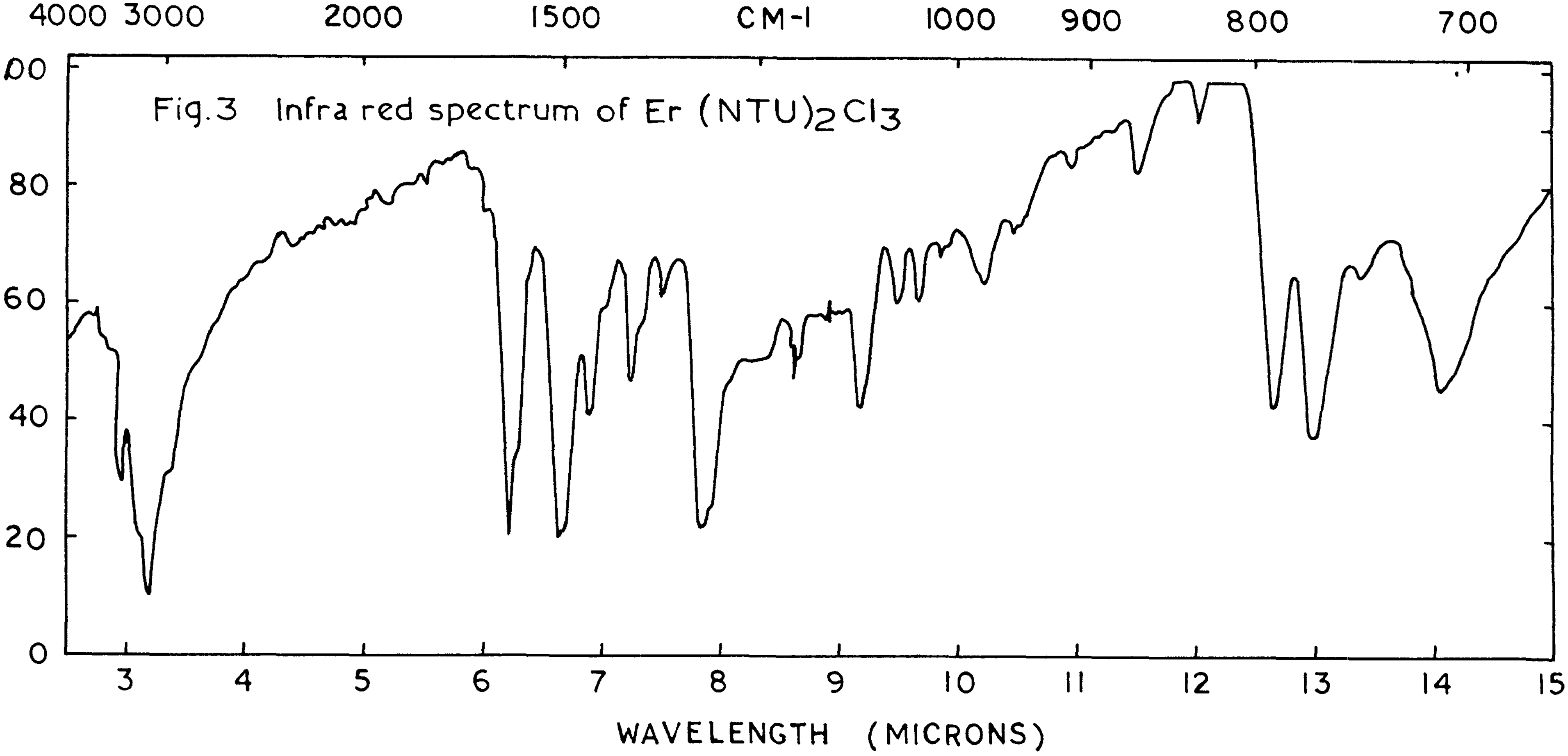


Fig.2 Infra red spectrum of $Dy(N.T.U.)_2Cl_3$

Fig. 3 Infra red spectrum of Er $(NTU)_2Cl_3$



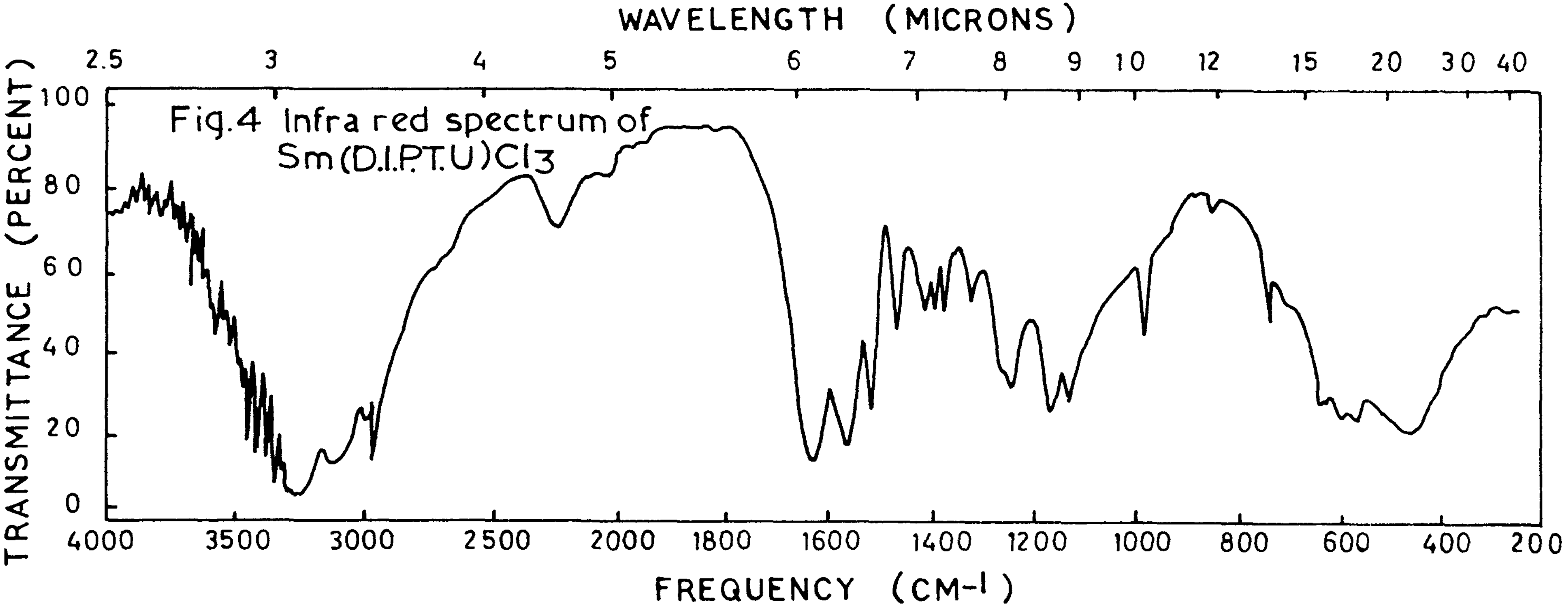


Fig.4 Infra red spectrum of $Sm(D.I.P.T.U)Cl_3$

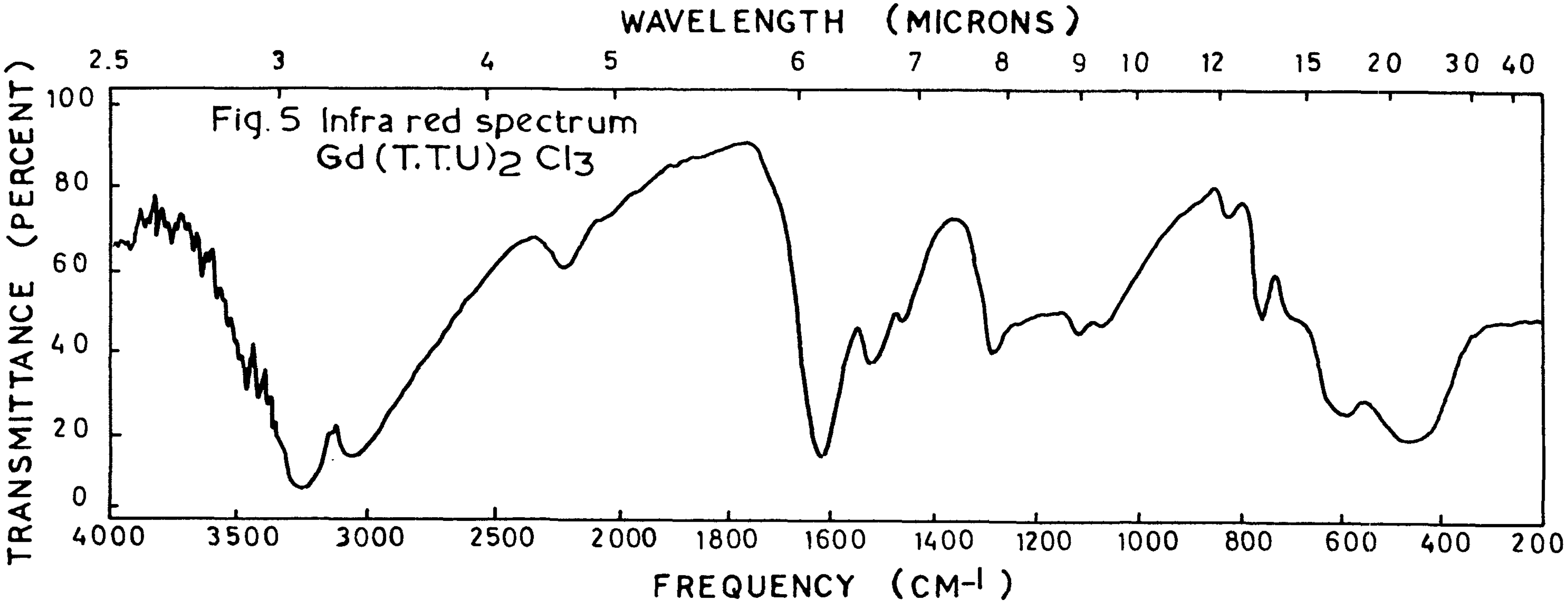


Fig. 5 Infra red spectrum $Gd(T.T.U)_2Cl_3$

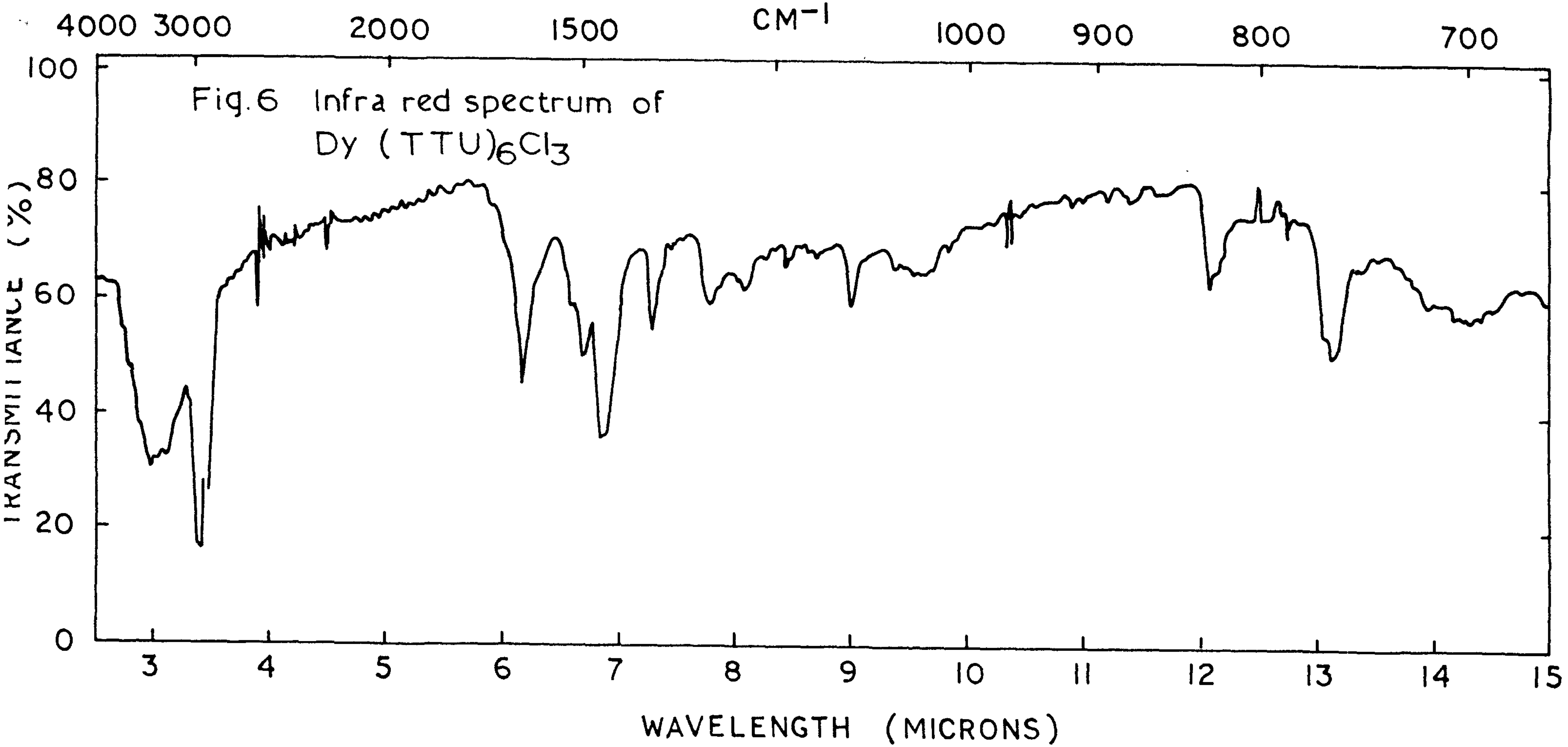


Fig.6 Infra red spectrum of Dy $(TTU)_6Cl_3$

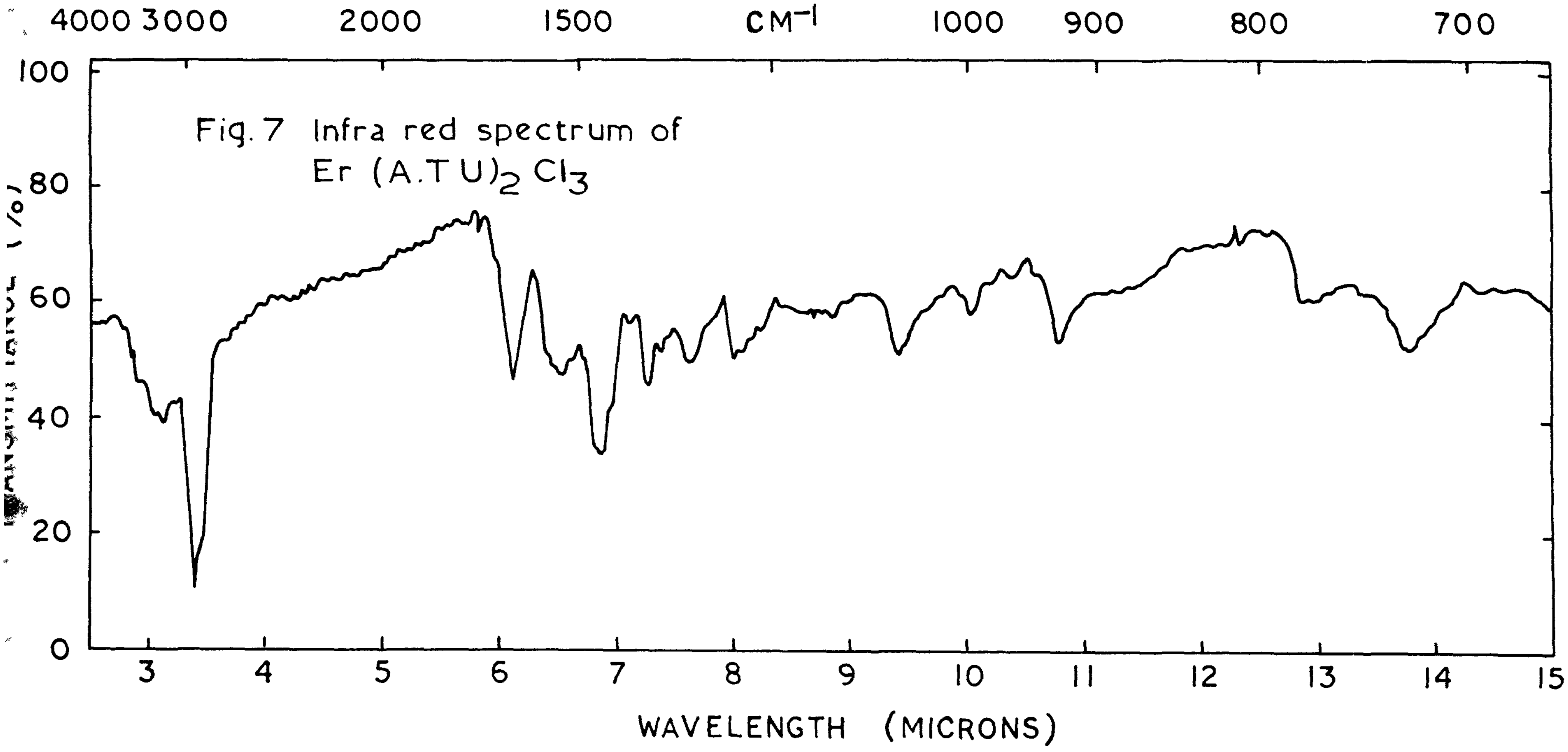


Fig. 7 Infra red spectrum of $Er(A.T.U)_2Cl_3$

the spectra of the complexes are as follows:

1. $Sm(NTU)_2Cl$: 610(s), 770(s), 790(s), 860(s), 950(m), 990(m), 1040(m), 1060(m), 1090(m), 1160(m), 1270(s), 1340(s), 1390(s), 1460(m), 1490(s), 1600(s), (Fig. 1).

2. $Dy(NTU)_2Cl_3$: 765(s), 790(s), 810(s), 1100(m), 1280(b&m), 1390(w), 1490(s), 1600(s), (Fig. 2).

3. $Er(NTU)_2Cl_3$: 770(s), 785(s), 855(s), 950(s), 1040(m), 1080(m), 1090(m), 1270(s), 1380(s), 1450(w), 1490(s), 1600(s), (Fig. 3).

4. $Sm(DIPTU)Cl_3$: 610(w), 705(s), 760(s), 860(s), 990(v.s), 1140(m), 1190(s), 1250(m), 1320(s), 1370(s), 1390(s), 1410(m), 1470(s), 1530(s), 1570(s), (Fig. 4).

5. $Gd(DIPTU)_4Cl_3$: 610(w), 705(m), 975(s), 1110(m), 1150(s), 1220(m), 1250(s), 1410(s), 1430(v.s), 1580(s).

6. $Gd(TTU)_2Cl_3$: 600-630(m&b), 770(s), 900(m), 1050(w), 1150(m), 1280(m), 1465(m), 1500(s), 1600(v.s), (Fig. 5).

7. $Dy(TTU)_6Cl_3$: 710(m&b), 765(s), 830(s), 1120(s), 1180(m), 1240(w), 1300(s), 1420(s), 1480(s), 1500(m), 1610(v.s). (Fig. 6).

8. $Gd(ATU)_2Cl_3$: 670(s), 730(s), 780(s), 930(v.s), 950(m), 970(s), 1000(s), 1070(s), 1140(m), 1250(s), 1320(s), 1360(s), 1410(m), 1430(s), 1540(m), 1630(v.s).

9. $Er(ATU)_2Cl_3$: 725(s), 860(m&b), 925(s), 950(m), 1060(s), 1250(b&m), 1320(b&m), 1380(s), 1460(s), 1540(m), 1640(s), (Fig. 7).

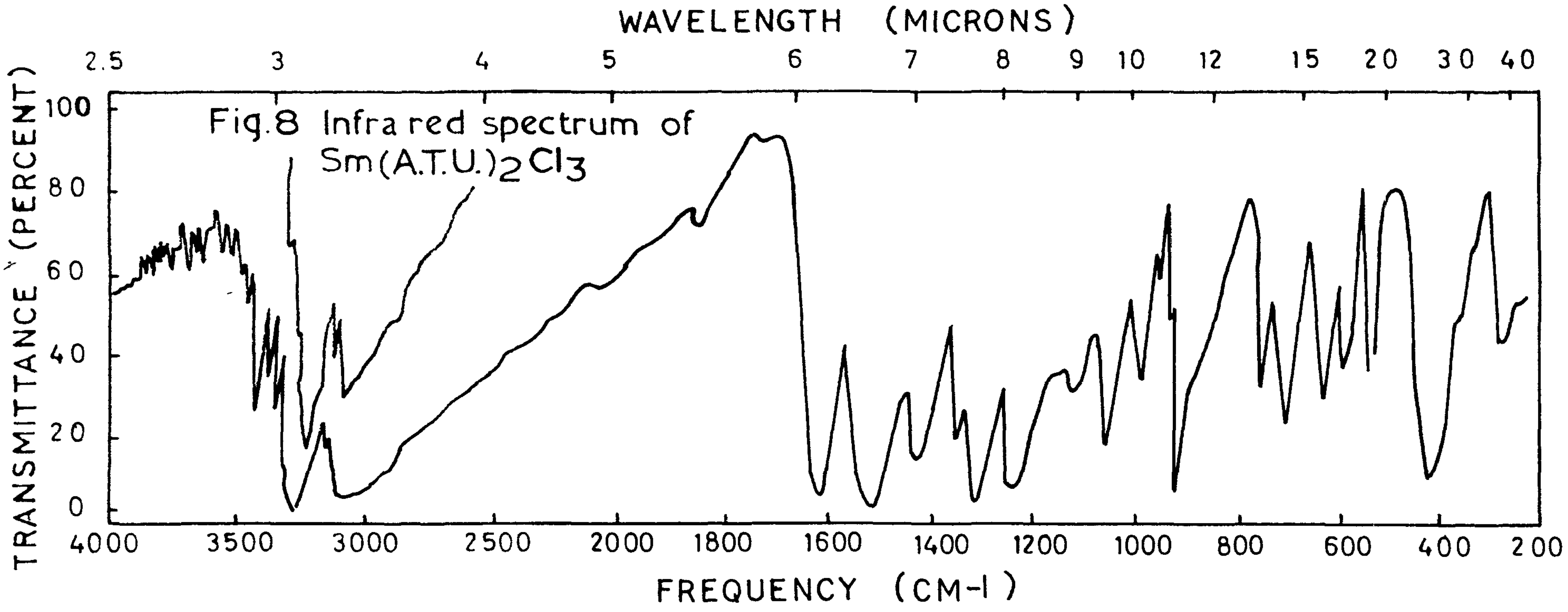


Fig.8 Infrared spectrum of $Sm(A.T.U.)_2Cl_3$

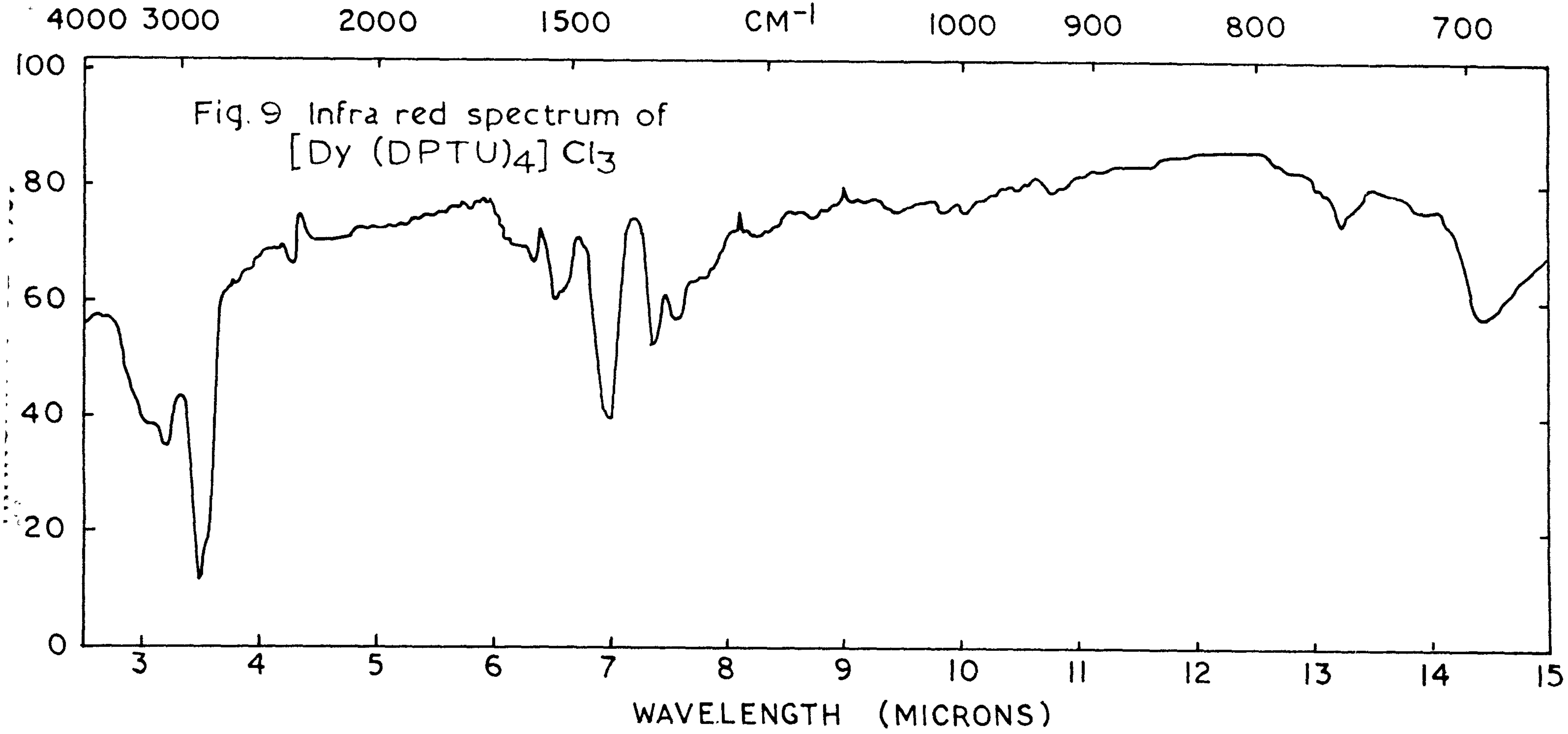


Fig. 9 Infra red spectrum of $[Dy(DPTU)_4]Cl_3$

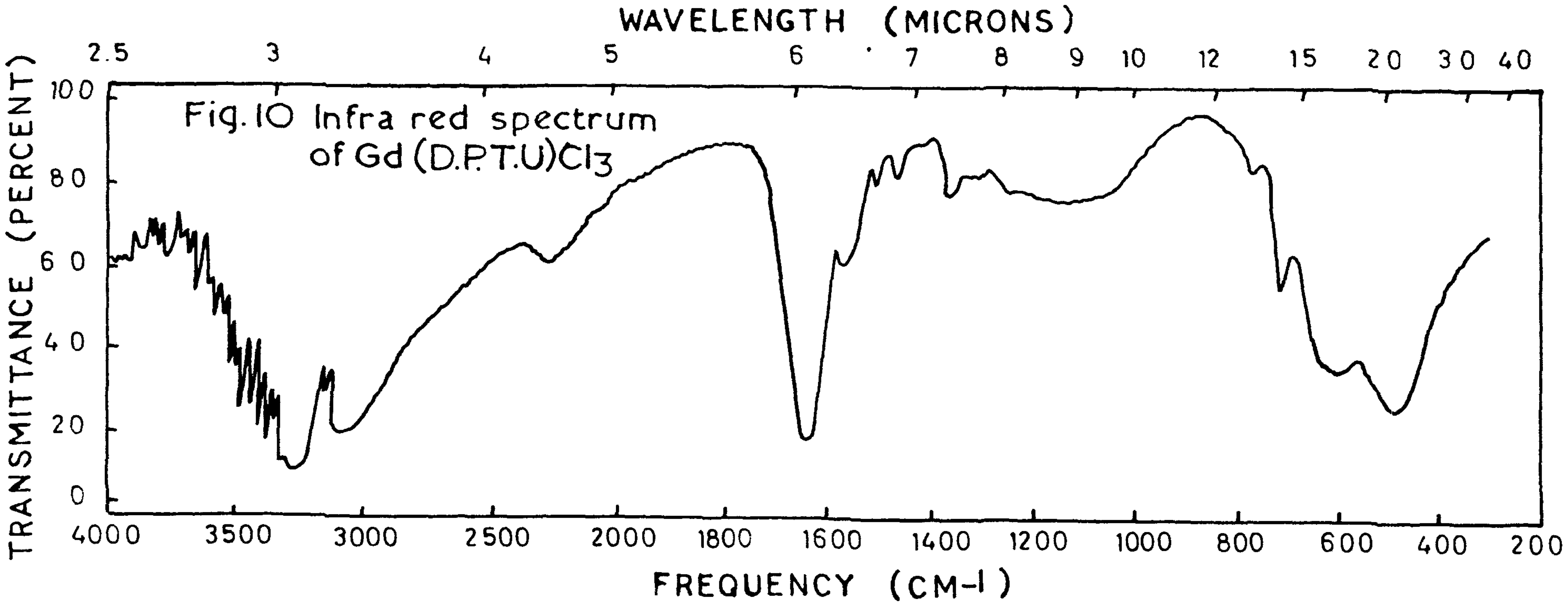


Fig. 10 Infra red spectrum of Gd (D.P.T.U)Cl_3

10. $Sm(ATU)_2Cl_3$: 630(s), 725(s), 780(s), 920(v.s), 950(w), 975(s), 1010(w), 1070(s), 1130(m), 1250(s), 1320(s),1360(s), 1410(m), 1440(s), 1540(s),1630(v.s), (Fig.8).

11. $Dy(ATU)_2Cl_3$: 690(s), 725(s), 850(m), 925(s), 1050(s),1250(b&m), 1320(m), 1380(s), 1450(s), 1540(m), 1630(s).

12. $Dy(DPTU)_4Cl_3$: 690(m), 760(s), 1320(m), 1360(s), 1440(s), 1510(m), 1570(m),(Fig.9).

13. $Gd(DPTU)Cl_3$: 720(s), 780(s), 1368(s), 1470(s), 1510(m), 1540(m), 1640(s),(Fig.10).

14. $Er(DPTU)Cl_3$: 760(s), 1360(s), 1370(m), 1460(s), 1510(m), 1570(m), 1650(s).

The details of the spectra of the substituted thioureas are given in Chapter II.

RESULTS AND DISCUSSION

Rare earth (III) ions react with substituted thioureas to give water soluble complexes. Amongst the substituted thioureas, diisopropyl thiourea forms 1:4 and 1:1 species with Gd^{3+} and Sm^{3+}, respectively, diphenyl thiourea: 1:1 and 1:4 with Gd^{3+}, Er^{3+}, and Dy^{3+}, respectively, allyl thiourea: 1:2 & 1:1 with Gd^{3+}, Dy^{3+}, Er^{3+} and Sm^{3+}, respectively, naphthyl thiourea: 1:2 with Dy^{3+}, Sm^{3+} and Er^{3+}, respectively, o-tolyl thiourea gives 1:2 and 1:6 species with Gd^{3+} and Dy^{3+}, respectively.

The results are summarised in table 1.

TABLE -1:

Rare earth complexes of substituted thioureas

Ligands*	Tripositive Rare Earth Chlorides**			
	Sm	Gd	Dy	Er
DIPTU	1:1 (light yellow)	1:4 (colourless)	-	-
ATU	1:1 (light pink)	1:2 (light yellow)	1:2 (light yellow)	1:2 (amethyst)
TTU	-	1:2 (light pink)	1:6 (light yellow)	-
NTU	1:2 (light yellow)	-	1:2 (yellow)	1:2 (buff)
DPTU	-	1:1 (light pink)	1:4 (bright yellow)	1:1 (buff)

* in order of decreasing nucleophility[13]

** in order of increasing atomic number and decreasing ionic radius

The complexes are generally colorless or light coloured and extremely hygroscopic. Attempts were made to prepare the entire series of rare earth complexes but with limited success and up-till now only a few complexes could be isolated in sufficiently pure form.

The formation of 1:1, 1:2, 1:4 and 1:6 species in rare earths may be explained on considering (a) order of nucleophility in the substituted thioureas which may be given[13] as DIPTU > ATU > TTU > NTU > DPTU (b) decrease in ionic radius with increase in atomic number (Sm^{3+} to Er^{3+}). With ligands having lower nucleophilic character, the formation of lower species is expected while with ligands having higher nucleophilic order, the formation of higher species is favoured. The contributions of nucleophility and ionic radius are very well exemplified by the results summarised in table 1 (typical examples; 1:1 species with Er^{3+}-DPTU and 1:4 species with Gd^{3+}-DIPTU). However, there are a few exceptions, e.g., the formation of 1:1 species with Sm^{3+} and DIPTU could not be explained on the basis of above considerations.

The infra red spectra of the substituted thioureas and the corresponding rare earth complexes were studied in the region 5 to 15 μ. The main features of the spectra of the complexes[14-17] in this region are:

(i) Ca.1600 cm^{-1}: The strong bands near this frequency in the substituted thioureas are attributed to NH_2 bending modes;[14,15] the bands remain unchanged on coordination. DIPTU and DPTU do not show any band at this frequency due to the absence of $-NH_2$ groups. The strong band at 1630 cm^{-1} in ATU may be assigned to C=C stretching and deformation vibrations of the allyl group, the bands remain uneffected on coordination.

(ii) Ca.1500 cm^{-1}: The N-H deformation and C-N antisymmetric stretching vibrations[14,15,17] observed near 1500 cm^{-1} in the substituted thioureas, in general, are shifted to higher frequencies to the extent of about 30 cm^{-1} in all cases.

(iii) Ca.750 cm^{-1}: The bands near 750 cm^{-1} are assigned to C-S stretching vibrations with a small contribution from C-N stretching modes.[17] They are shifted to lower frequencies by 20 to 30 cm^{-1} in all cases except DPTU where the bands are almost unshifted on coordination, and TTU where a small increase from 5 to 10 cm^{-1} is observed. The observed frequencies in this region (in the various complexes) are summarised in Table 2.

TABLE -2:

Infra red frequencies of substituted thioureas and their complexes in the region ca.750 cm^{-1}.

Metal	DIPTU	ATU	TTU	NTU	DPTU
	750(s)	740(s)	760(s)	775(s)	760(s)
Sm^{3+};	705(s)	725(s)	-	770(s)	-
Gd^{3+};	705(m)	730(s)	770(s)	-	760(s)
Dy^{3+};	-	725(s)	765(s)	765(s)	760(s)
Er^{3+};	-	725(s)	-	770(s)	760(s)

An interesting feature of the substituted thioureas is the decrease in NH deformation and C-N antisymmetric stretching vibrations(CN,NH) and increase in (C-S) stretching vibrations with decrease in nucleophility of the compounds. This shows the strengthening of C-S double bond and decrease in coordination ability of sulphur as we move from DIPTU to DPTU. The observed changes in the spectra of the complexes in these regions are summarised in Table 3.

TABLE -3:

Spectral shifts in the i.r. frequencies of substituted thioureas complexes in the regions of NH deformations, CN stretchings and C-S stretchings.

	(CN,NH) (cm^{-1})	(CS) (cm^{-1})
DIPTU	1570	705
ATU	1540	725
TTU	1500	765
NTU	1490	770
DPTU	1510	760

On the basis of the shifts in the region, 1500-1600 cm^{-1}, it seems certain that the coordination in the rare earth complexes does not take place through nitrogen. This conclusion is further strengthened by the fact that the lowering of C-S stretching frequencies occurred/on coordination (except TTU and DPTU complexes), indicating thereby a weakening of C=S and strengthening of C-N bonds on complex formation. However, on the basis of present information there is no conclusive evidence regarding the nature of bonding in rare earth-o-tolyl thiourea complexes.

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CHAPTER - VI:

INTERACTION OF SOME RARE EARTHS WITH 2, MERCAPTOBENZTHIAZOLE.

Interaction of Some Rare Earths With 2, Mercaptobenzthiazole

2, mercaptobenzthiazole has been used as an analytical reagent for the last so many years. This is due to its extensive tendency to form stable complexes with a large number of metal ions. A fairly long list of references is available in chemical literature regarding its interaction with various metals such as Cd, Bi, Hg(II), Ni, Zn, Tl, Cu(II), Pt(II & IV), Pd(II), Rh, Os, Ru etc.[1] However, a critical survey of the literature (1940-1960) would indicate that only a few references are available on the various aspects of the coordination chemistry of these complexes. This may probably due to nonavailability of the techniques such as i.r., and n.m.r. which later proved to be excellent tools for ascertaining the nature of the bonding in the complexes in general. The main interest in the chemistry of 2, mercaptobenzthiazole lies in its property of exhibiting in two tautomeric forms namely the thioketo and the thioenol. Studies of Bellamy[2] and others[3,4] on the infra red spectrum gave evidence for the existence of thioketo form (N-C=S) in the solid compound. However, the infra red spectral studies of the complexes with 2, mercaptobenzthiazole indicate the absence of band ca. 1500 cm^{-1} attributed to -N-C=S stretching vibrations. As regard to the nature of the complexes formed, they may be formed either by the replacement of a proton (from $\overset{N}{\diagdown}\underset{|}{C} - SH$ or $\overset{NH}{\diagdown}\underset{|}{C}{=}S$) by the metal or direct coordination with RH or a rare possibility of formation of a chelate structure involving both sulphur and nitrogen and, the last but not the least the formation of a polymeric structure through bridging involving one of the coordinating atoms. The exploration of this area of research has made the chemistry of this ligand very interesting. Wilson and Merchant[5] carried out a critical study of the reaction of this compound with platinum metals, and on the evidence obtained from i.r. and n.m.r. studies they suggested the presence of a coordination bond in which the metal is directly linked to RH where H is an imino proton.

The work described in the following pages mainly describes the results of the studies on the interaction of 2, mercaptobenzthiazole (MBT) with some trivalent rare earth chlorides such as Gd^{3+}, Dy^{3+}, Sm^{3+}, Pr^{3+}, Nd^{3+} Er^{3+} and Tm^{3+}. The complexes are synthesised and characterised on the basis of analytical data and an attempt has been made to ascertain the nature of bonding on the basis of i.r. studies.

Preparation of Rare Earths -2, Mercaptobenzthiazole Complexes.

To an aqueous solution of rare-earth chloride (about 1%) was added an excess of 2-mercaptobenzthiazole (M.B.T.) solution (1% in acetone) with constant stirring, the excess of the reagent added is indicated by the appearence of a yellow precipitate. The whole mixture was then heated over a water bath and evaporated slowly to just dryness, cooled and the cooled mass was then treated with about 20 ml. of water, warmed for about 20 mts and filtered. The light coloured filtrate was concentrated and then again treated with a slight excess of 2, mercaptobenzthiazole solution and the whole operation (evaporation to dryness and treating the dried mass with water) was repeated. The concentrated aqueous solution thus obtained, was kept for crystallisation. After 24-48 hours crystals of the complex appeared. They were separated from the main liquor and dried in a vacuum desiccator over CaO.

Analytical Data:

1. Mono(mercaptobenzthiazole) samarium(iii) chloride. Sm(M.B.T.)Cl_2. Light pink crystals, highly soluble in water sparingly soluble in ethanol. Calc. for $C_7H_4NS_2$ $SmCl_2$: C-21.7, H-1.0, N-3.6, S-16.5, Sm-38.8, Cl-18.3. Found: C-18.9, H-1.3, N-3.6, S-16.3, Sm-37.9, Cl-18.2.

2. Mono(mercaptobenzthiazole)gadolinium(iii) chloride. Gd(M.B.T.)Cl_2. Light yellow crystals, soluble in water sparingly soluble in ethanol. Calc. for $C_7H_4NS_2\ GdCl_2$: C-21.3, H-1.0, N-3.55, S-16.2, Gd-39.9, Cl-18.0. Found: C-20.7, H less than 1%, N-3.4, S-16.0, Gd-38.9, Cl-17.8.

3. Mono(mercaptobenzthiazole) erbium(iii) chloride. Er(M.B.T.)Cl_2. Light brown crystals, soluble in water. Calc. for $C_7H_4NS_2ErCl_2$: C-20.75, H-1.0, S-15.8, N-3.5, Er-41.3, Cl-17.6, Found: C-20.3, H-1.3, N-3.5, S-15.6, Er-39.6, Cl-17.5.

4. Mono(mercaptobenzthiazole) dysprosium(iii) chloride. Dy(M.B.T.)Cl_2. Pinkish yellow crystals, highly soluble in water. Calc. for $C_7H_4NS_2\ DyCl_2$: C-21.0, H-1.0, N-3.5, Cl-17.8, S-16.0, Dy-40.6. Found: C-19.8, H less than 1%, N-3.2, Cl-17.7, S-16.3, Dy-39.7.

5. Mono(mercaptobenzthiazole) thullium(iii) chloride. Tm(M.B.T.)Cl_2. Dirty pink crystals soluble in water. Calc. for $C_7H_4NS_2\ TmCl_2$: C-20.7, H-1.0, N-3.4, S-15.8. Found: C-20.3, H-1.6, N-3.4, S-15.6.

6. Mono(mercaptobenzthiazole) praseodymium(iii) chloride. Pr(M.B.T.)Cl_2. Light green crystals, highly soluble in water. Calc. for $C_7H_4NS_2\ PrCl_2$: C-22.2, H-1.05, N-3.7, S-16.9, Pr-37.2, Cl-18.8 Found: N-3.6, S-16.9, Pr-36.8, Cl-18.6.

7. Mono(mercaptobenzthiazole) neodymium(iii) chloride. Nd(M.B.T.)Cl_2. Light pink crystals, highly soluble in water. Calc. for $C_7H_4NS_2$ $NdCl_2$: N-3.7, S-16.5, Nd-37.8, Cl-18.6, Found: N-3.5, S-16.2, Nd-36.6, Cl-18.8.

C,H,N and S analyses were carried out by the Australian Microanalytical Service, Melbourne. Also, some of the samples were analysed at the microanalytical lab. A.M.U., Aligarh.

Chlorine was estimated gravimetrically as AgCl, and rare earths were estimated by heating the complex in an electric furnace (maintained at 800°C) and weighing the residue as rare earth trioxide.

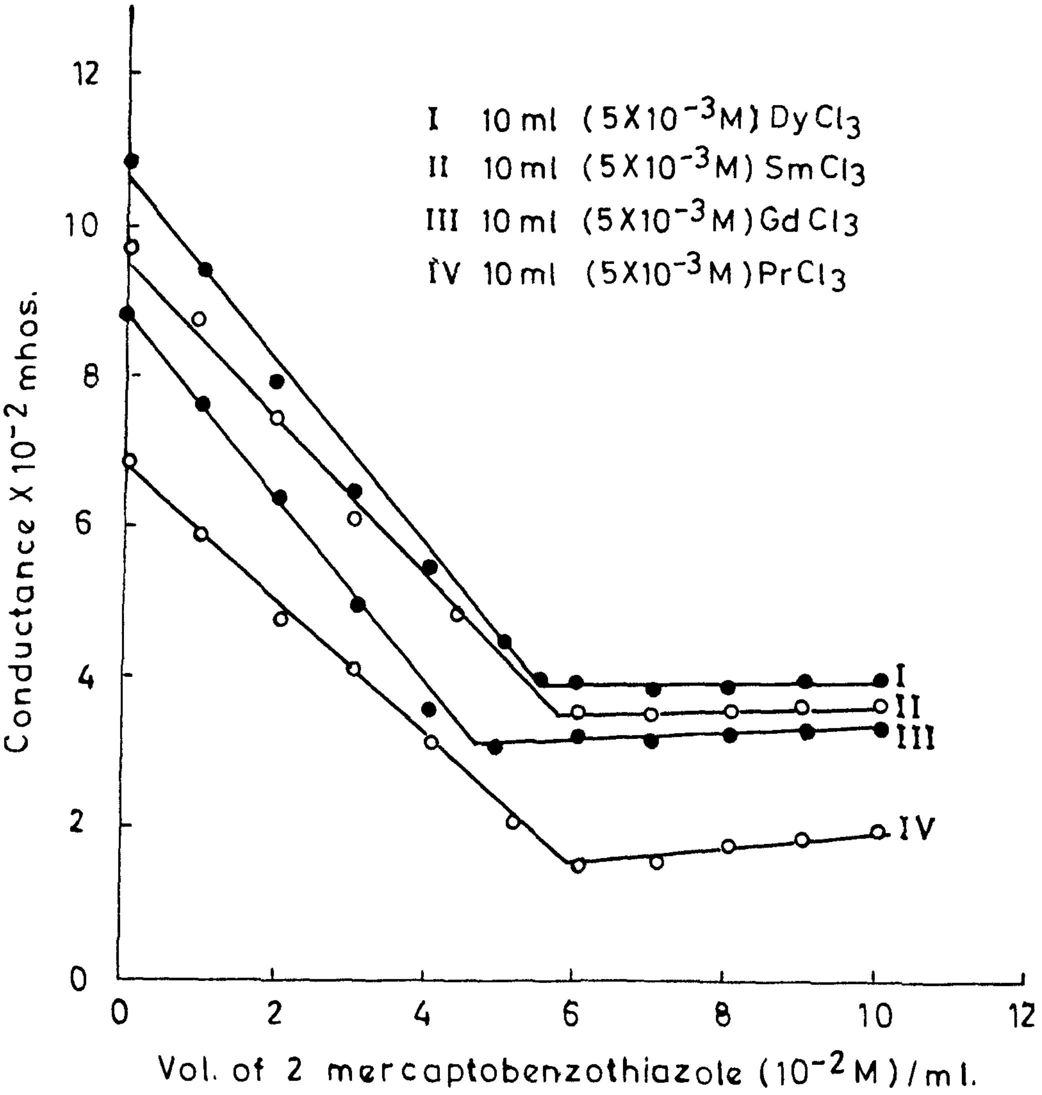


Fig. 1 Conductometric Titrations

Systems: Rare Earth (III) Chloride-2, Mercaptobenzothiozole

EXPERIMENTAL

Rare earth oxides (spectroscopically pure) were obtained from Jhonson and Matthey (London) and their trichlorides were prepared by dissolving in HCl. 2, mercaptobenzthiazole (Reagent grade) was a B.D.H. product and was purified and crystallised from AnalaR acetone.

Conductometric studies:

Conductometric titrations were performed with a Philips conductivity bridge (type PR9500), using a dip type cell (cell const. 1.52).

Solutions of rare earth trichlorides of varying concentrations were used and only direct titrations (R.E. in the cell) were carried out using alcoholic solution of 2, mercaptobenzthiazole as the titrant (typical curves fig.1).

Infra red spectra of the complexes:

The infra red spectra of the complexes were recorded (in the wave length range 3 to 16 µ) with a Perkin Elmer Infra red spectrometer, type 221 using standard KBr technique.

The infra red spectral data of the rare earths —— 2, mercaptobenzthiazole complexes are given as follows:

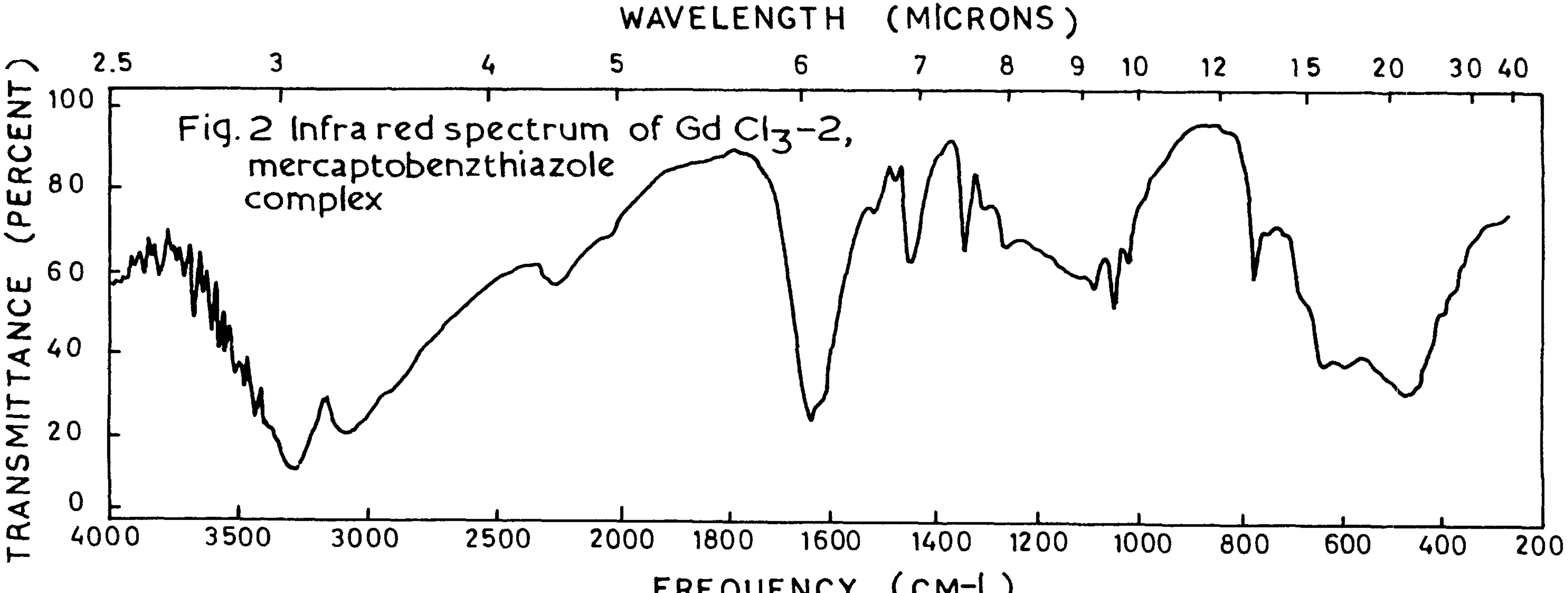


Fig. 2 Infrared spectrum of Gd Cl_3-2, mercaptobenzthiazole complex

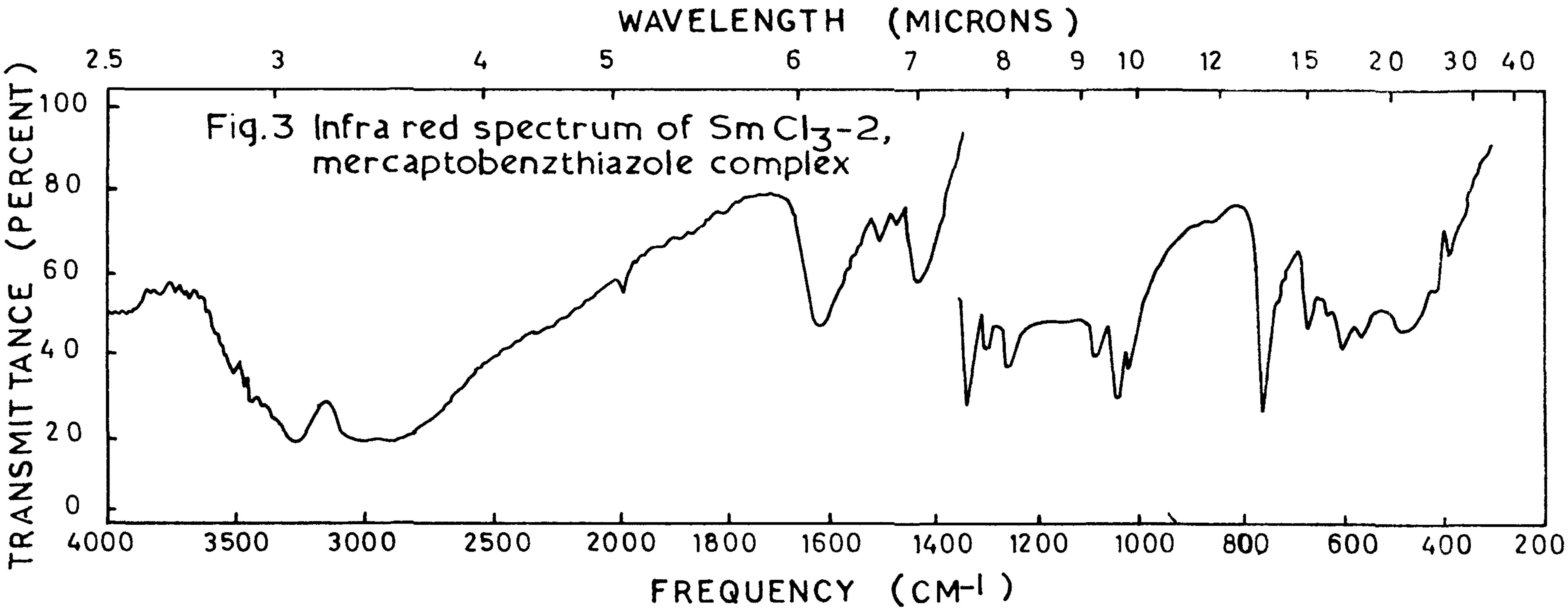


Fig.3 Infra red spectrum of $SmCl_3$-2, mercaptobenzthiazole complex

1. 2, mercaptobenzthiazole: 3100(s), 1600(m), 1500(s), 1460(m), 1420(s), 1310(s), 1270(m), 1240(m), 1120(m), 1080(s), 1030(s), 1010(s), 846(m), 745(s), 660(s).

2. Gd(M.B.T.)Cl$_2$: 3200(b&m), 1430(m), 1320(w), 1620(v.s), 660(m), 550(b&m). (Fig.2)

3. Sm(M.B.T.)Cl$_2$: 3200(b&m), 1600(m&b), 1480(m), 1450(w), 1430(s), 1320(v.s), 1290(s), 1245(m), 1080(m), 1035(s), 1020(m), 730(v.s), 670(s), 605(s), 580(m), (Fig.3)

4. Dy(M.B.T.)Cl$_2$: 3200(b&m), 3060(m&b), 1625(v.s), 1430(m), 1320(w), 630(m), 660(m), 540(m).

5. Pr(M.B.T.)Cl$_2$: 3200(b&m), 1605(v.s), 1430(w), 1320(w), 1060-1100(b&w), 560(b&m).

6. Nd(M.B.T.)Cl$_2$: 3200(m), 1610(s), 1430(w), 1325(w),1030(m), 1035(s), 1020(w), 560(m).

7. Tm(M.B.T.)Cl$_2$: 3200(m), 1620(s), 1430(w), 1330(m), 660(m), 560(m).

RESULTS AND DISCUSSION

Rare earth (III) ions form 1:1 complex species with 2, mercaptobenzthiazole: Sm^{3+}(light pink), Gd^{3+} (light yellow), Er^{3+}(light brown), Dy^{3+}(pinkish yellow), Tm^{3+}(dirty pink), Pr^{3+}(light green) and Nd^{3+} (light pink). The complexes are soluble in water but in general, slightly soluble in alcohol and other organic solvents.

The conductometric titrations were carried out by taking R.E.(III) chloride in the cell and using 2, mercaptobenzthiazole solution (in alcohol) as the titrant. The conductometric titration curves indicate sharp breaks at 1:1 molar ratio (typical curve fig.1).

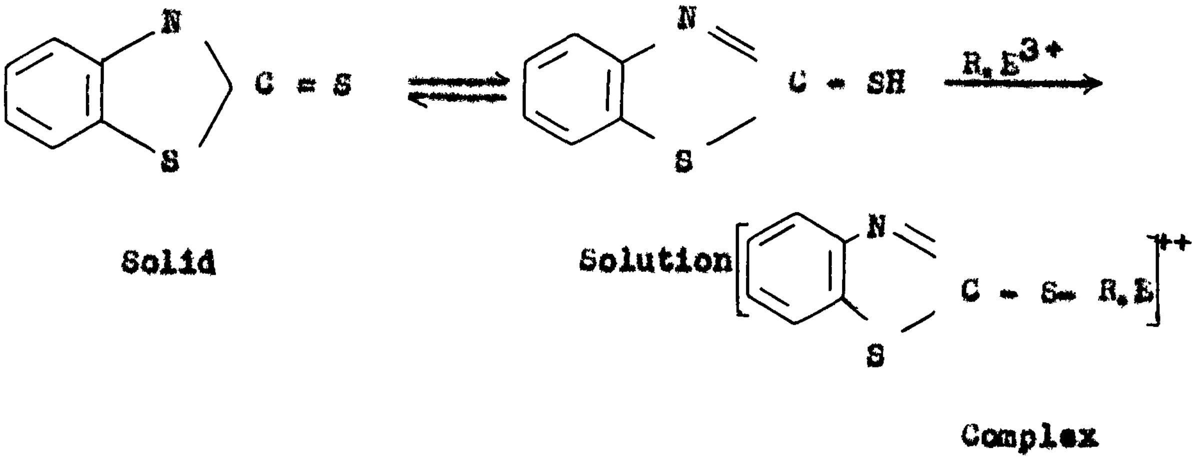
The results of chemical analysis indicate the formation of the complexes of the type ,R.E.(R') Cl$_2$ by the interaction of the ligand (R'H) with(R.E.)Cl$_3$, e.g., displacement of one hydrogen by the tripositive rare earth.

2- mercaptobenzthiazole is capable of exhibiting thioketol-thiol isomerism involving-NH-C=S and -N=C-SH groups. The infra red spectra studies were carried out to ascertain which hydrogen (-SH or -NH) has been replaced by the R.E. to give a simple salt like structure.

2, mercaptobenzthiazole shows a strong stretching vibration at 1500 cm^{-1} which corresponds to -NH-C=S indicating thereby the presence of thioketo group.[2] An examination of the i.r. spectra of the complexes indicates the absence of any strong band ca.1600 cm^{-1} showing thereby the structure has been changed probably from thioketo to thioenol form.

Although there are no other outstanding changes in the spectra of the complexes as compared to that of the ligand (R'H). But there are two changes which may be qualitatively correlated with the strengthening of C-N bond and weakening of C=S bond. (1) bands at 1460,1420 and 1310 cm^{-1} observed in the ligand and are assigned to -N-C=S symmetric and antisymmetric stretching vibrations with major contribution from C-N and N-H deformations, are slightly shifted to higher frequencies (10-20 cm^{-1}). The plausible explanation of this change may be the strengthening of C-N bond; (2) the band observed at 745 cm^{-1} in the ligand assigned to delocalised C=S stretching vibrations is not observed at this wave number in the complexes. This indicates (i) replacement of a proton by tripositive rare earth ion (ii) the formation of $d_{\pi}-d_{\pi}$ bond using d_{π} level of the acceptor atom (sulphur). This may be attributed to stabilisation of M-S bond resulting in the change of C-S stretching vibrations.

Despite the absence of a clear cut interpretation regarding the nature of bonding in these complexes, the results of infra red spectral studies can be summed up by the two foregoing conclusions: (i) evidence of strengthening of C=N bond and weakening of C=S bond (ii) little evidence of the elimination of imino proton by the R.E. ions. On the basis of available information, a possible course for the reaction may be depicted as:



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CHAPTER - VII:

STUDIES ON SULPHUR AND NITROGEN LIGATED COMPLEXES OF PALLADIUM(II).

Studies on Sulphur and Nitrogen Ligated Complexes of Palladium(II).

The coordination chemistry of palladium has been extensively investigated.[1] A major portion of the work carried out on Pd(II and IV) complexes deals with nitrogen containing ligands[2-6], and only a limited number of references are available on their complexes with sulphur containing ligands.[7-8] Amongst the references worth mentioning are those on the Pd(II) complexes of thiourea and thiocyanate. Spacu and Camboli[9,10] published a series of papers on the interaction of palladium(II) thiocyanate with heterocyclic amines and reported the preparation of the complexes of the type: $[Pd(am)_2(SCN)_2]$ $[Pd(am)_2](SCN)_2$, $[Pd(am)_4]$ $[Pd(SCN)_4]$, $[Pd(thiourea)_4\ Pd(SCN)_4]$ etc. On the basis of infra red studies, they concluded the presence of M-S bond in these complexes. Chatt and Coworkers[11,12,13] synthesised and studied the properties of a number of Pd(II) complexes with ligands containing tertiary arsine and phosphine coordinating groups. The stereochemistry of the compounds with sulphur and heavy atoms donors is based upon the formations of ligand π bonds obtained by the overlapping of a filled d orbital of palladium(II) and a vacant d orbital of the heavy atom e.g., S, P, As, etc., thus resulting in $d_\pi - d_\pi$ hybridisation.[14]

The kinetic studies on the substitution reactions of square planar metal complexes have been an area of extensive research for the last two decades, although with the advent of 'trans effect' by Chernyaev[15] in 1926 a large number of square planar complexes of Pt(II) were synthesised, principally by Russian chemists who also employed this effect in differentiating cis and trans isomers of the type Pt A_2X_2.[16-18] The main bulk of the recent work has, however, been carried out by Basolo, Pearson, Gray and others.[19,20] Their investigations are mainly devoted to the stereochemistry of square planar Pt(II) complexes including the study of the kinetics of Pd(II) square planar substitution reactions.

Basolo et al[21] carried out the kinetic studies on the mechanism of substitution reactions of Pt(II)-ammine with various nucleophiles such as thiourea, pyridine etc. According to the authors, the reactions studied fall in two categories: (i) those that are first order in the complex but zero order in the reactants and all of nearly the same rate; (ii) those that are first order in both the complex and the reactant and faster than those of the first category. In general, the reactants of the first category (i) are low in trans effect series whereas the category (ii) has a higher trans effect. A 'dissociation mechanism' has been proposed for these substitution reactions of 'square complexes'. In another paper, Basolo and coworkers[22] studied the substitution reactions of $[Pt(dien)X]^+$ and $[Pt(tripy)X]^+$ with pyridine and observed the relative reactivities of replaceable ligands following the order: $NO_3^- > Cl^- > Br^- > I^- > SCN^- > NO_2^-$, as observed in octahedral complexes of Co(III) except for an inversion in the reactivities of the halides. In the same publication, the studies on analogous Pd(II) complexes have also been described and it is found that $[Pd(dien)X]^+$ react 10^4 to 10^6 times faster than the corresponding Pt(II) complexes. Ni(II) complexes are again some what more reactive than Pd(II) complexes. Kinetic studies[23] are also reported of the alkyl and the aryl compounds of the Ni(II) group of the type $[MClR(PR'_3)_2]$ where M is: Ni(II), Pd(II) and Pt(II); R is: alkyl, aryl or hydrogen and R' = alkyl, with pyridine. The relative rates of attainment of equilibrium of trans$[MCl(o\text{-}tolyl)(PEt_3)_2]$, with pyridine are approximately $5x10^6$: 10^5:1 for Ni(II), Pd(II), and Pt(II) respectively. The effect on the rates of equiliberation of different groups undergoing replacement shows that trans labilising abilities of these ligands decrease as follows: $PMe_3 > PEt_3 \approx \overset{+}{H} > PPr_3 >$ Me - phenyl $\approx$ p-methoxy phenyl $\approx$ p-chlorophenyl > biphenyl > o-tolyl > mesityl $\approx Cl^-$. Both the electrostatic (polarisation) and π bonding theories of trans effect were applied to explain these results. It has also been found that solvent and/or reactant are involved in rate determining step. The paper also reports K_1 and K_2 values of a number of such reactions in ethyl alcohol, which are interrelated by the expression;

$$K_{obs} = K_1 + K_2[py]$$

Where K_{obs} is a pseudo-first order rate constant, K_1 is the first order rate constant for the solvent controlled reaction and K_2 is a second order rate constant for reactions with pyridine. Baddley and Basolo[24] pointed out the importance of steric factors in substitution reaction of metal complexes by illustrating the reaction of $[Pd(Et_4dien)Cl]^+$ with various reagents and showed that except OH^- the rate of reaction does not depend on L, the reagent. This unique behaviour of OH^- was attributed to rapid acid-base equilibrium, forming the more reactive aminod species $Pd(Et_4dien-H)Cl$ -an S_NI CB mechanism.

The work described in this chapter deals with:

The preparations of some palladium(II) complexes with sulphur and nitrogen containing ligands such as those with substituted thioureas and thiourea-heterocyclic amines.

ii) The determination of the composition of the complexes by spectrophotometry.

iii) The infra red spectral studies to ascertain the nature of bonding in these complexes.

iv) The kinetic studies on the interaction of heterocyclic amines with tetrakis(thiourea) *palladium(II)* chloride, using spectrophotometric and potentiometric methods. The kinetic studies permit: (a) a comparison of the rates of reaction of amines with $Pd(tu)_4Cl_2$ (b) a detailed information regarding the mechanism of substitution of pyridine with $Pd(tu)_4Cl_2$ and (c) an estimation of trans effects of various amines e.g.,pyridine picolines, lutidines, o-phenanthroline and 2,2' dipyridyl.

EXPERIMENTAL

Reagents: Palladium(II) chloride (Jhonson and Matthey product) was used for the preparation of palladium(II) complexes. Thiourea, diphenyl thiourea, naphthyl thiourea diisopropyl thiourea and o-tolyl thiourea were all 'Light ' products. The compounds were purified by recrystallisation either from water (in case of thiourea) or from acetone.

Pyridine, o-phenanthroline and 2,2'dipyridyl were all Analytical grade B.D.H. products. 2-, 3- and 4 picolines, 2,4 and 2,6 lutudines were all reagent grade B.D.H. products and were purified by redistillation. The standard solution of the amines were prepared by titrating pH metrically against standard HNO_3, using calomel and glass electrodes.

Preparation of the Complexes

1. Tetrakis(thiourea)palladium(II) chloride:

About 50 ml solution of 1% palladium(II) chloride in HCl was taken in an Erlenmeyer flask and about 5g. of solid thiourea was added to it, the resulting mixture was heated over a water bath till all the thiourea was dissolved. Any insoluble residue left was filtered out, the filtrate was diluted by adding 50 ml. of water and evaporated to one half of its volume. The resulting solution was kept for crystallisation and after about 72 hours, red crystals of the complex appeared, separated from the main liquor, washed with acetone and dried in a desiccator over CaO.

Tetrakis(thiourea)palladium(II)chloride:

$Pd(tu)_4Cl_2$. Red crystals, soluble in water but insoluble in acetone and other organic solvents. Anal. Calc. for $C_4H_{16}N_8S_4$ $PdCl_2$: C-9.9, H-3.3, N-23.1, S-26.6; Found: C-10.1, H-3.3, N-23.2, S-26.5.

2. Palladium(II)-substituted thiourea complexes:

An excess of 1% Pd(II) chloride solution (in HCl) was added to a 2% substituted thiourea solution in acetone contained in an Erlenmeyer flask with vigorous shaking. An orange or red precipitate (depending upon the substituted thiourea) settled down at the bottom of the flask. The contents of the flask were heated over a water bath for about 15 minutes and the mixture was then allowed to stand for about one hour. The clear supernatant liquid was separated from the main bulk of the precipitate by decantation. The precipitate was then treated with about 25 ml of 50% ethanol and warmed slightly, allowed to stand for about 15 minutes and centrifuged. During centrifugation, the precipitate was washed 2-3 times with small aliquots of 25% ethanol, the precipitate was then dissolved in acetone, concentrated by heating over a water bath and kept for crystallisation. After 2-3 hours, dark coloured crystals of the complex were appeared, separated from the main liquor and dried in a vacuum desiccator and recrystallised from acetone.

The preparation of palladium(II) chloride complexes with naphthyl thiourea (NTU), s-diphenylthiourea (DPTU) o-tolyl thiourea (TTU) and diisopropyl thiourea (DIPTU) were carried out by the above method. However, all attempts to prepare corresponding allyl thiourea (ATU) complex failed due to the formation of an oily mass which was difficult to be dried.

Analytical Data:

i) Tris(naphthyl thiourea)mono chloro Pd(II)chloride. $[Pd(NTU)_3Cl]Cl$. Dark orange crystals, insoluble in water but soluble in organic solvents, m.p. 190°C. Calc. for $C_{33}H_{30}N_6S_3$ $PdCl_2$: C-50.5, H-3.8, N-10.7, S-12.2; Found: C-49.8, H-4.1, N-10.4, S-11.3; Cl (ionisable)-Calc: 4.5, Found: 4.1.

ii) Tris(diphenyl thiourea)monochloro Pd(II) chloride. $[Pd(DPTU)_3Cl]Cl$. Dark orange crystals, insoluble in water but soluble in organic solvents, m.p. 160°C. Calc. for $C_{39}H_{36}N_6S_3PdCl_2$: C-55.0, H-4.2, N-9.9, S-11.3; Found: C-54.6, H-4.3, N-10.1, S-11.3; Cl (ionisable)- Calc: 4.1, Found: 3.6.

iii) Tris(o-tolyl thiourea)monochloro Pd(II) chloride.
$[Pd(TTU)_3Cl]Cl$. Brownish red crystals, insoluble in water but soluble in organic solvents, m.p. 86°C. Calc. for $C_{24}H_{30}N_6S_3PdCl_2$: C-41.1, H-4.4, N-12.4, S-13.7; Found: C-39.6, H-5.2, N-12.1, S-11.8; Cl (ionisable)-Calc: 5.2, Found: 4.7.

iv) Tris(di-isopropyl thiourea) monochloro Pd(II) chloride.
$[Pd(DIPTU)_3Cl]Cl$. Orange crystals, soluble in organic solvents, m.p. 170°C. Calc. for $C_{21}H_{48}N_6S_3$ $PdCl_2$: C-38.3, H-7.3, N-12.7, S-14.6; Found: C-37.75, H-7.5, N-12.4, S-14.4 Cl (ionisable)-Calc.: 5.4, Found: 5.2.

The ionizable Cl^- ion was estimated by dissolving the complex in absolute alcohol and precipitating it as AgCl with $AgNO_3$ solution. The precipitate was filtered, washed several times with dil. HNO_3 and weighed. The concentrarion of Cl^- estimated was, however, found to be considerably lower than the theoretical value.

3. Bis(thiourea) bis(pyridine) Pd(II) chloride:

About 10 ml. of pyridine (AnalaR) was added dropwise to an aqueous solution of tetrakis(tu)Pd(II) chloride (50 ml of $1x10^{-1}M$), with constant stirring. The resulting solution was heated over a water bath for about one hour and the concentrated dark coloured solution so obtained was kept for crystallisation. After about 24 hours, light brown crystals of the complex were appeared, separated from the main liquor, washed with acetone and dried in a vacuum desiccator over CaO.

Bis(thiourea) bis(pyridine) palladium(II) chloride.
$[Pd(tu)_2(py)_2]Cl_2$. Brown crystals, soluble in water but insoluble in alcohol and acetone. Anal. Calc. for $C_{12}H_{18}N_6S_2PdCl_2$: C-29.5, H-3.7, N-17.2, S-13.1; Found: C-28.7, H-3.8, N-17.4, S-13.2.

4. Bis(thiourea) mono(o-phen)Pd(II) chloride:

To an aqueous solution of $Pd(tu)_4Cl_2$(50 ml of $1x10^{-1}M$) was added 50 ml. of o-phenanthroline (2%) solution in ethanol, the whole mixture was heated over a water bath for about 45 mts. and then filtered to eliminate any insoluble residue. The filtrate was allowed to stand for about 48 hours when orange crystals of the complex appeared, separated and soak dried with a filter paper and kept in a vacuum desiccator over CaO.

Bis(thiourea)mono(o-phen)palladium(II) chloride.
$[Pd(tu)_2(o\text{-}phen)]Cl_2$. Orange crystals, soluble in water, slightly soluble in alcohol and acetone. Anal. Calc. for $C_{14}H_{16}N_6S_2PdCl_2$: C-33.0, H-3.1, N-16.5, S-12.6; Found: C-32.3, H-4.3, N-15.8, S-12.5.

5. The preparation of bis(thiourea)mono(dipyridyl) palladium(II) chloride was carried out in the same manner as described in case of o-phenanthroline complex.

Bis(thiourea) mono(dipyridyl) palladium(II) chloride. $[Pd(tu)_2(dipy)]Cl_2$. Pink crystals, soluble in water, insoluble in absolute alcohol and acetone. Anal. Calc. for $C_{12}H_{16}N_6S_2PdCl_2$: C-29.7, H-3.3, N-17.3, S-13.2; Found: C-30.8, H-3.5, N-17.3, S-13.1.

<u>Spectrophotometric measurements:</u>

The spectrophotometric studies were carried out by using a Bausch and Lomb Spectronic (20) transistorised spectrophotometer and 1 cm. diameter cuvettes.

The selection of the wave lengths was made by plotting the spectra in the region 350-625 m μ (Vosburg and Cooper's method). The composition of the complexes was determined by applying Job's method of continuous variation and also by the method involving the expression[25]

$$\text{Log}\,\frac{A_a - A_o}{A_\alpha - A_a} = \log K_f + n \log \left[X^{-\nu}\right] \quad \text{———} \quad (1)$$

for an equilibrium mixture involving two complexes

$$\left[Pd(L)_4\right]^{2+} + nX \underset{K_f}{\rightleftharpoons} \left[Pd(L)_4X_n\right]^{2-n\nu}$$

where A_o = absorbancy of the complex, $Pd(L)_4$, containing no X^-

A_a = absorbancy of the complex containing $M(L)_4X^{2-}$ at a time t, A = absorbancy of the complex containing sufficient X^- to convert all $[Pd(L)_4]^{2+}$ to $[Pd(L)_4X_n]^{2-n\nu}$.

The plot of log $\frac{A_a - A_o}{A_\infty - A_a}$ versus log $X^{-\nu}$ has a slope equal to n. The value of K_f can be calculated from eqn. (1).

Kinetic measurements:

(a) Spectrophotometric method:

The kinetic studies on the interactions of heterocyclic amines with tetrakis(thiourea) palladium(II) chloride were carried out spectrophotometrically. The rate const K in such cases is given by the expression[26]:

$$K_{obs} = \frac{2.303}{t} \log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$$

where K_{obs} is the observed first order rate constant

$(O.D)_\infty$ - is the maximum absorbance value for the system

$(O.D.)_t$ - is the absorbance value at a time t

$(O.D.)_o$ - is the initial absorbance value

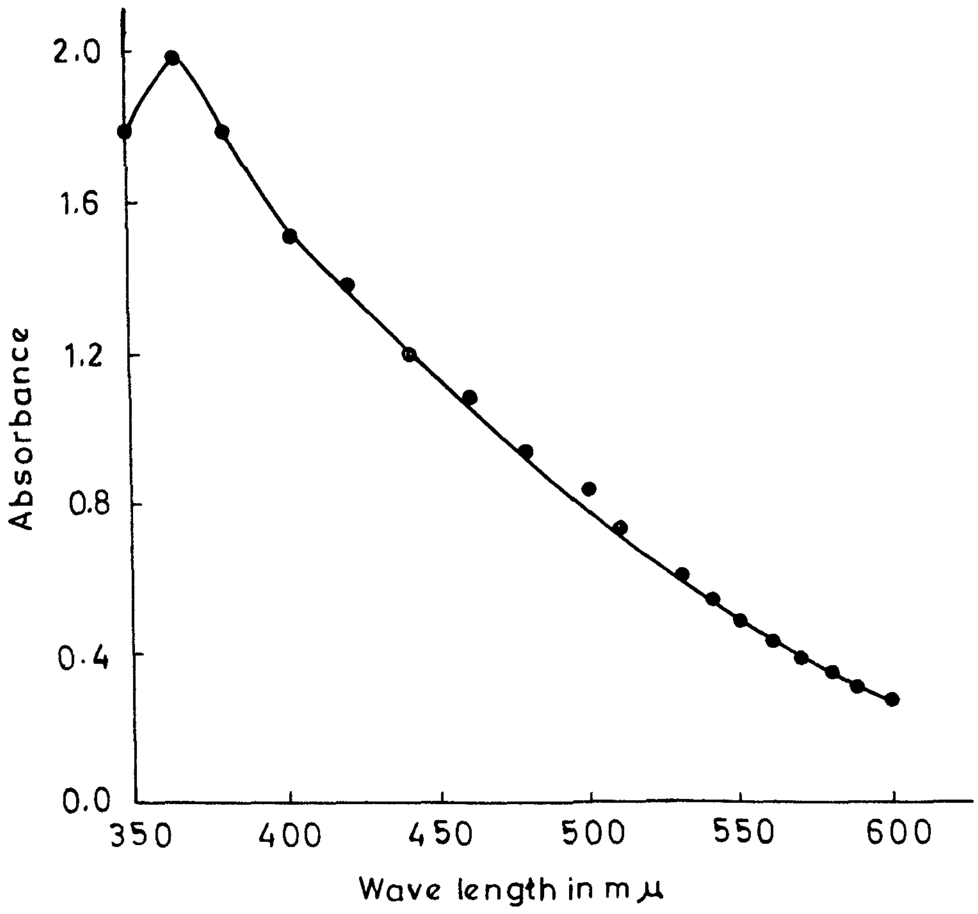


Fig. 1 Visible Spectrum Of The Complex, $Pd(tu)_4Cl_2$

The λ max of the complex, $[Pd(tu)_4]Cl_2$, was observed at 360 m u (Fig.1). In the kinetic studies carried out for the systems: $[Pd(tu)_4]Cl_2$ + L (where L = pyridine, 2,3, and 4 picolines, 2,4 and 2,6 lutidines, 2,2' dipyridyl and o-phenanthroline); the selection of the wavelength was made at 600 m μ where thiourea complex and the substituted amine complex have vast difference in absorbancies, the latter absorbing more strongly. The absorbance of the pyridine complex (A_∞) was obtained by keeping the mixture overnight and measuring the absorption until a reasonably constant value was obtained. In case of 2,4 and 2,6 lutidines, it was found that the solutions were subjected to precipitation immediately after achieving maximum absorbance. The spectrophotometric data for the various systems are given in tables 2A to 5E (vide Fig.2(a) to 5(e)) and the K_{obs} values are summarised in tables 6A and 6B.

(b) Potentiometric method.

The reaction kinetics of the substitution reactions involving tetrakis(thiourea) palladium (II) chloride and heterocyclic amines were also studied potentiometrically. The theoretical aspects and experimental verification of this method have already been discussed while dealing with the kinetics of the interactions of heterocyclic amines with tris(thiourea) copper(I) iodide (vide chapter III). In brief, the potentiometric method is based upon the fact that there could exist a linear relationship between the concentration of thiourea and the e.m.f., involving $Ag-Ag_2S$ as an indicator electrode at the reaction mixture's pH (~8). Taking advantage of this characteristic of $Ag-Ag_2S$ electrode, the first order rate reaction was determined by plotting $\log \frac{E_t}{E_\infty - E_t}$ vs. t, where E_∞ and E_t are respectively, the e.m.f. values at equilibrium and at a time, t. The method was applied for the systems: $[Pd(tu)_4]Cl_2$ + py, $[Pd(tu)_4]Cl_2$ + picolines (2,3 and 4), $[Pd(tu)_4]Cl_2$ + lutidines (2,4 and 2,6) $[Pd(tu)_4]Cl_2$ + dipy and $[Pd(tu)_4]Cl_2$ + o-phen. The potentiometric data for the various systems are given in tables 8A to 15D.

The plots of $\log \frac{E_t}{E_\infty - E_t}$ vs. t, were found to be linear (fig.8A to 15D), the K_{obs} values were obtained by multiplying 2.3 times the slopes of the linear plots. The K_{obs} values are summarised in table 16A.

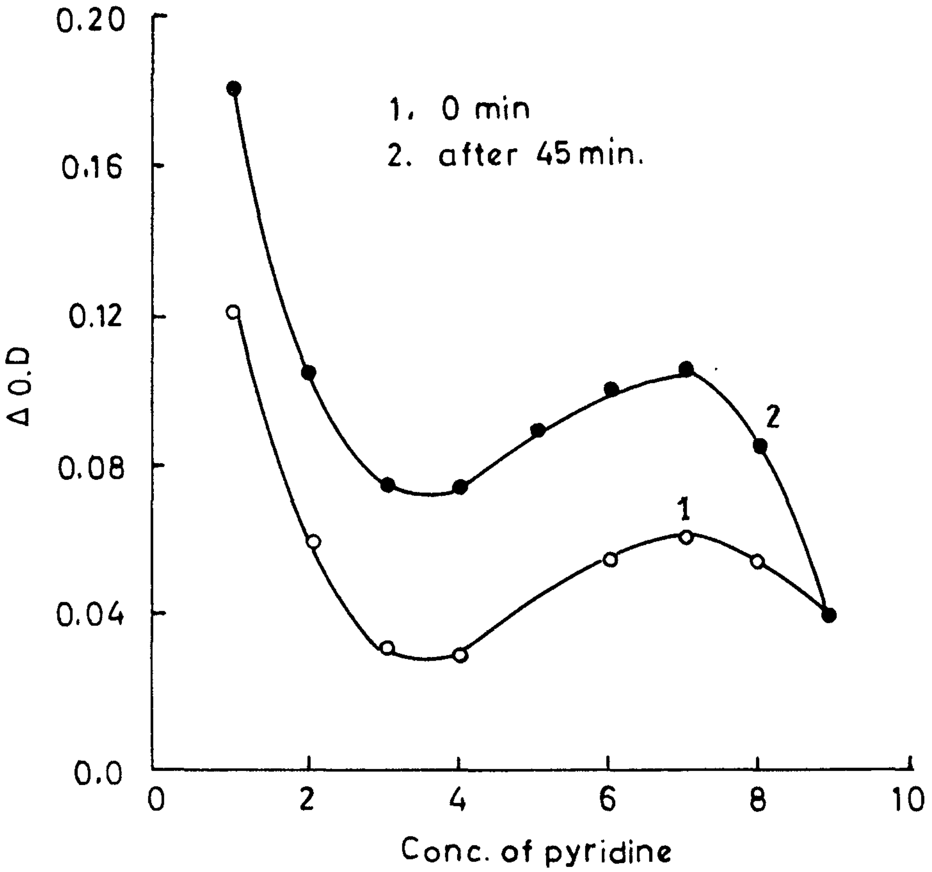


Fig. 1a Job's Method Of Continuous Variation

$\frac{M}{1000}$ Complex + $\frac{M}{1000}$ py at 600 mμ

$[Pd\ tu_4]Cl_2 + 2\,py \rightarrow [Pd(tu_2\,py_2)]Cl_2 + 2\,tu$

(Vide table 1a)

T A B L E -1A:

Absorbance data of the Job's method of continuous variation as applied to the system: $[Pd(tu)_4]Cl_2$ + pyridine ,

Conc. of the complex $[Pd(tu)_4]Cl_2$ = $1x10^{-3}M$

Conc. of the pyridine = $1x10^{-3}M$

Conc. of KCl = $1x10^{-1}M$

Wave length selected = 600 m μ

Vol.of the complex (in ml.)	Vol.of the pyridine (in ml.)	O.D.* $(A_2)_o$	O.D. $(A_2)_t$	**Vol.of the complex	Vol.of H_2O	O.D. A_1	$(A_2)_o$- A_1	$(A_2)_t$- A_1
1	9	0.065	0.08	1	9	0.025	0.040	0.055
2	8	.085	.115	2	8	.030	.055	.085
3	7	.10	.140	3	7	.040	.06	.10
4	6	.10	.140	4	6	.045	.055	.095
5	5	.095	.140	5	5	.05	.045	.090
6	4	.09	.135	6	4	.06	.03	.075
7	3	.10	.140	7	3	.065	.035	.075
8	2	.135	.180	8	2	.075	.060	.105
9	1	.20	.260	9	1	.08	.120	.18

* absorbance just after mixing the solutions

** absorbance after 45 mts.

(Vide Fig.1A)

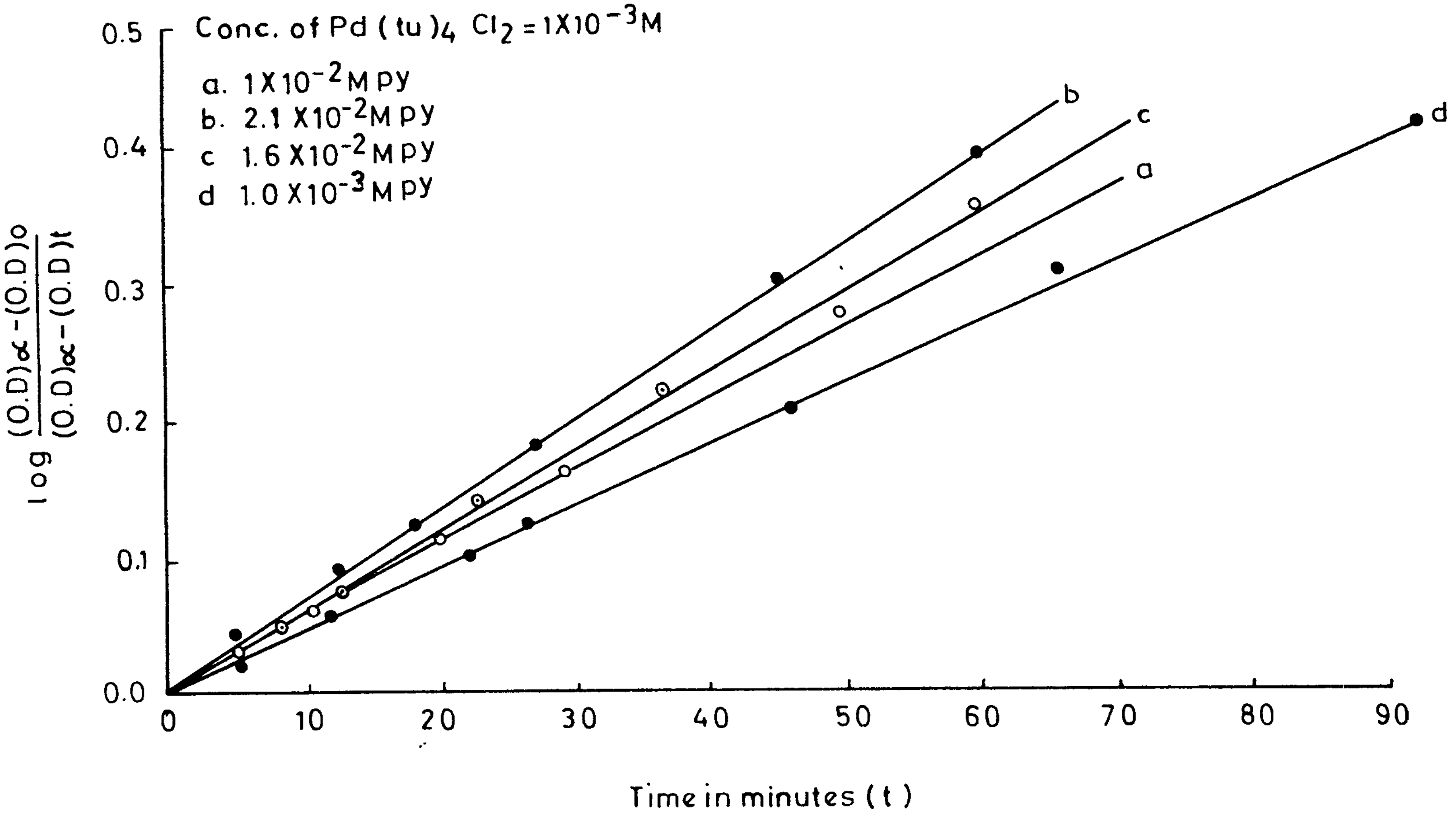


Fig 2 Plot Between Log $\frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$ and Time(t)

(Vide table 2A to 2D)

Kinetic Data (Spectrophotometric method)

The first order rate was determined by plotting log $\frac{(O.D)_{\infty} - (O.D)_{o}}{(O.D)_{\infty} - (O.D)_{t}}$ versus t, where $(O.D)_{\infty}$, $(O.D)_{o}$ and $(O.D)_{t}$ are defined earlier. Values of rate constants were calculated from 2.30 times the slopes of the linear rate plots. In the following tables are given the values of the terms: t, O.D., log $\frac{(O.D)_{\infty} - (O.D)_{o}}{(O.D)_{\infty} - (O.D)_{t}}$ for the various systems.

TABLE -2A.

Spectrophotometric data for the first order rate law.

System: $Pd(tu)_4Cl_2$ + py.

Conc. of the complex = $1x10^{-3}$M
Conc. of pyridine = $1x10^{-2}$M
Conc. of KCl = $1x10^{-1}$M
Temp. = 20°C
$(O.D)_{\infty}$ = 0.75
$(O.D)_{o}$ = 0.18

Time in minutes	O.D.	log $\frac{(O.D)_{\infty} - (O.D)_{o}}{(O.D)_{\infty} - (O.D)_{t}}$	$K_{obs.}$ min.$^{-1}$
5	0.22	0.0334	
10	.25	.0569	
15	.39	.0934	
20	.31	.1139	$1.15x10^{-2}$
30	.35	.1538	
45	.40	.2095	
50	.44	.2672	
70	.50	.3579	

(Vide Fig.2a)

T A B L E -2B:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

Conc. of the complex = $1x10^{-3}M$

Conc. of the pyridine = $2.1x10^{-2}M$

Conc. of KCl = $1x10^{-1}M$

Temp. = $20^{o}C$

$(O.D)_\infty$ = 0.80

$(O.D)_o$ = 0.16

Time in (minutes)	O.D.	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} $min.^{-1}$
5	0.3	0.0492	
13	.285	.0934	
18	.32	.1239	$1.53x10^{-2}$
27	.38	.1818	
45	.476	.3010	
60	.54	.3927	

(Vide Fig.2(b))

TABLE -2C:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

Conc.of the complex = $1x10^{-3}M$

Conc. of pyridine = $1.6x10^{-2}M$

Conc. of KCl = $1x10^{-1}M$

Temp. = $20^{0}C$

$(O.D)_{\infty}$ = 0.90

$(O.D)_{o}$ = 0.23

Time in (minutes)	O.D.	$\log \frac{(O.D)_{\infty} - (O.D)_{o}}{(O.D)_{\infty} - (O.D)_{t}}$	K_{obs} min.$^{-1}$
8	0.29	0.0453	
12	.33	.0719	
22	.40	.399	$1.34x10^{-2}$
37	.49	.2122	

(Vide Fig.2(c))

TABLE-2D:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2 + py.$

Conc. of the complex = 1×10^{-3}M

Conc. of pyridine = 1×10^{-3}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\infty$ = 1.0

$(O.D)_0$ = 0.24

Temp. = 20°C

Time in (minutes)	O.D	$\log \frac{(O.D)_\infty - (O.D)_0}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
5	0.27	0.0170	8.6×10^{-3}
11	.34	.0607	
22	.39	.0969	
27	.41	.1139	
46	.51	.1931	
66	.62	.3010	
92	.70	.4031	

(Vide Fig.2(d))

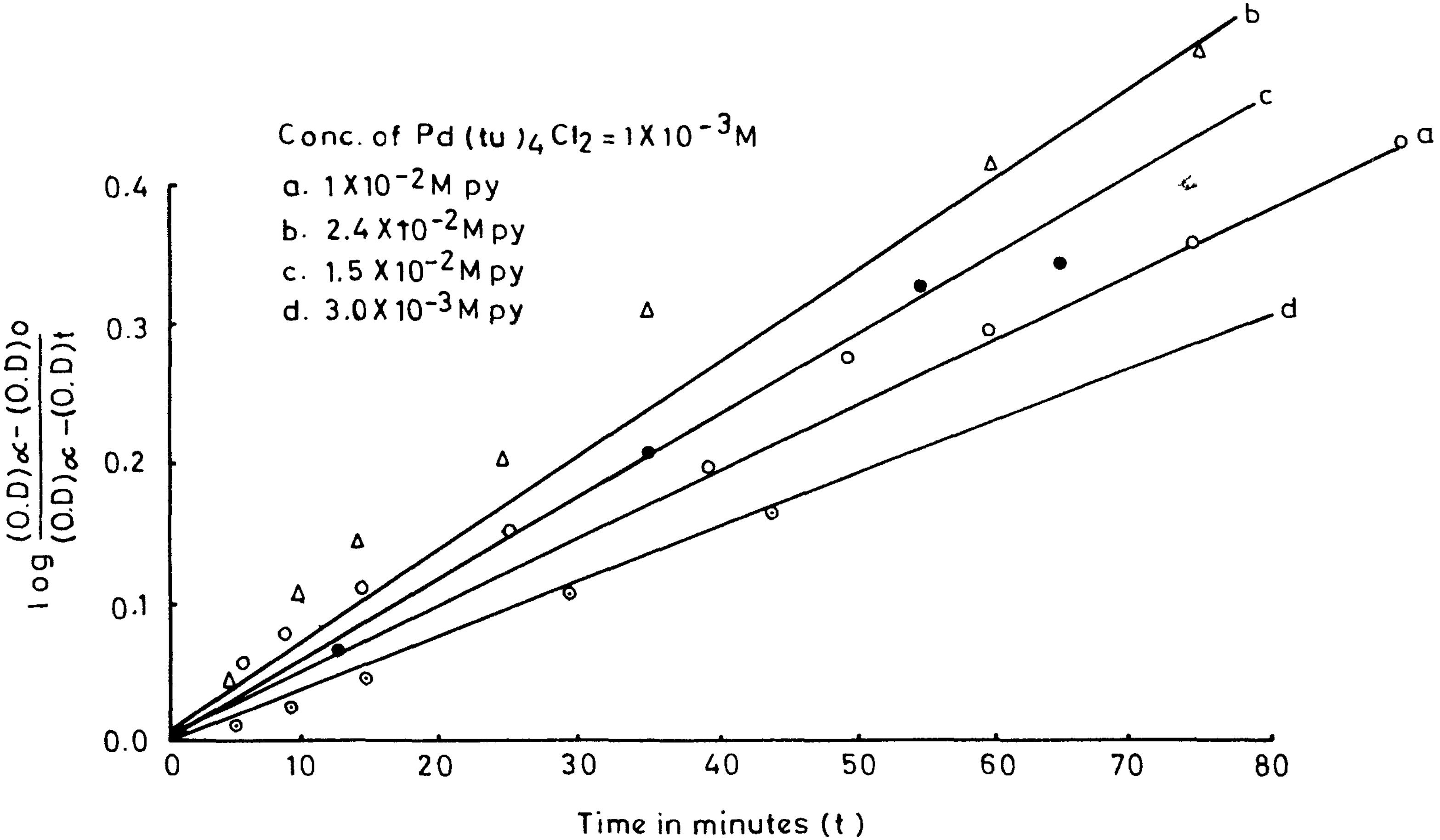


Fig. 3 Plot Between Log $\frac{(O.D)_\alpha - (O.D)_o}{(O.D)_\alpha - (O.D)_t}$ and (t)

(Vide table 3A to 3D)

T A B L E -3A:

Spectrophotometric data for the first rate law.

System: $[Pd(tu)_4]Cl_2$ + py

Conc. of the complex = $1x10^{-3}M$

Conc. of pyridine = $1x10^{-2}M$

Conc. of KCl = $1x10^{-1}M$

$(O.D)_\infty$ = 0.75

$(O.D)_o$ = 0.18

Temp. = 20^oC

Time in (minutes)	O.D.	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
5	0.23	0.0531	
10	.27	.0755	
15	.30	.1038	
25	.35	.1538	
40	.41	.2304	$1.2554x10^{-2}$
50	.44	.2788	
55	.46	.3010	
65	.50	.3579	
80	.54	.4314	

(Vide Fig.3(a)

TABLE -3B$_1$

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py

Conc. of the complex = 1×10^{-3}M

Conc. of pyridine = 2.4×10^{-2}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\infty$ = 0.80

$(O.D)_0$ = 0.18

Time in (minutes)	O. D.	$\log \frac{(O.D)_\infty - (O.D)_0}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
3	0.24	0.044	
10	.31	.1004	
20	.36	.1461	
25	.41	.2041	1.64×10^{-2}
45	.50	.3139	
60	.56	.4150	
75	.60	.4914	
90	.66	.435	

(Vide Fig.3(b)

TABLE -3C.

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

Conc. of the complex = $1x10^{-3}M$

Conc. of pyridine = $1.6x10^{-2}M$

Conc. of KCl = $1.0x10^{-1}M$

$(O.D)_\infty$ = 0.90

$(O.D)_o$ = 0.19

Temp. = 25°C

Time in (minutes)	O.D.	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
6	0.27	0.0492	
12	.33	.0934	
25	.40	.1492	$1.38x10^{-2}$
35	.47	.2175	
50	.54	.3010	
55	.58	.3424	

(Vide Fig.3(c)

TABLE -3D:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

Conc. of the complex = 1×10^{-3}M

Conc. of pyridine = 3×10^{-3}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\infty$ = 1.0

$(O.D)_o$ = 0.18

Temp. = 25°C

Time in (minutes)	O.D	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
5	0.22	0.0212	
10	.27	.0492	
15	.30	.0682	1.07×10^{-2}
30	.39	.1271	
40	.45	.1761	

(Vide Fig. 3(d))

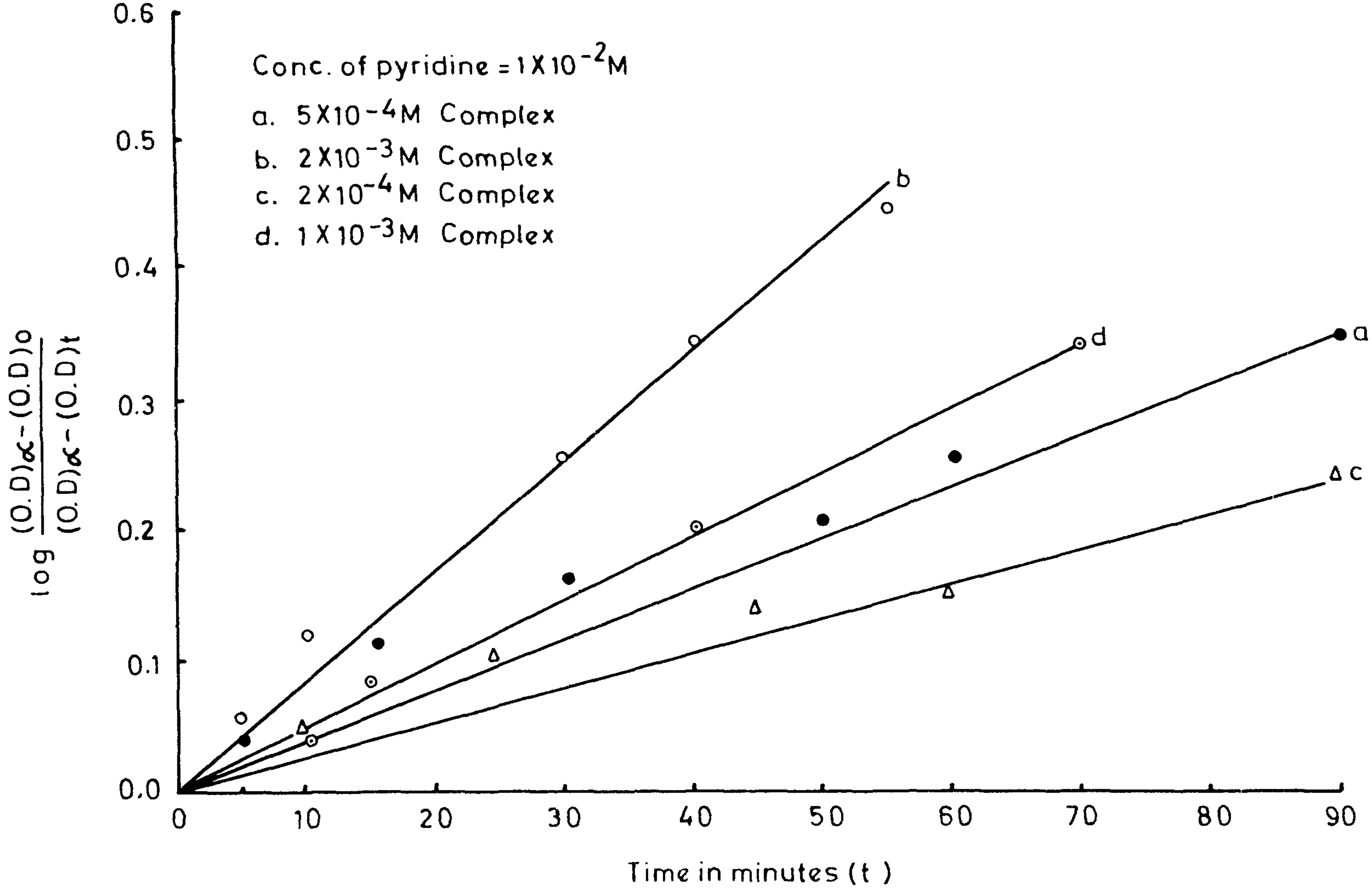


Fig. 4 Plot Between Log $\frac{(O.D)_{\alpha} - (O.D)_{o}}{(O.D)_{\alpha} - (O.D)_{t}}$ and (t)

Vide table 4A, 4B, 4C, & 4D

T A B L E -4A:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

Conc. of the complex = $2x10^{-3}M$

Conc. of pyridine = $1x10^{-2}M$

Conc. of KCl = $1x10^{-1}M$

$(O.D)_\infty$ = 1.0

$(O.D)_o$ = 0.33

Temp. = 24°C

Time in (minutes)	O.D	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
5	0.39	0.0453	
10	.49	.1173	
20	.58	.2041	$8.3x10^{-3}$
30	.63	.2553	
40	.70	.3483	
55	.76	.4472	
100	.86	.6812	

Vide Fig.4(a)

TABLE -4B:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py

Conc. of the complex = 5×10^{-4}M

Conc. of pyridine = 1×10^{-2}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\alpha$ = 0.60

$(O.D)_o$ = 0.15

Temp. = 24°C

Time in (minutes)	O.D	$\log\frac{(O.D)_\alpha - (O.D)_o}{(O.D)_\alpha - (O.D)_t}$	K_{obs} min^{-1}
5	0.20	0.0511	
10	.23	.0828	
15	.25	.1139	4.0×10^{-3}
30	.29	.1673	
50	.32	.2041	
60	.35	.2553	
90	.40	.3522	

(Vide Fig.4(b))

TABLE -4C:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

Conc. of the complex = 2×10^{-4}M

Conc. of pyridine = 1×10^{-2}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\infty$ = 0.40

$(O.D)_o$ = 0.10

Temp. = 24°C

Time in (minutes)	O.D.	$\log\frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
10	0.13	0.0414	
15	.15	.0792	
25	.16	.0969	
45	.18	.1335	2.1×10^{-3}
60	.19	.1553	
90	.23	.2455	

(Vide Fig.4(c))

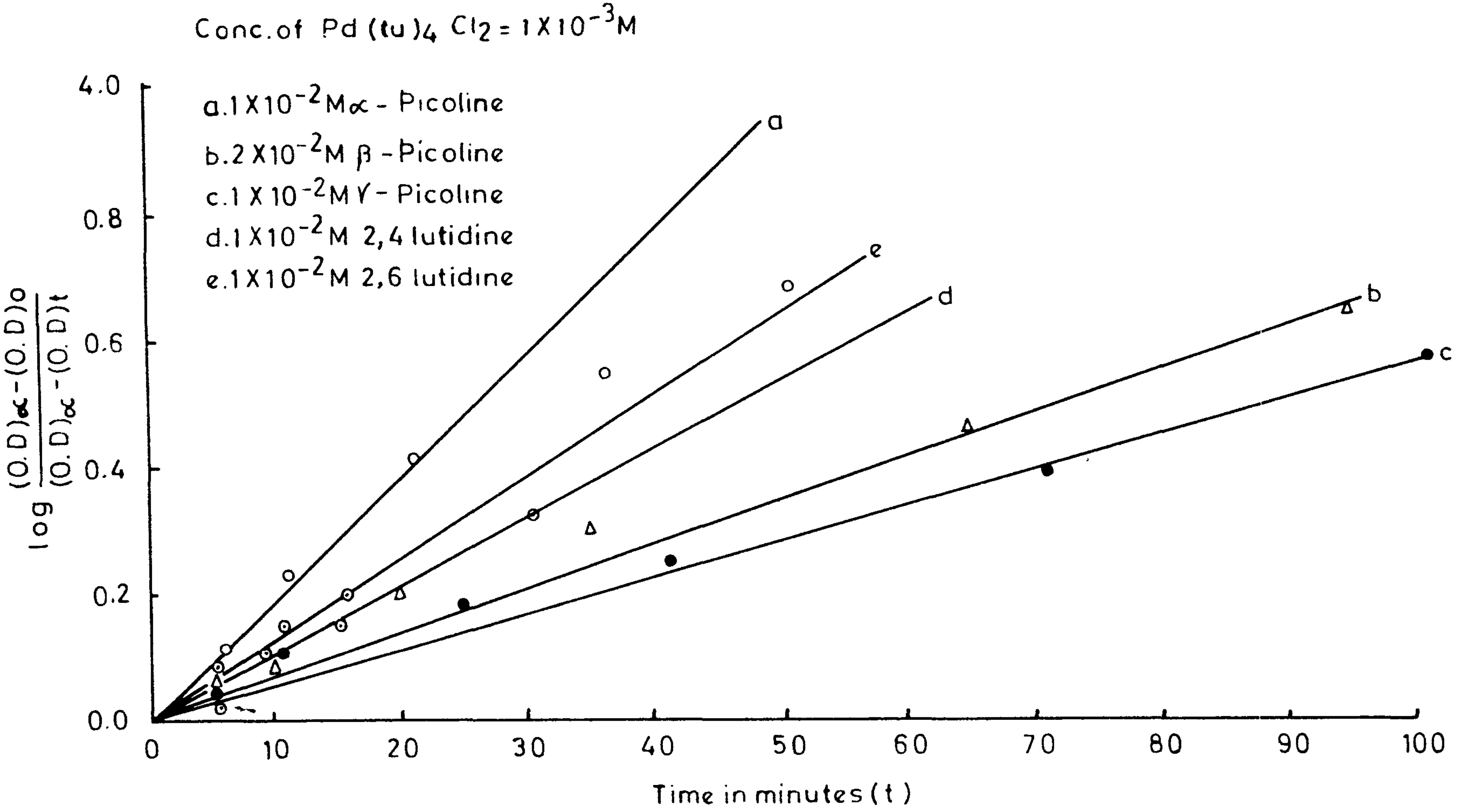


Fig. 5 Plot Between Log $\frac{(O.D)_\alpha - (O.D)_o}{(O.D)_\alpha - (O.D)_t}$ and (t)

(Vide table 5 A to 5E)

TABLE -5A:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,pic

Conc. of the complex = 1×10^{-3}M

Conc. of 2 picoline = 1×10^{-2}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\infty$ = 1.05

$(O.D)_o$ = 0.54

Temp. = 25°C

Time in (minutes)	O.D	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
7	0.70	0.1153	
12	.75	.2304	
22	.85	.4065	2.0×10^{-2}
37	.90	.5315	
52	.94	.6656	
112	1.0	1.0086	

(Vide Fig.5(a))

TABLE -58:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2 + 3,pic$

Conc. of the complex = 1×10^{-3}M

Conc. of 3 picoline = 2×10^{-2}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\infty = 0.90$

$(O.D)_o = 0.26$

Temp. = 25°C

Time in (minutes)	O.D.	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
5	0.35	0.0645	
10	.39	.0969	
20	.50	.2041	0.66×10^{-2}
35	.58	.3010	
65	.68	.4624	
95	.75	.6294	

(Vide Fig.5(b)

TABLE -5C:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 4,pic.

Conc. of the complex = $1x10^{-3}M$

Conc of 4-picoline = $1x10^{-2}M$

Conc. of KCl = $1x10^{-1}M$

$(O.D)_\infty$ = 0.90

$(O.D)_0$ = 0.20

Temp. = 25°C

Time in (minutes)	O.D.	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
5	0.285	0.0531	
10	.35	.1038	
25	.44	.1818	
42	.51	.2553	$0.546x10^{-2}$
72	.62	.3979	
102	.71	.5682	

(Vide Fig.5(c))

TABLE -5D:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,4 lutidine

Conc. of the complex = 1×10^{-3}M

Conc. of 2.4 lutidine = 1×10^{-2}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\alpha$ = 1.25

$(O.D)_o$ = 0.75

Temp. = 25°C

Time in (minutes)	O.D.	$\log \frac{(O.D)_\alpha - (O.D)_o}{(O.D)_\alpha - (O.D)_t}$	K_{obs} min^{-1}
5	0.85	0.0969	
10	.87	.1173	
15	.90	.1553	
20	.94	.2041	1.1×10^{-2}
30	1.1	.5185	

(Vide Fig.5(d))

TABLE -5E:

Spectrophotometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,6 lutidine

Conc. of the complex = 5×10^{-4}M

Conc. of 2,6 lutidine = 1×10^{-2}M

Conc. of KCl = 1×10^{-1}M

$(O.D)_\infty = 0.60$

$(O.D)_o = 0.43$

Temp. = 25°C

Time in (minutes)	O.D.	$\log \frac{(O.D)_\infty - (O.D)_o}{(O.D)_\infty - (O.D)_t}$	K_{obs} min^{-1}
5	0.45	0.0531	
10	.48	.1492	1.27×10^{-2}
15	.495	.2041	

(Vide Fig.5(e))

TABLE -6A:

Values of K_{obs} at various *pyridine* concentrations (in presence of 0.1M KCl).

Temp.	Conc. of the Complex $[Pd(tu)_4]Cl_2$	Conc. of py	$K_{obs} X10^{-2}$ min^{-1}	Table	Fig.
20°C	$1x10^{-3}M$	$1x10^{-3}M$	0.86	2B	2(b)
"	"	$1x10^{-2}M$	1.15	2A	2(a)
"	"	$1.6x10^{-2}M$	1.34	2C	2(c)
"	"	$2.1x10^{-2}M$	1.53	2B	2(b)
25°C	"	$3.0x10^{-3}M$	1.07	3D	3(d)
"	"	$1.0x10^{-2}M$	1.25	3A	3(a)
"	"	$1.5x10^{-2}M$	1.38	3C	3(c)
"	"	$2.4x10^{-2}M$	1.64	3B	3(b)
24°C	$2.0x10^{-3}$	$1.0x10^{-2}M$	0.83	4A	4(a)
"	$5.0x10^{-4}$	"	0.40	4B	4(b)
"	$2.0x10^{-4}$	"	0.21	4C	4(c)

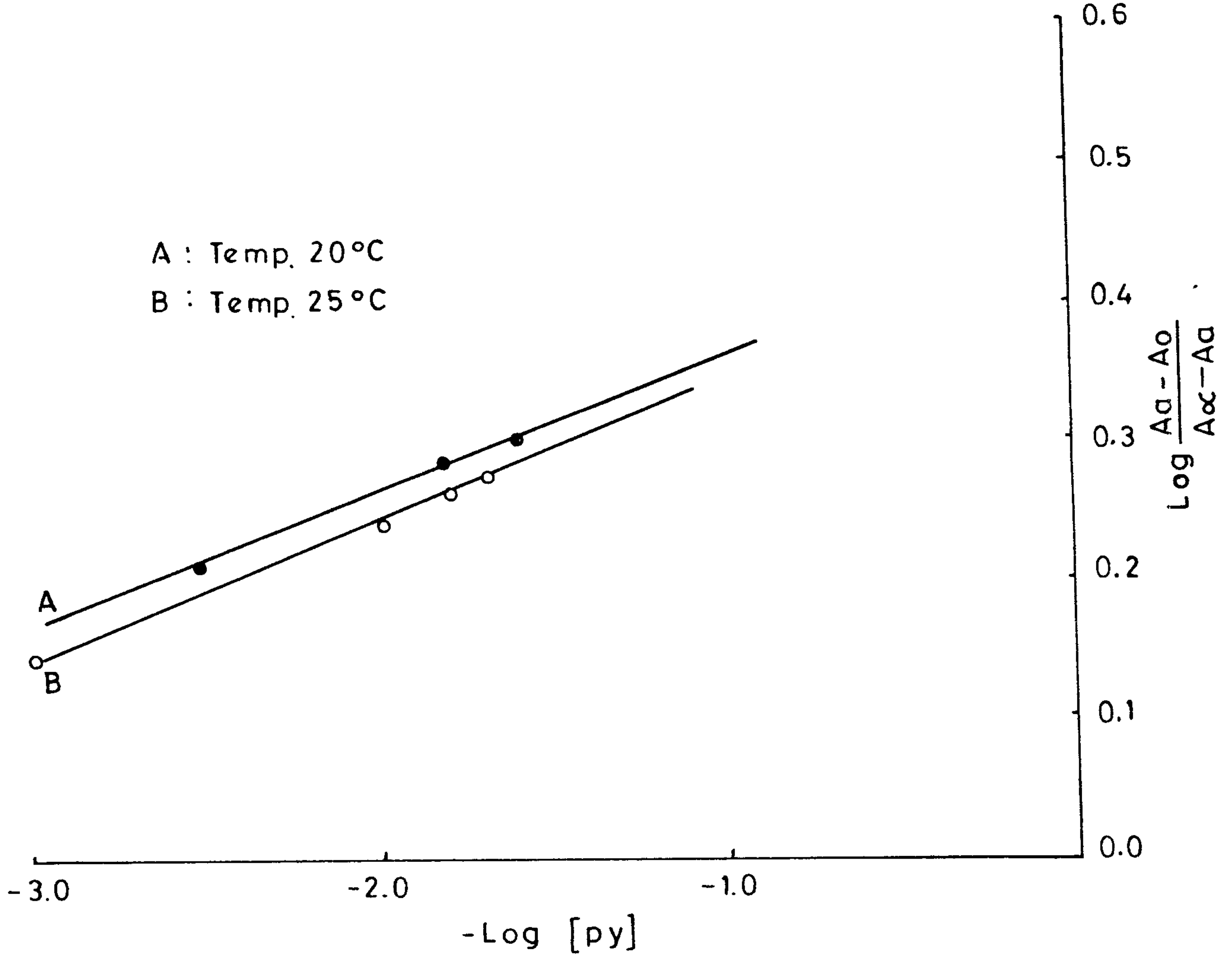


Fig. 7 Plot Of Log $\frac{Aa - Ao}{A\alpha - Aa}$ Vs. Log [py]

TABLE -6B:

Values of K_{obs} for picolines and lutidines
(in presence of 0.1M KCl)

Temp.	Conc. of the complex $[Pd(tu)_4]Cl_2$	Conc. of the amine	$K_{obs.} \times 10^{-2}$ min^{-1}	Table	Fig.
25°C	$1.0 \times 10^{-3}M$	$1 \times 10^{-2}M$ (2-picoline)	2.0	5A	5(a)
"	"	$2 \times 10^{-2}M$ (3-picoline)	0.66	5B	5(b)
"	"	$2 \times 10^{-2}M$ (4-picoline)	0.545	5C	5(c)
"	"	$1 \times 10^{-2}M$ (2,4 lutidine)	1.1	5D	5(d)
"	$5 \times 10^{-4}M$	$1 \times 10^{-2}M$ (2,6 lutidine)	1.27	5E	5(e)

TABLE -7A:

Spectrophotometric data for calculating n and K_f from the slope of the plot and equation(1), respectively.

Conc. of the complex $[Pd(tu)_4]Cl_2$ = $1 \times 10^{-3}M$
Conc. of KCl = $1 \times 10^{-1}M$
Temp. = 20°C

A_∞	A_o	A_a	$\frac{A_a - A_o}{A_\infty - A_a}$	$\log \frac{A_a - A_o}{A_\infty - A_a}$	py	$\log [py]$
1.0	0.08	0.65	1.62	0.2095	$3 \times 10^{-3}M$	-2.5229
0.90	0.08	0.62	1.92	0.2833	$1.5 \times 10^{-2}M$	-1.8239
0.80	0.08	0.56	2.0	0.3010	$2.4 \times 10^{-2}M$	-1.6198

Value of n from the slope of the plot of $\log \frac{A_a - A_o}{A_\infty - A_a}$ vs. $\log [py]$ = 1.0

Value of K_f from the equation (1) = 2.917

(Vide Fig.7A)

TABLE -7B:

Spectrophotometric data for calculating n and K_f from the slope of the plot and equation (1), respectively.

Conc. of the complex $[Pd(tu)_4]Cl_2$ = $1x10^{-3}M$
Conc. of KCl = $1x10^{-1}M$
Temp. = 25^oC

A_∞	A_o	A_a	$\frac{A_a - A_o}{A_\infty - A_a}$	$\log \frac{A_a - A_o}{A_\infty - A_a}$	$[py]$	$\log [py]$
0.92	0.08	0.57	1.41	0.15	$1x10^{-3}$	-3
0.68	0.08	0.46	1.74	0.24	$1x10^{-2}$	-2
0.90	0.08	0.62	1.90	0.279	$1.6x10^{-2}$	-1.796
0.80	0.08	0.54	1.80	0.255	$2.1x10^{-2}$	-1.68

Value of n from the slope of the plot of $\log \frac{A_a - A_o}{A_\infty - A_a}$ vs. $\log [py]$ = 1.0

Value of K_f, from the equation(1) = 2.818

(Vide Fig.7B)

Kinetic Data (Potentiometric method)

The first order rate was determined by plotting $\log \frac{E_t}{E_\infty - E_t}$ versus t, where E_∞ and E_t are defined earlier. Values of rate constants were calculated from 2.30 times the slopes of the linear rate plots. In the following tables are given the values of the terms: t, E_t and $\log \frac{E_t}{E_\infty - E_t}$ for the various systems.

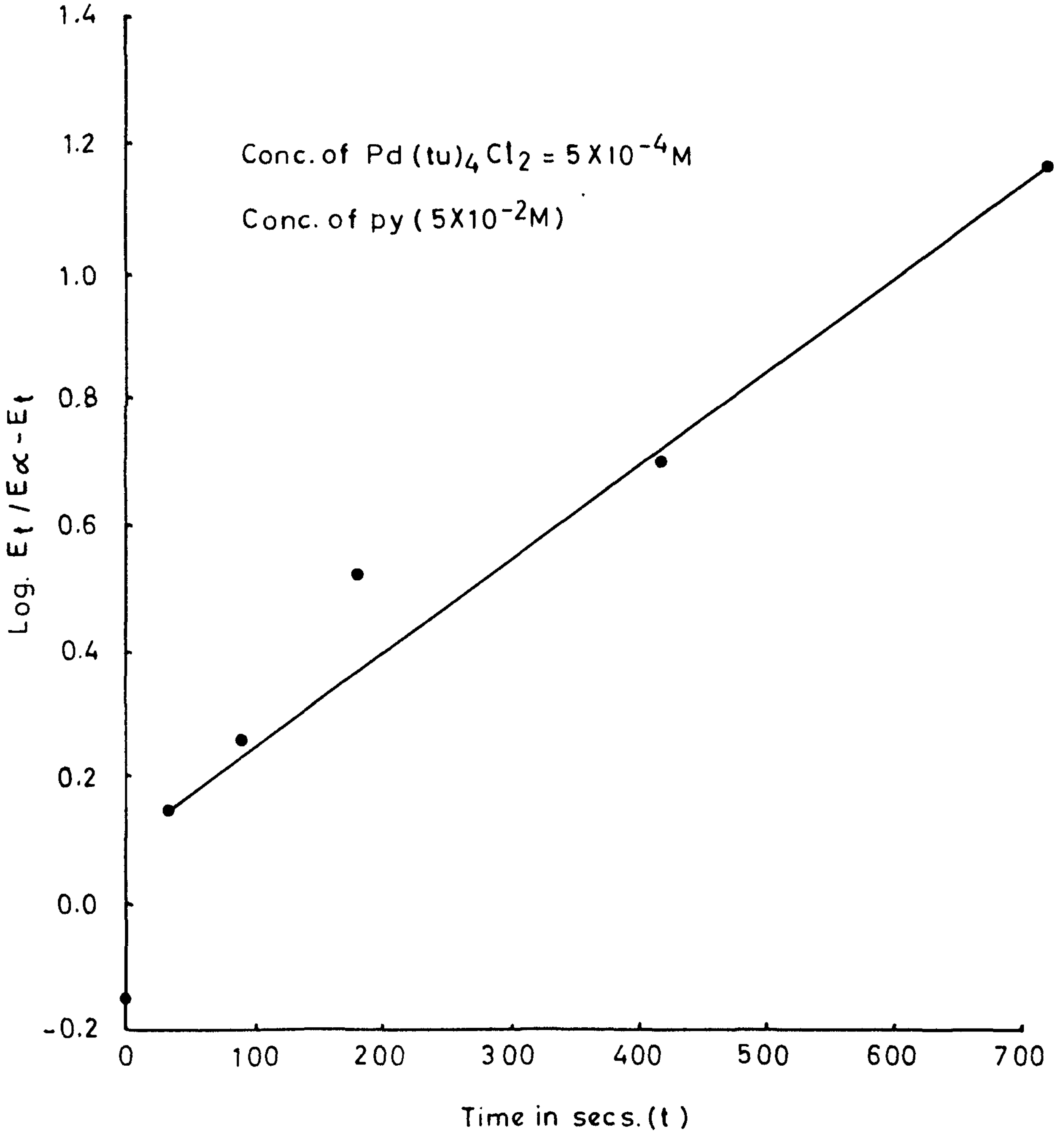


Fig 8 A Plot $E_t / E_\alpha - E_t$ Vs. (t)
(Vide table 8A)

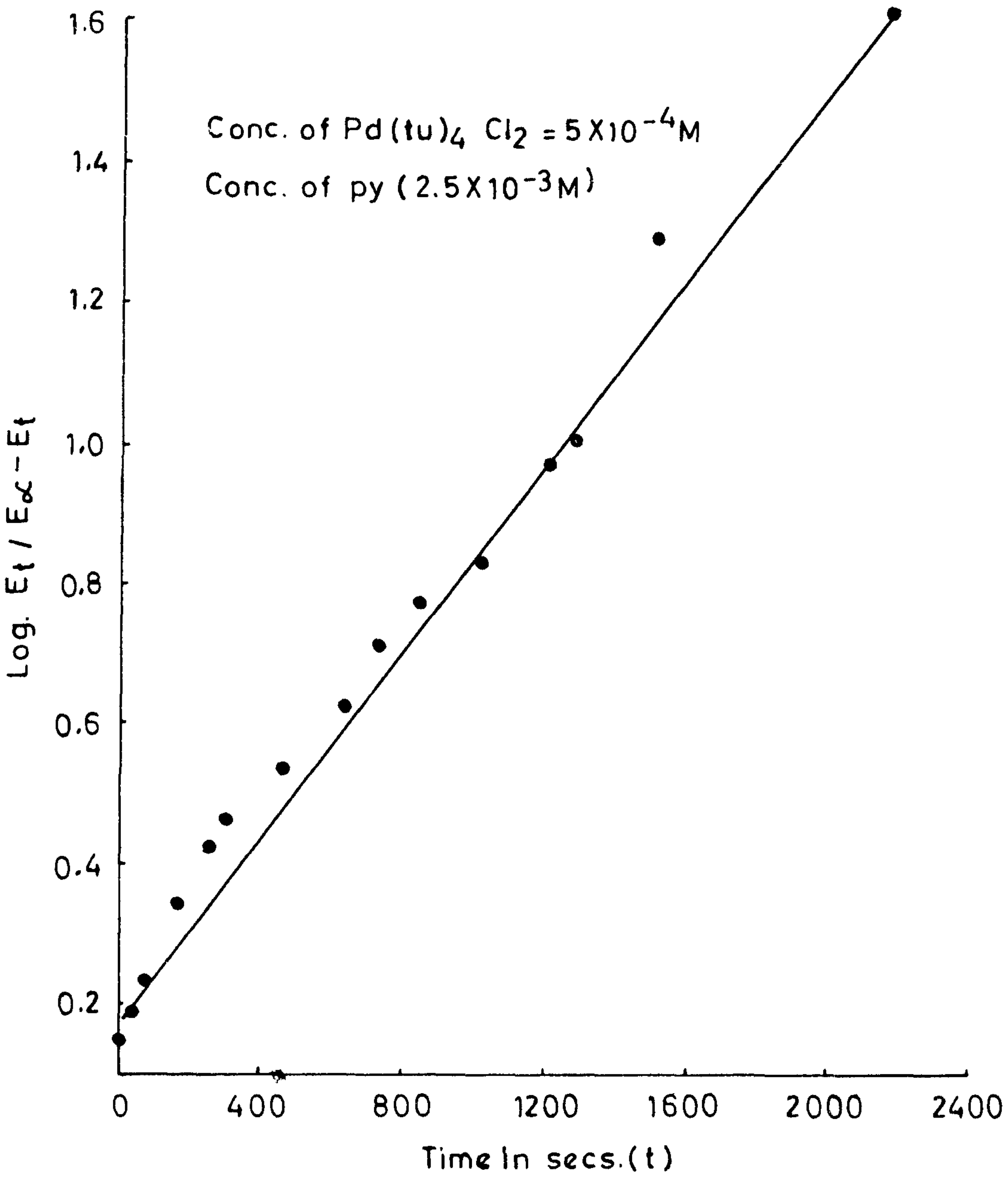


Fig. 8B Plot $Et / E_{\alpha} - Et$ Vs. (t) ·

(Vide table 8 B)

TABLE-8A.

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

25 ml($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml ($1x10^{-1}$M) pyridine

Temp. = 25°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ $sec.^{-1}$
0	20	-0.1467	
30	28	.1461	
90	31	.2601	$3.47x10^{-3}$
180	37	.5267	
420	40	.6990	
720	45	1.1761	
1620	48	-	

(Vide Fig.8A)

TABLE-8B.

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + py.

50 ml($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 50 ml.($5x10^{-3}$M) pyridine

Temp. = 35°C.

Time in Seconds	Potentials, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ $sec.^{-1}$
0	72	0.1413	
15	74	.1702	
60	78	.2293	
150	85	.3383	
240	90	.4227	
300	92	.4587	$1.495x10^{-3}$
450	96	.5351	
630	101	.6326	
720	104	.7160	
840	106	.7700	
1020	108	.8293	
1200	112	.9700	
1380	115	1.0065	
1500	118	1.293	
2160	121	1.6057	
2340	124	-	

(Vide Fig. 8B)

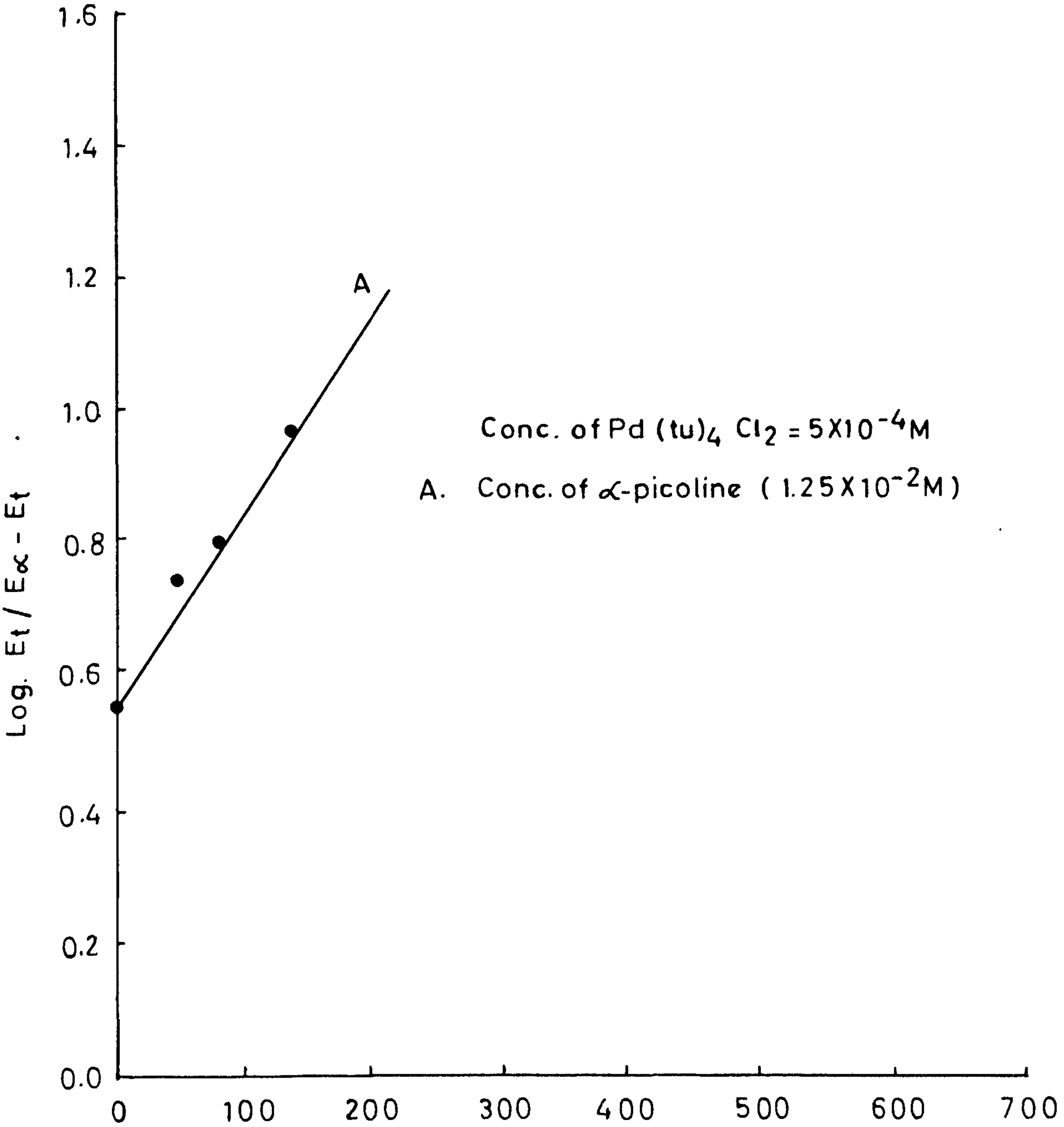


Fig 9A Plot Et / Eα - Et Vs. (t)

(Vide table 9 A)

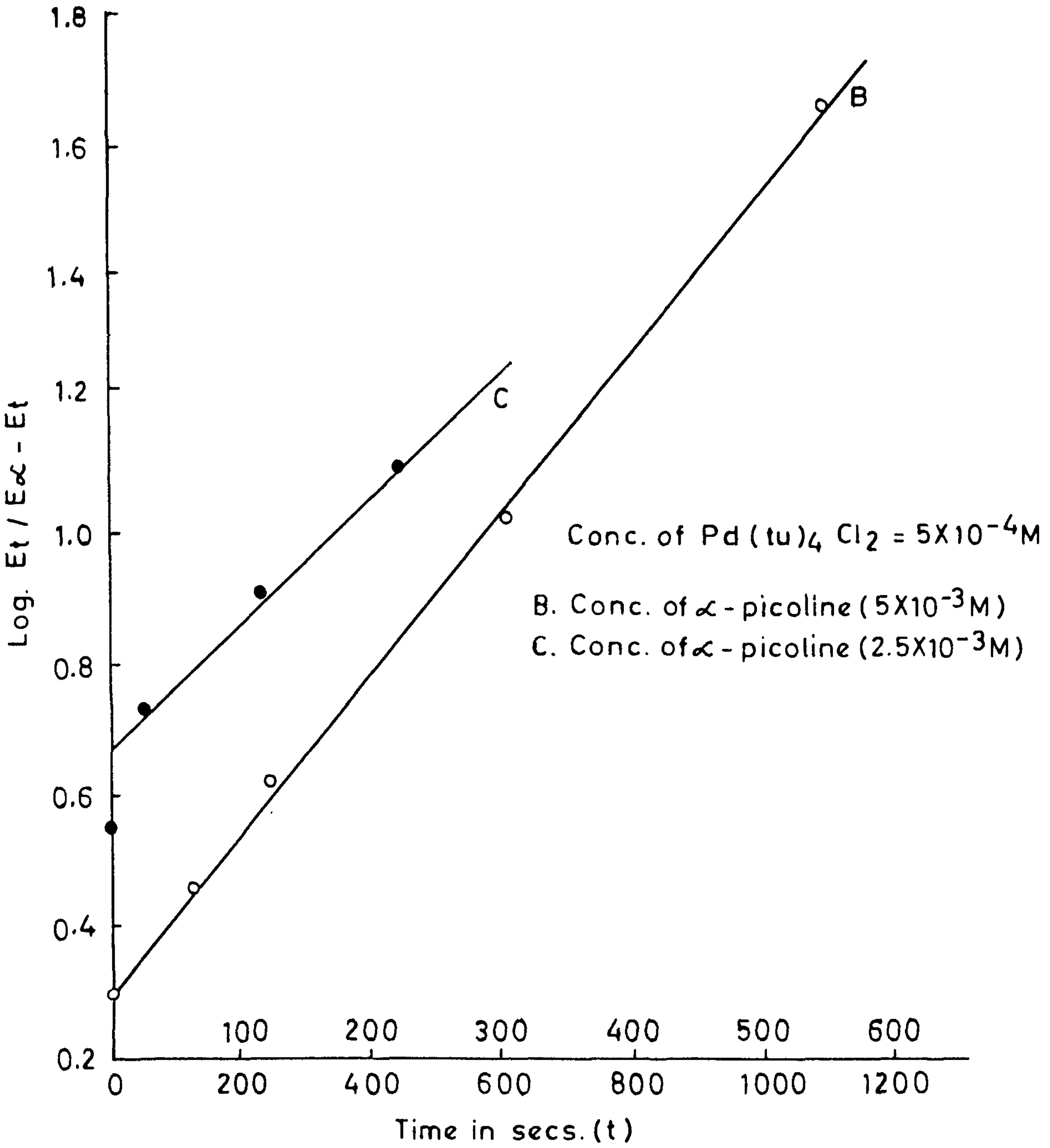


Fig.9B&C Plot $E_t / E_\alpha - E_t$ Vs. (t)

(Vide table 9B & C)

TABLE -9A:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,picoline.

25 ml($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml($2.5x10^{-2}$M) 2-picoline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log\frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	83	0.5574	
45	90	.7501	
75	92	.8177	$6.9x10^{-3}$
135	96	.9823	
375	100	1.2218	
795	106		

(Vide Fig.9A)

TABLE -9B:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,picoline.

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($1x10^{-2}$M) 2-picoline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log\frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	62	0.2873	
60	70	.4649	$5.75x10^{-3}$
120	76	.6255	
300	86	1.0314	
540	92	1.6628	
2280	94	-	

(Vide Fig.9B)

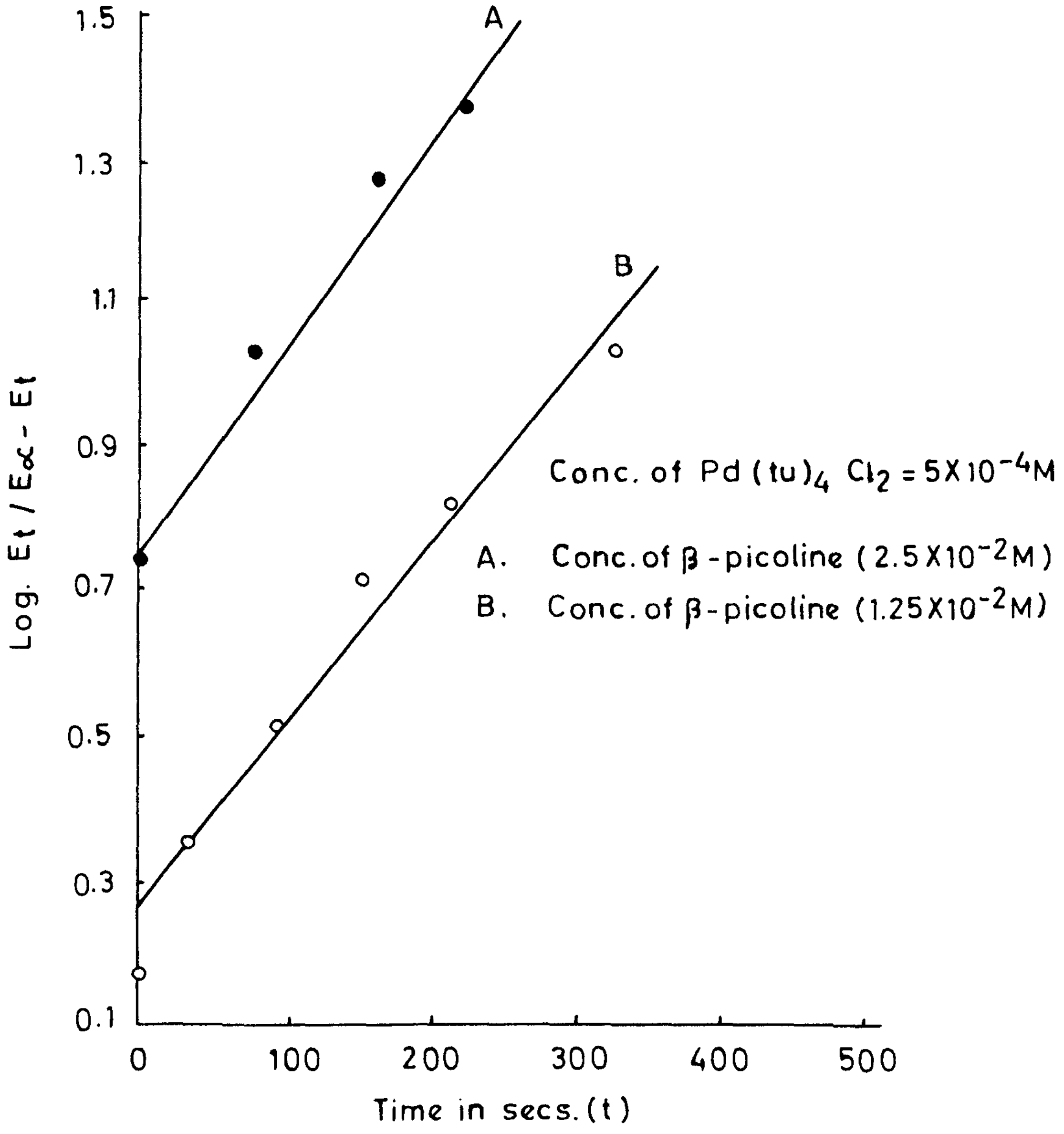


Fig. 10A & B Plot Et / E_α - Et Vs. (t)

(Vide table 10A & B)

TABLE-9C:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,picoline.

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($5.0x10^{-3}$)2-picoline

Temp. = 35°C

Time in Seconds	Potential,E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ $sec.^{-1}$
0	66	0.5576	
46	70	.7312	
226	74	.9150	$2.15x10^{-3}$
436	77	1.1083	
1246	80	1.426	
2026	82	1.9133	
2926	83	-	

(Vide Fig.9C)

TABLE-10A:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$+ 3 picoline.

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml ($2.5x10^{-2}$M)3-picoline

Temp. = 35°C.

Time in Seconds.	Potential,E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ $sec.^{-1}$
0	82	0.7677	
75	88	1.0414	
225	92	1.3617	$5.98x10^{-3}$
495	96	-	

(Vide Fig.10A)

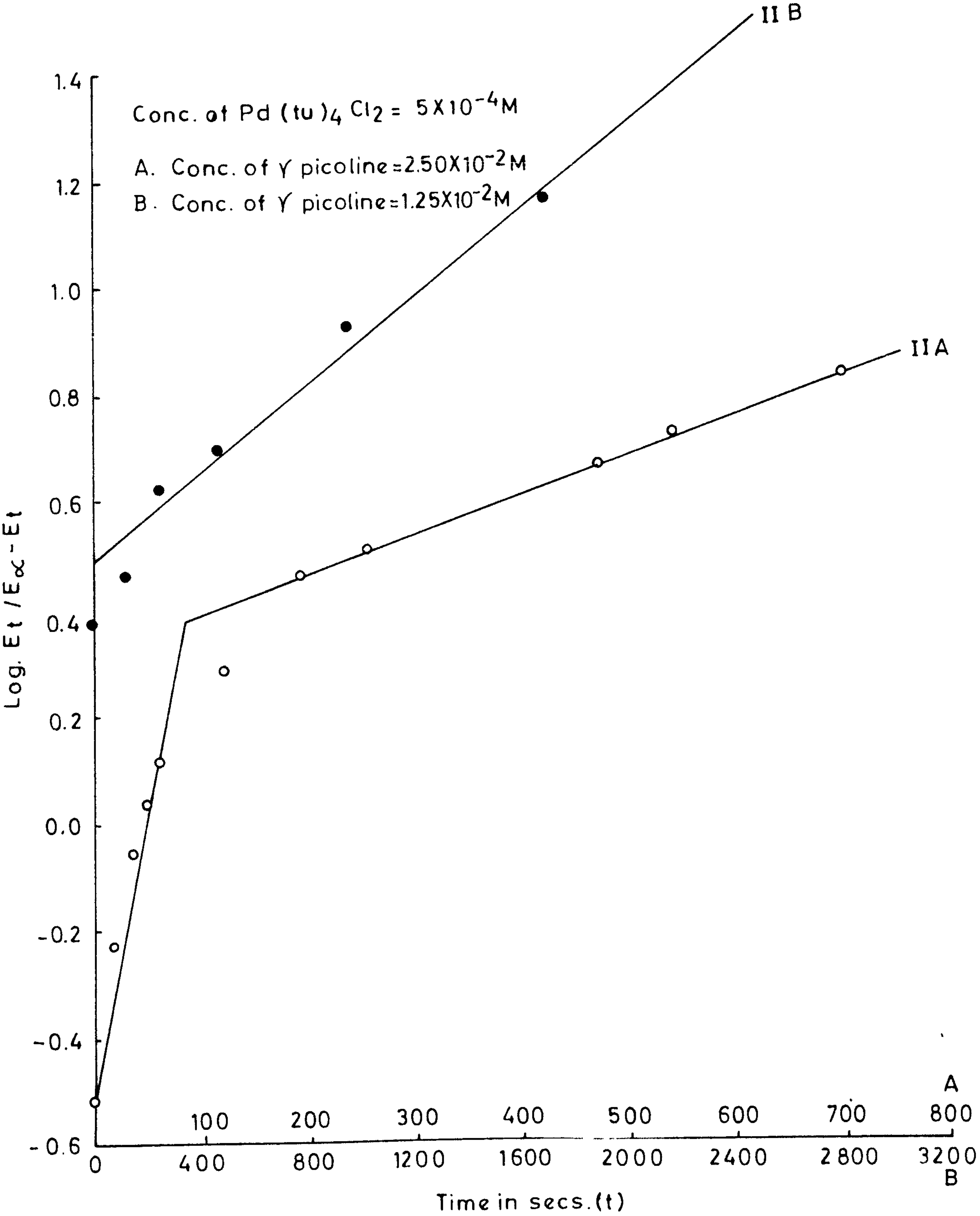


Fig. 11 Plot Et / E∝ - Et Vs.(t)

(Vide table 11A &11B)

TABLE -10B.

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2.picoline.

25 ml.(1×10^{-3}M) $[Pd(tu)_4]Cl_2$ + 25 ml.(5×10^{-2}M)3-picoline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	64	0.1727	
30	74	.3507	
90	82	.5139	
150	90	.7238	5.75×10^{-3}
210	93	.8224	
330	98	1.037	
570	103	1.4107	
1110	107	-	

(Vide Fig.10B)

TABLE -11A.

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 4 picoline.

25 ml.(1×10^{-3}M) $[Pd(tu)_4]Cl_2$ + 25 ml.(5×10^{-2})4-picoline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	24	-0.5229	
60	38	-0.2397	
120	48	-0.0670	
180	54	0.0334	
240	59	.117	5.325×10^{-3}
480	69	.2947	
780	78	.4771	
1920	86	.6792	
1020	80	.5229	
2160	88	.7404	
2820	91	.8451	
3540	94	.9731	
8340	104	-	

(Vide Fig.11A)

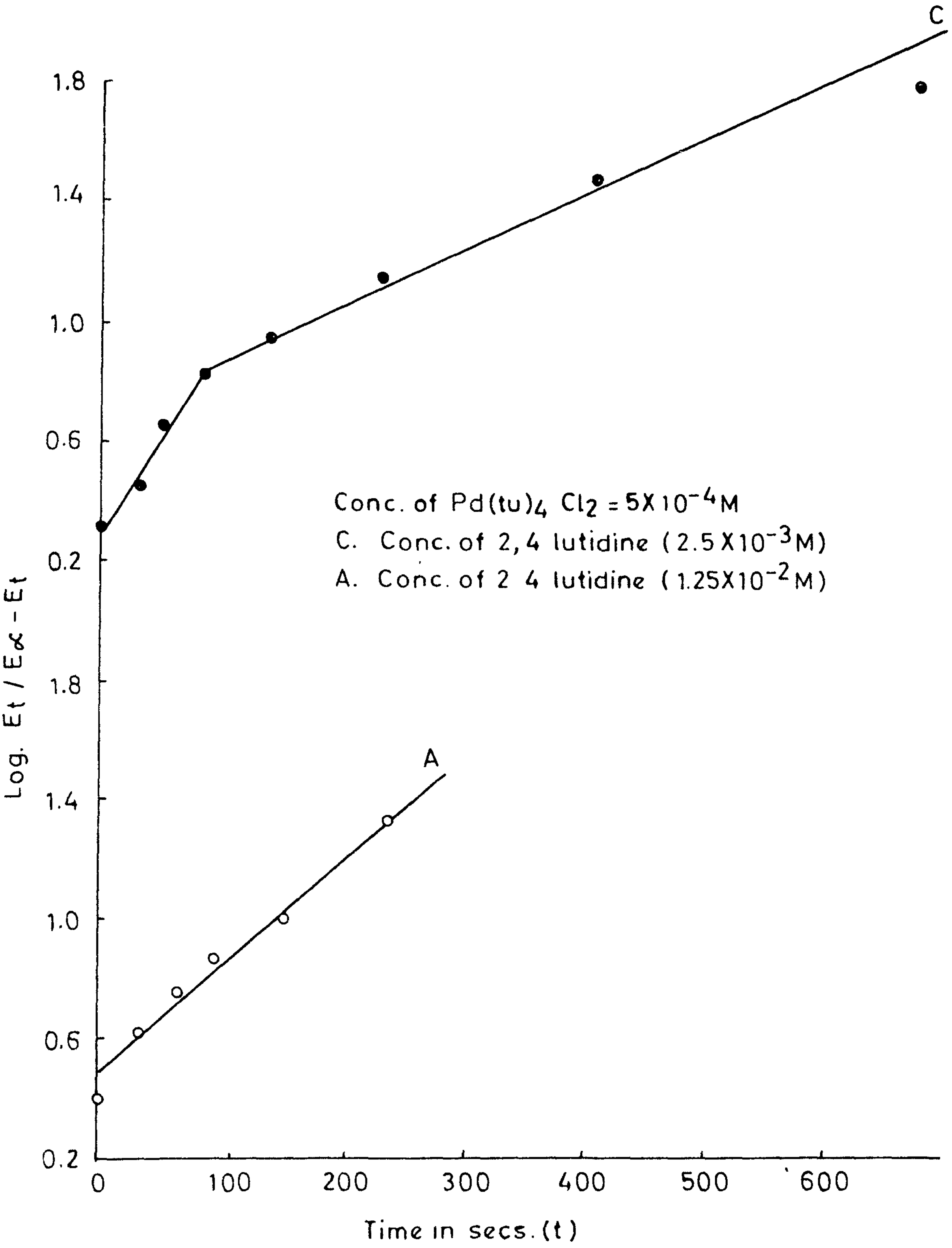


Fig. 12A & C Plot $E_t/E_\alpha - E_t$ Vs. (t)

(Vide table 12A & C)

TABLE -11B:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 4 picoline.

25 ml.$(1x10^{-3}M)$ $[Pd(tu)_4]Cl_2$ + 25 ml.$(2.5x10^{-2}M)$4-picoline

Temp. = 35°C.

Time in Seconds.	Potential, E (in m.V.)	$\log\frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	68	0.3853	
30	72	.4771	
60	78	.6369	3.77x10^{-3}
120	80	.699	
240	86	.9345	
420	90	1.176	
720	93	1.4914	
1560	96	-	

(Vide Fig.11B)

TABLE -12A:

Potentiometric data for the first order rate law:

System: $[Pd(tu)_4]Cl_2$+ 2,4, lutidine

25 ml.$(1x10^{-3}M)$ $[Pd(tu)_4]Cl_2$ + 25 ml.$(2.5x10^{-2}M)$2,4, lutidine

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log\frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	98	0.4114	
30	110	.6264	
60	116	.7635	7.75x10^{-3}
90	120	.8751	
150	128	1.004	
240	130	1.3357	
480	134	1.8261	
1080	136	-	

(Vide Fig.12A)

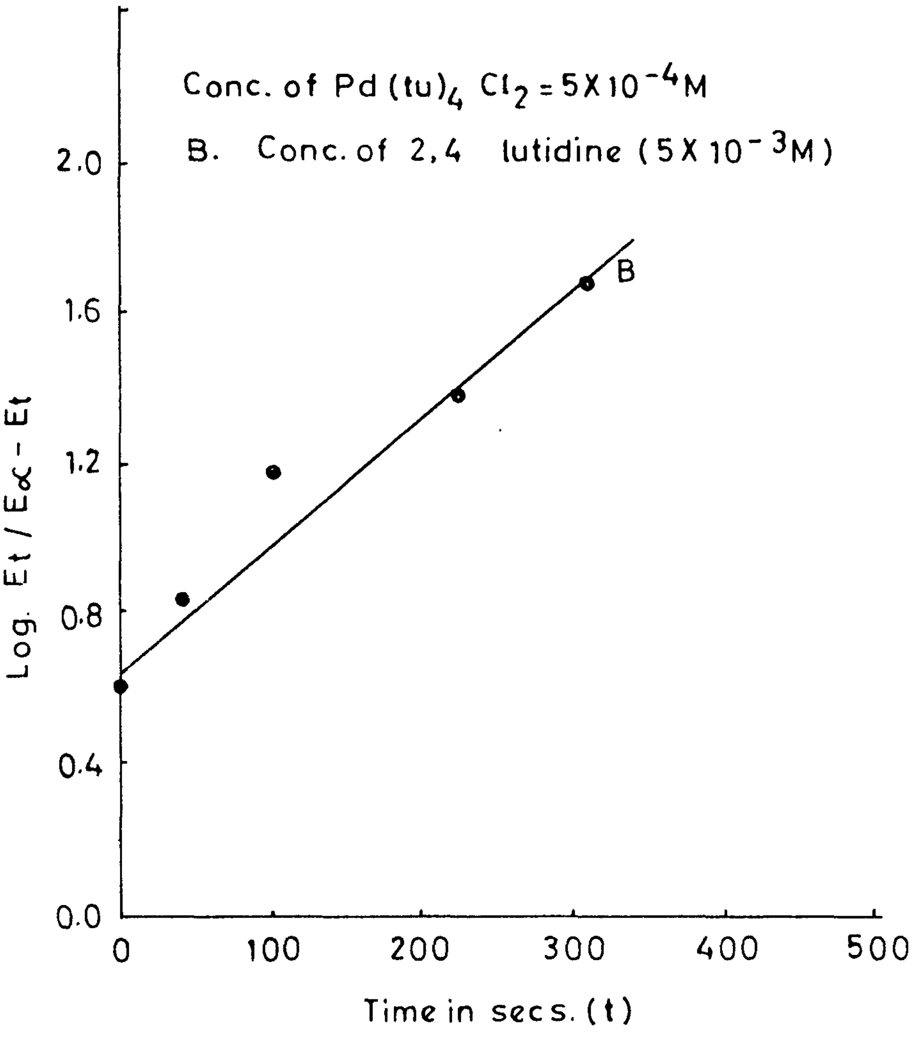


Fig 12 B Plot Et / E$_\alpha$ - Et Vs. (t)

(Vide table 12 B)

T A B L E -12B:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ +2,4, lutidine

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($1x10^{-2}$M)2,4, lutidine.

Temp. = 35^{o}C.

Time in seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	118	0.6095	
40	128	0.85519	
100	138	1.1857	7.66x10^{-3}
190	142	1.4533	
310	144	1.6813	
940	147	-	

(Vide Fig.12B)

T A B L E -12C:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,4, lutidine

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($5x10^{-3}$M)2,4, lutidine.

Temp. = 35^{o}C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	84	0.3222	
30	96	.4451	
50	102	.6662	
80	108	.8293	
140	112	.9700	
230	116	1.1614	
680	120	1.4771	1.47x10^{-3}
1100	124	1.7853	

(Vide Fig.12C)

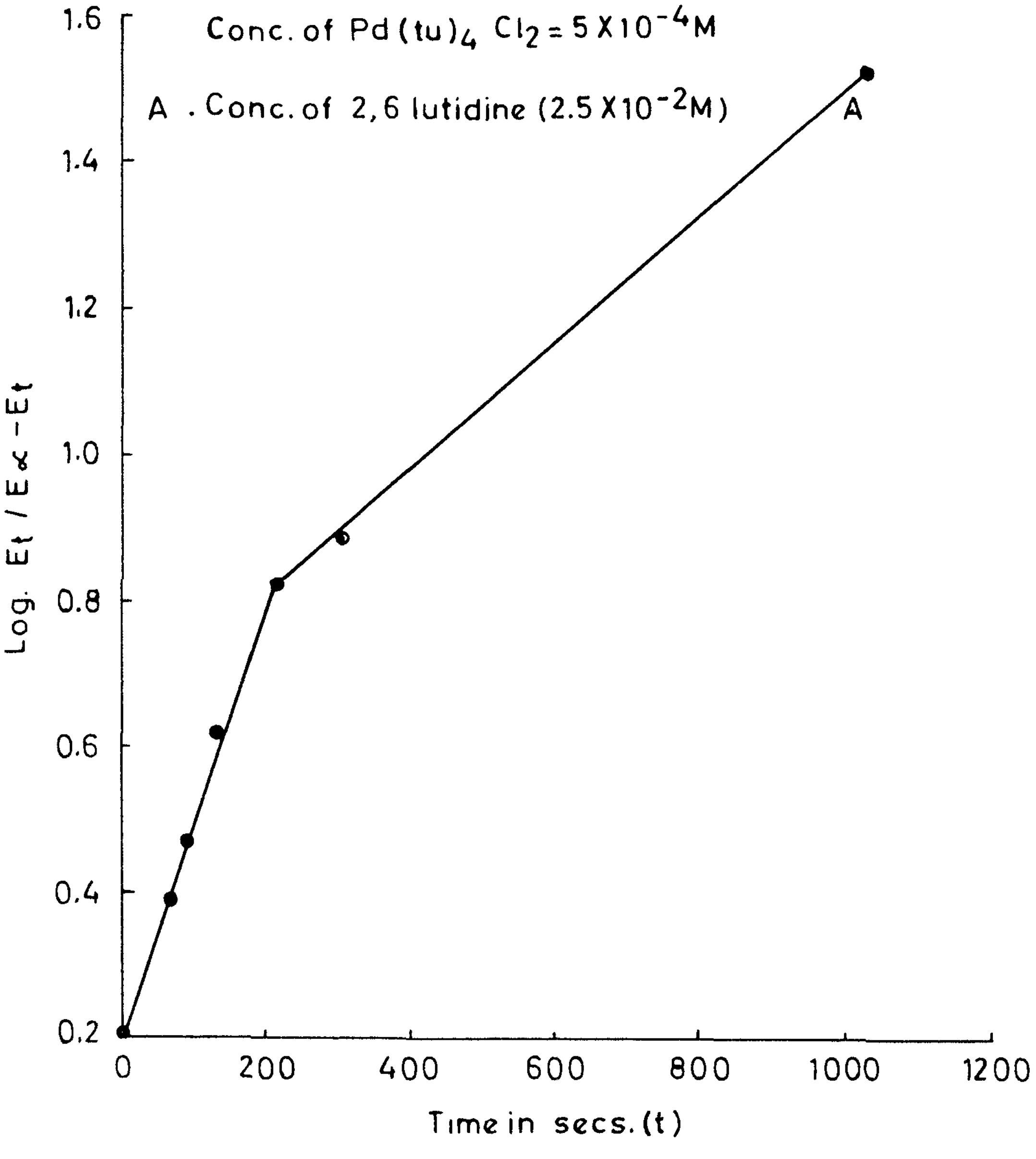


Fig.13A Plot $E_t/E_\infty - E_t$ Vs. (t)

(Vide table 13A)

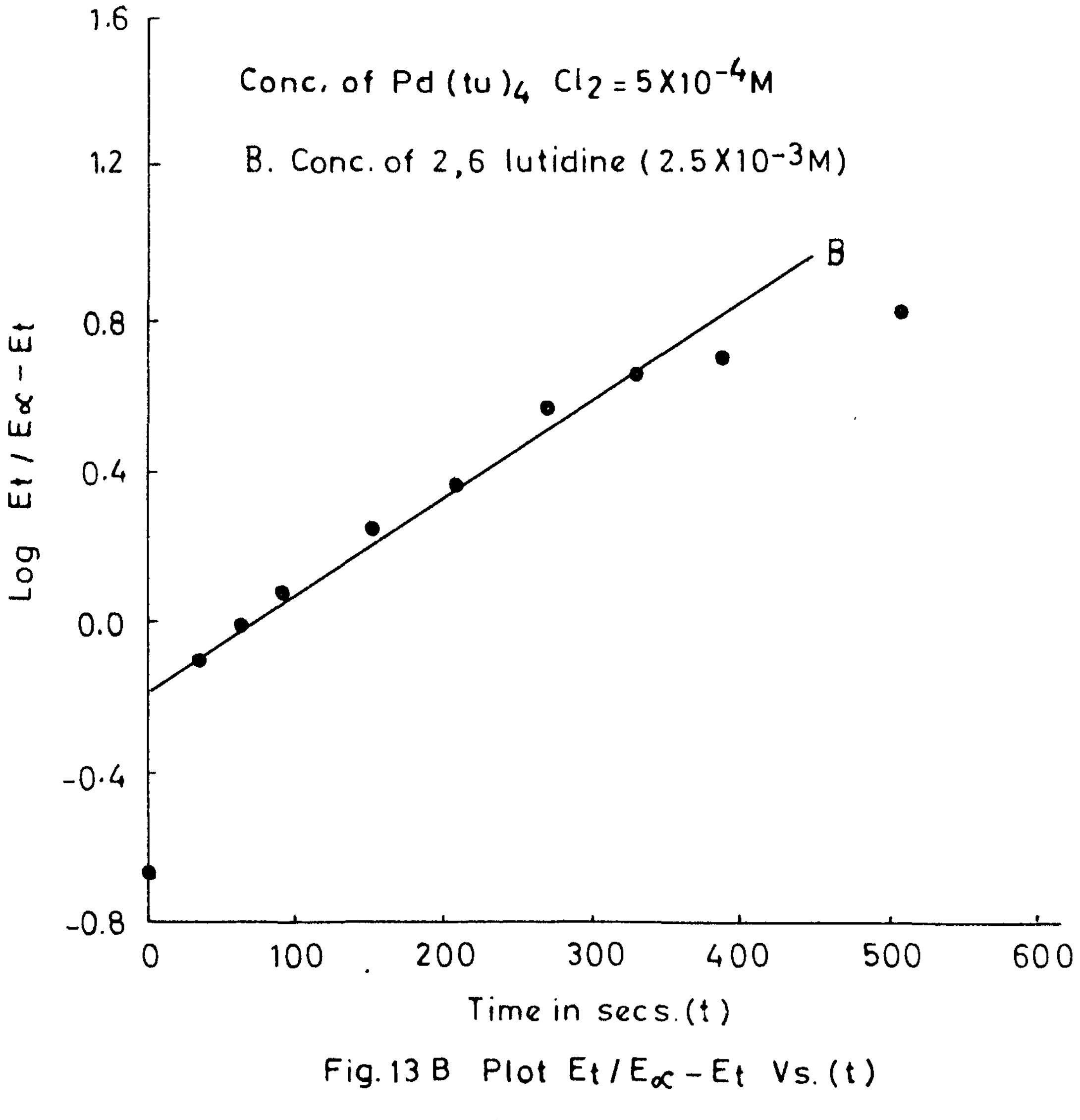


Fig. 13 B Plot Et / E$_\alpha$ - Et Vs. (t)

(Vide table 13 B)

TABLE -13A:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,6, lutidine

25 ml($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml($5x10^{-2}$M)2,6, lutidine

Temp. = 35°C.

Time in seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	86	0.2021	
60	100	.3939	
90	108	.4771	
120	113	.6217	$6.9x10^{-3}$
210	122	.8311	
300	124	.8893	
1020	136	1.5315	
2100	140	-	

(Vide Fig.13A)

TABLE -13B:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ +2,6, lutidine

25 ml.($1x10^{-3}$) $[Pd(tu)_4]Cl_2$ + 25 ml.($5x10^{-3}$M) 2,6, lutidine

Temp. = 35°C.

Time in seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	20	-0.6532	
30	42	- .1093	
60	54	- .0158	
90	60	- .0792	
150	70	+0.2630	
210	78	.3870	
270	84	.5093	
330	90	.6532	$6.9x10^{-3}$
390	92	.7085	
510	98	.8362	
750	106	1.4232	
1770	110	-	

(Vide Fig.13B)

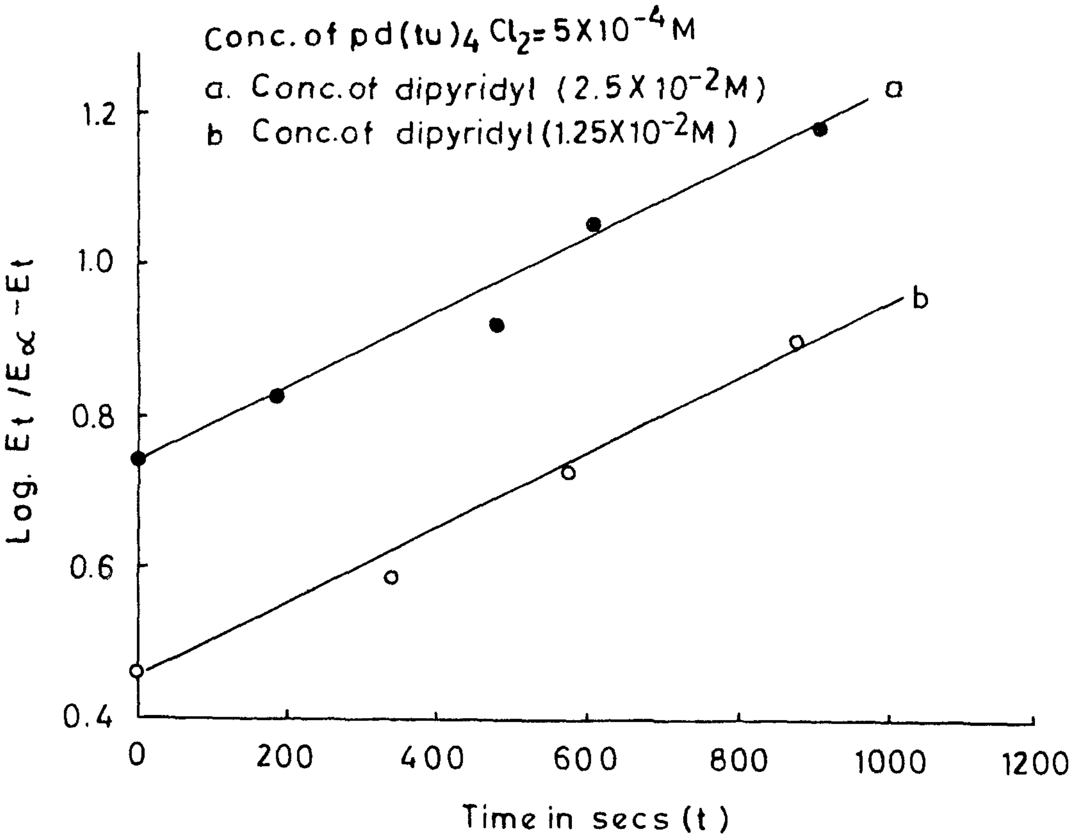


Fig.14A&B Plot Et / E$_\alpha$ -Et Vs (t)

(Vide table 14A&B)

TABLE -14A:

Potentiometric data for the first order rate law.
System: $[Pd(tu)_4]Cl_2$ + 2,2' dipyridyl.

25 ml.($1x10^{-3}M$) $[Pd(tu)_4]Cl_2$ + 25 ml.($5x10^{-2}M$) dipyridyl

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	90	0.7501	
180	86	.8304	
480	84	.9243	
600	81	1.0634	$1.15x10^{-3}$
900	79	1.1986	
2100	74	-	

(Vide Fig.14A)

TABLE -14B:

Potentiometric data for the first order rate law.
System: $[Pd(tu)_4]Cl_2$+2,2' dipyridyl.

25 ml.($1x10^{-3}M$) $[Pd(tu)_4]Cl_2$ + 25 ml.($2.5x10^{-2}M$) dipyridyl

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	48	0.4771	
330	51	.5937	
570	54	.7324	
870	57	.9108	
2010	60	1.1761	
4250	64	-	$1.15x10^{-3}$

(Vide Fig. 14B)

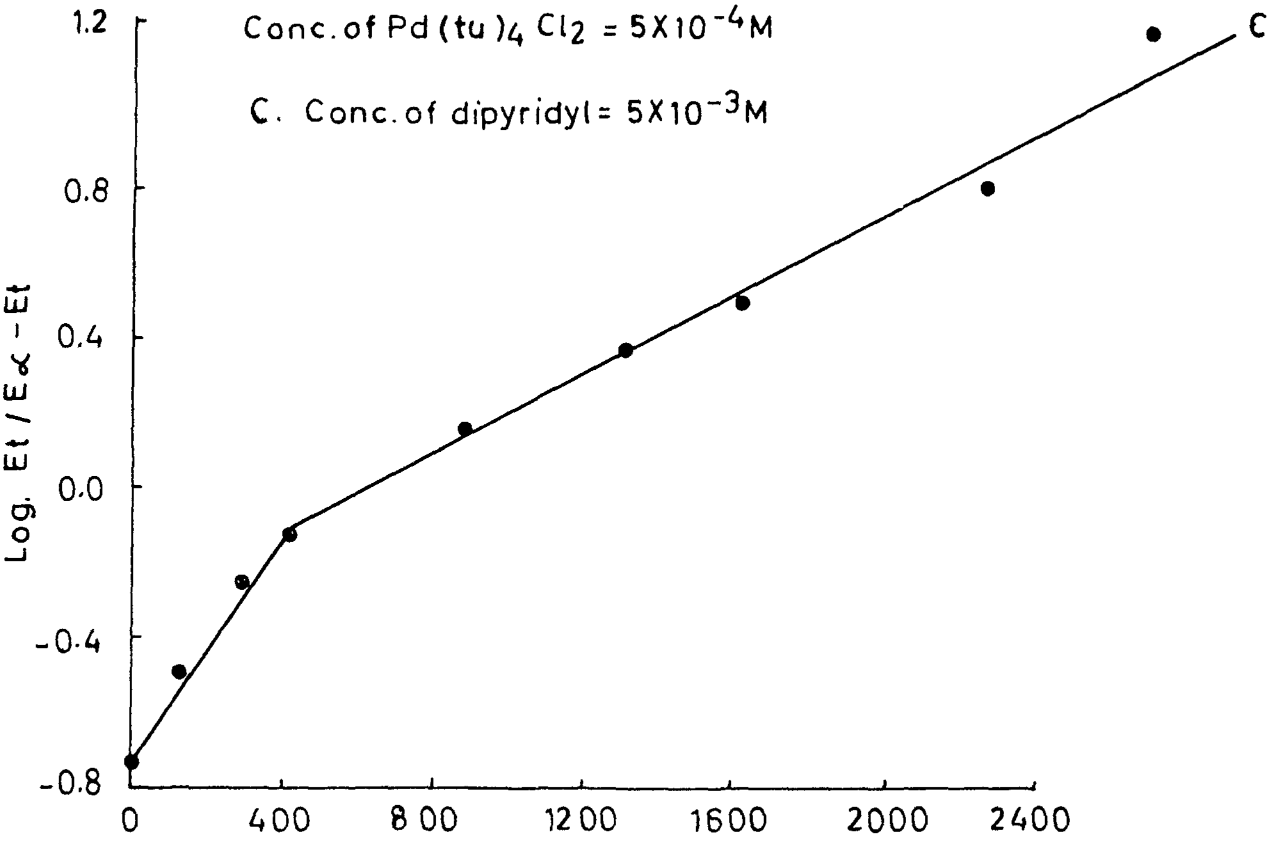


Fig. 14C Plot $E_t/E_\alpha - E_t$ Vs. (t)

(Vide table 14C)

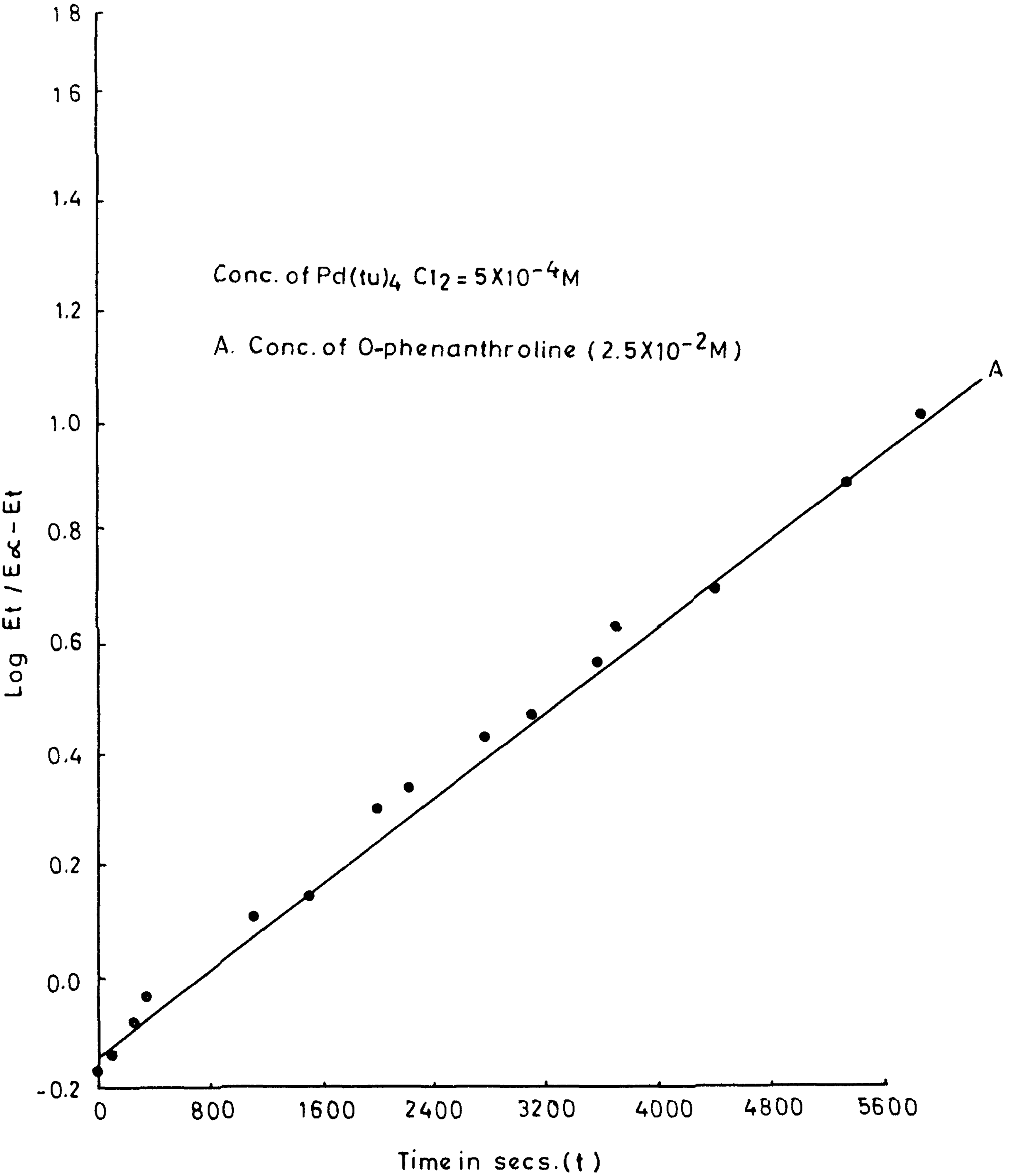


Fig. 15 A

(Vide table 15A)

TABLE -14C:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + 2,2'dipyridyl.

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml. ($1x10^{-2}$M) dipyridyl

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	6	-0.7869	
120	9	- .5082	
300	14	- .2341	
420	16	- .1383	
900	23	+0.1856	
1320	27	.3900	
1620	29	.5082	1.15x10^{-3}
2280	33	.8195	
2700	36	1.255	
3030	38	-	

(Vide Fig.14C)

TABLE -15A:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + o-phenanthroline.

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($5x10^{-2}$M)o-phenanthroline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	71	0.7374	
60	76	0.9777	2.3x10^{-3}
180	78	1.1139	
720	82	1.6128	
1080	84	-	

(Vide Fig.15A)

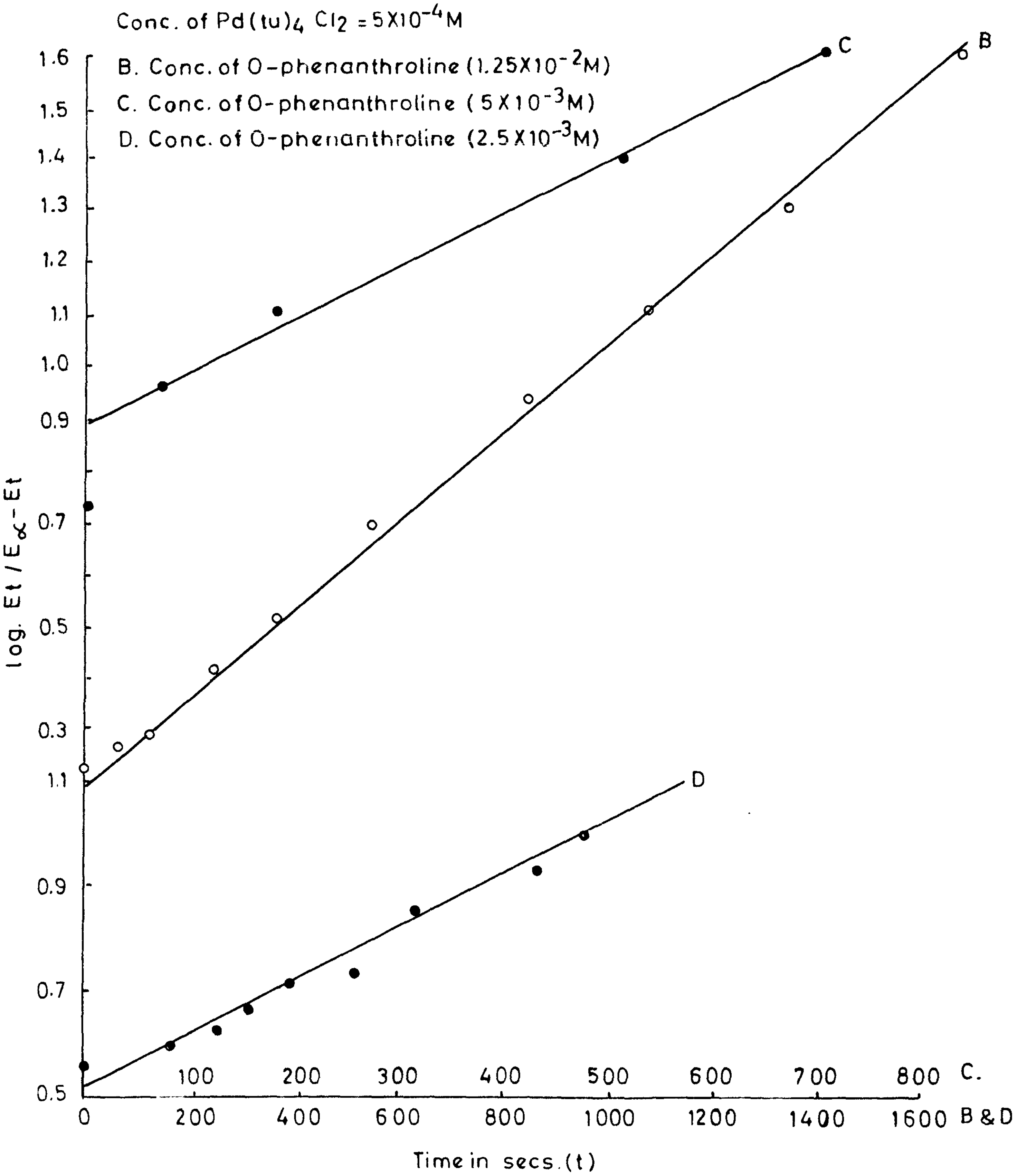


Fig.15 B, C and D

(Vide table 15B, C and D)

TABLE -15B:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + o-phenanthroline

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($2.5x10^{-2}$M)o-phenanthroline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ $sec.^{-1}$
0	80	0.231	
60	83	.2756	
120	84	.2908	
240	92	.4197	$1.97x10^{-3}$
360	98	.5288	
540	106	.7031	
840	114	.943	
1080	118	1.1177	
1350	121	1.3046	
1680	124	1.6163	
2280	127	-	

(Vide Fig.15B)

TABLE -15C:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$- o-phenanthroline

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($1x10^{-2}$M)o-phenanthroline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log \frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ $sec.^{-1}$
0	184	0.5572	
150	178	.5972	
240	174	.6277	
300	170	.6622	$1.15x10^{-3}$
390	164	.7234	
510	160	.7727	
630	154	.8653	
870	150	.9457	
980	147	1.0212	
1560	136	1.0921	
2490	133	-	

(Vide Fig.15C)

T A B L E -15D:

Potentiometric data for the first order rate law.

System: $[Pd(tu)_4]Cl_2$ + o-phenanthroline

25 ml.($1x10^{-3}$M) $[Pd(tu)_4]Cl_2$ + 25 ml.($5x10^{-3}$M)o-phenanthroline

Temp. = 35°C.

Time in Seconds	Potential, E (in m.V.)	$\log\frac{E_t}{E_\infty - E_t}$	$K_{obs.}$ sec.$^{-1}$
0	38	-0.1836	
90	40	.1461	
270	44	.0725	
390	46	.0362	
1110	54	+0.1092	6.9x10^{-4}
1530	56	.1461	
2010	64	.301	
2250	66	.3424	
2760	70	.43	
3090	72	.4771	
3570	76	.5798	
3690	78	.6368	
4410	80	.699	
5340	85	.8880	
5850	88	1.0414	
7230	92	1.3617	
8550	94	1.6721	
9570	96	-	

(Vide Fig.15C)

TABLE -16A:

Comparison of some rates of reactions of tetrakis(thiourea) palladium(II)chloride($5x10^{-4}$M in $1x10^{-1}$M KCl) with heterocyclic amines in aqueous solutions at 35°C.

Conc. of amines	$K_{obs.}$ sec.$^{-1}$	Figure and Table
py($5x10^{-2}$M)	$3.47x10^{-3}$	8 A
($2.5x10^{-3}$M)	$1,49x10^{-3}$	8 B
2 pic.($1,25x10^{-2}$M)	$6,90x10^{-3}$	9 A
($5x10^{-3}$M)	$5,75x10^{-3}$	9 B
($2,5x10^{-3}$M)	$2,15x10^{-3}$	9 C
3 pic.($2,5x10^{-2}$M)	$5.92x10^{-3}$	10 A
($1.25x10^{-2}$M)	$5.75x10^{-3}$	10 B
4 pic.($2.5x10^{-2}$M)	$6.32x10^{-3}$	11 A
($1.25x10^{-2}$M)	$3.77x10^{-3}$	11 B
2,4 L ($1,25x10^{-2}$M)	$7,76x10^{-3}$	12 A
($5x10^{-3}$M)	$7,66x10^{-3}$	12 B
($2.5x10^{-3}$M)	$1,47x10^{-3}$	12 C
2,6 L ($2.5x10^{-2}$M)	$6.9x10^{-3}$	13 A
($2.5x10^{-3}$M)	$6.9x10^{-3}$	13 B
dipy ($2.5x10^{-2}$M)	$1.15x10^{-3}$	14 A
($1.25x10^{-2}$M)	$1.15x10^{-3}$	14 B
o-phen.($2.5x10^{-2}$M)	$2.3x10^{-3}$	15 A
($1.25x10^{-2}$M)	$1.97x10^{-3}$	15 B
($5x10^{-3}$M)	$1.15x10^{-3}$	15 C
($2.5x10^{-3}$M)	$6.9x10^{-4}$	15 D

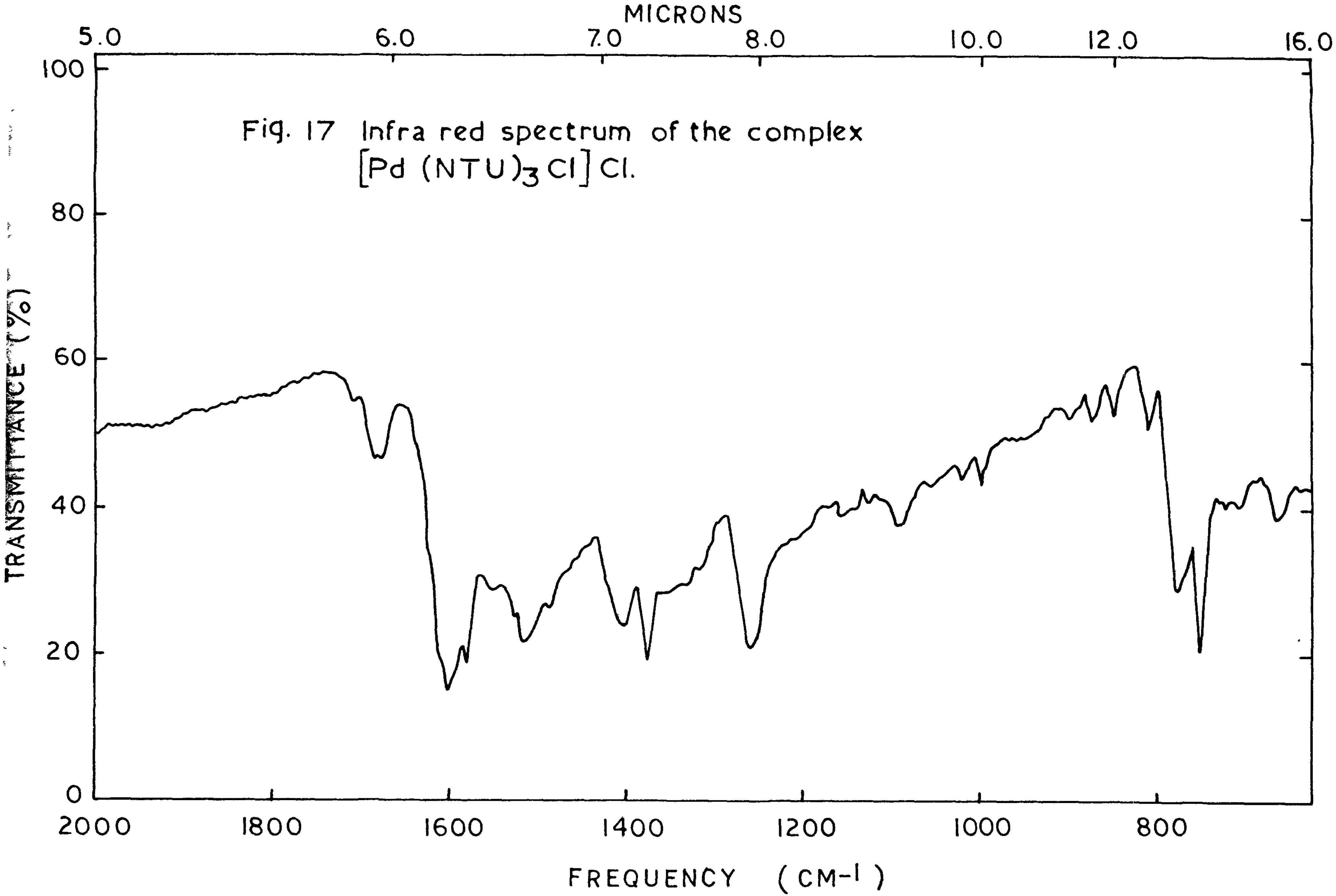


Fig. 17 Infra red spectrum of the complex
$[Pd(NTU)_3Cl]Cl$.

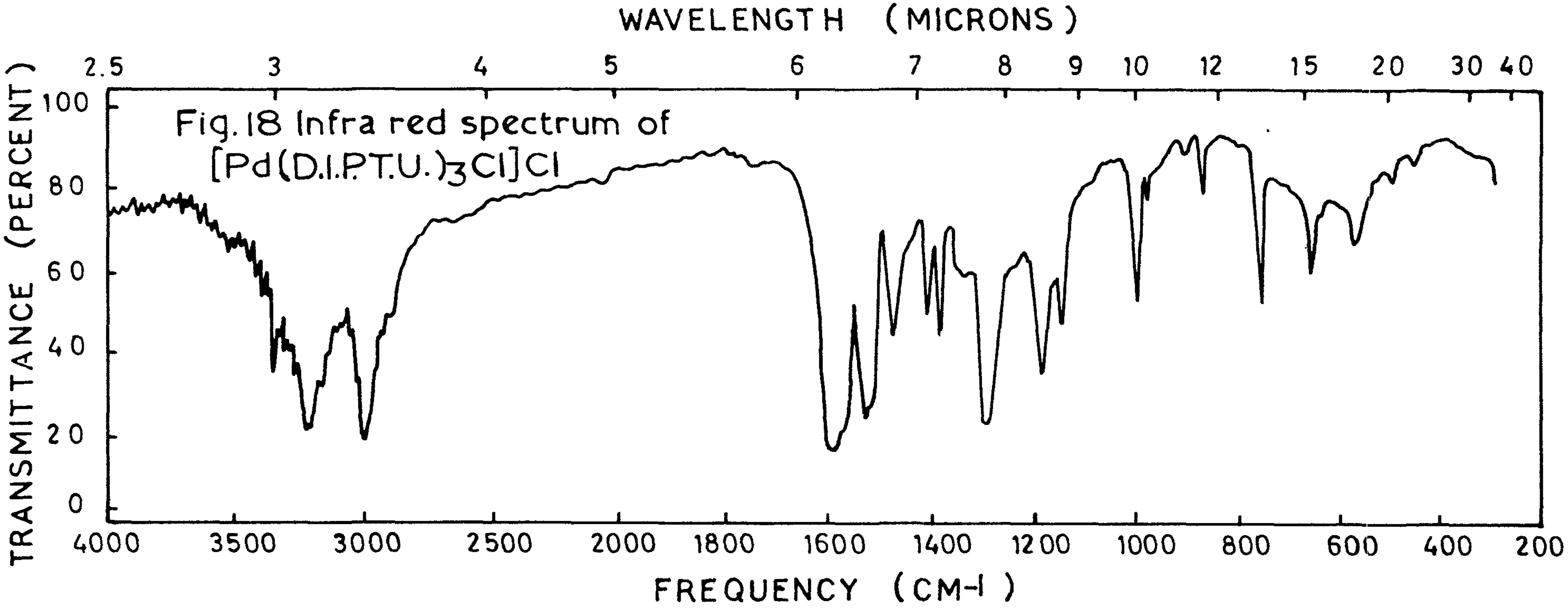


Fig. 18 Infra red spectrum of $[Pd(D.I.P.T.U.)_3Cl]Cl$

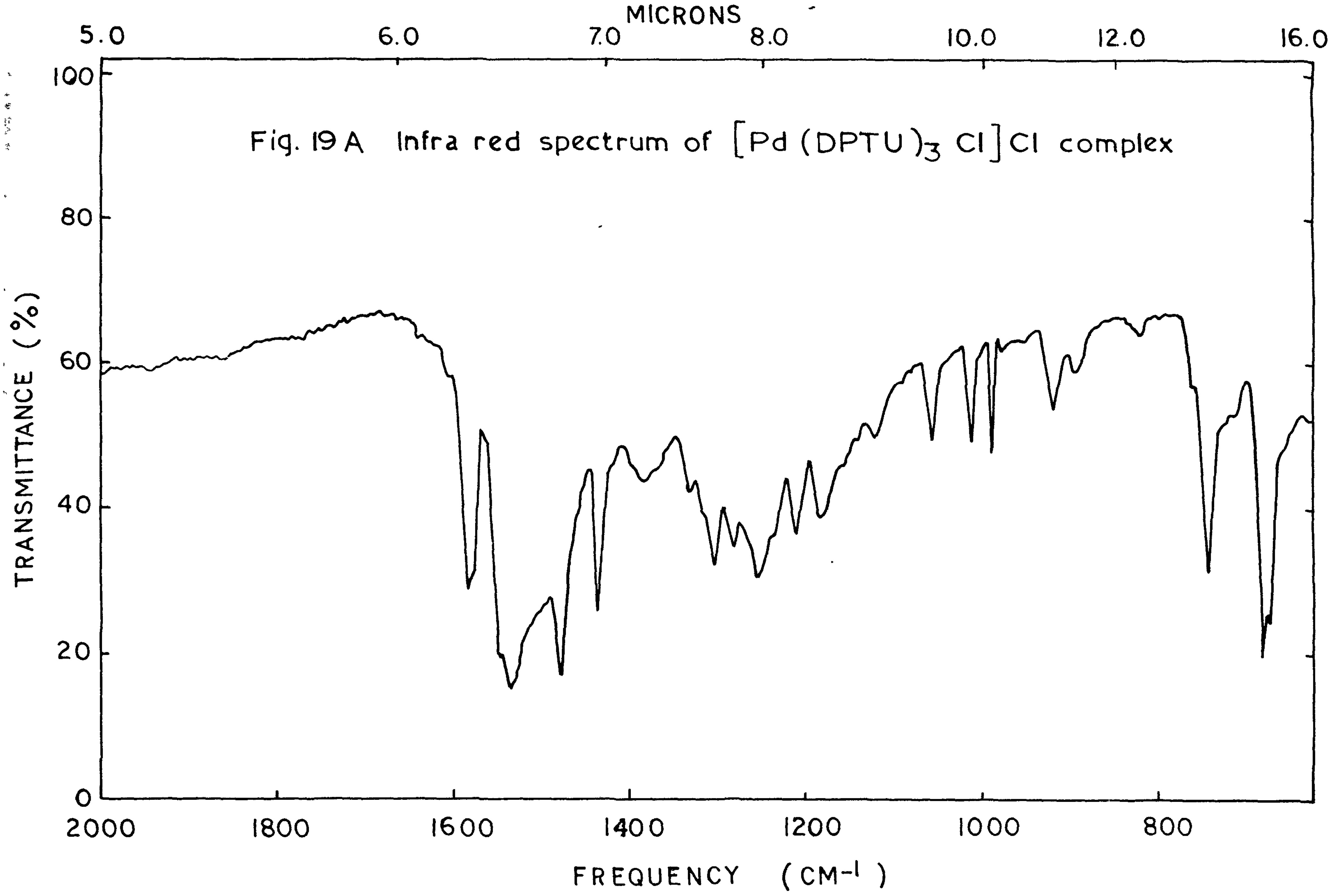


Fig. 19 A Infra red spectrum of $[Pd(DPTU)_3Cl]Cl$ complex

Infra red spectral data for palladium(II) complexes.

Infra red spectra of the complexes were taken with a Perkin Elmer 237 spectrometer, in the region 2.5 to 15 μ employing the standard KBr technique, using spectral grade KBr. Far infra spectra (16 to 40 μ) were recorded with a Perkin Elmer IR-10 spectrometer, using nujol mull films and CsI prism.

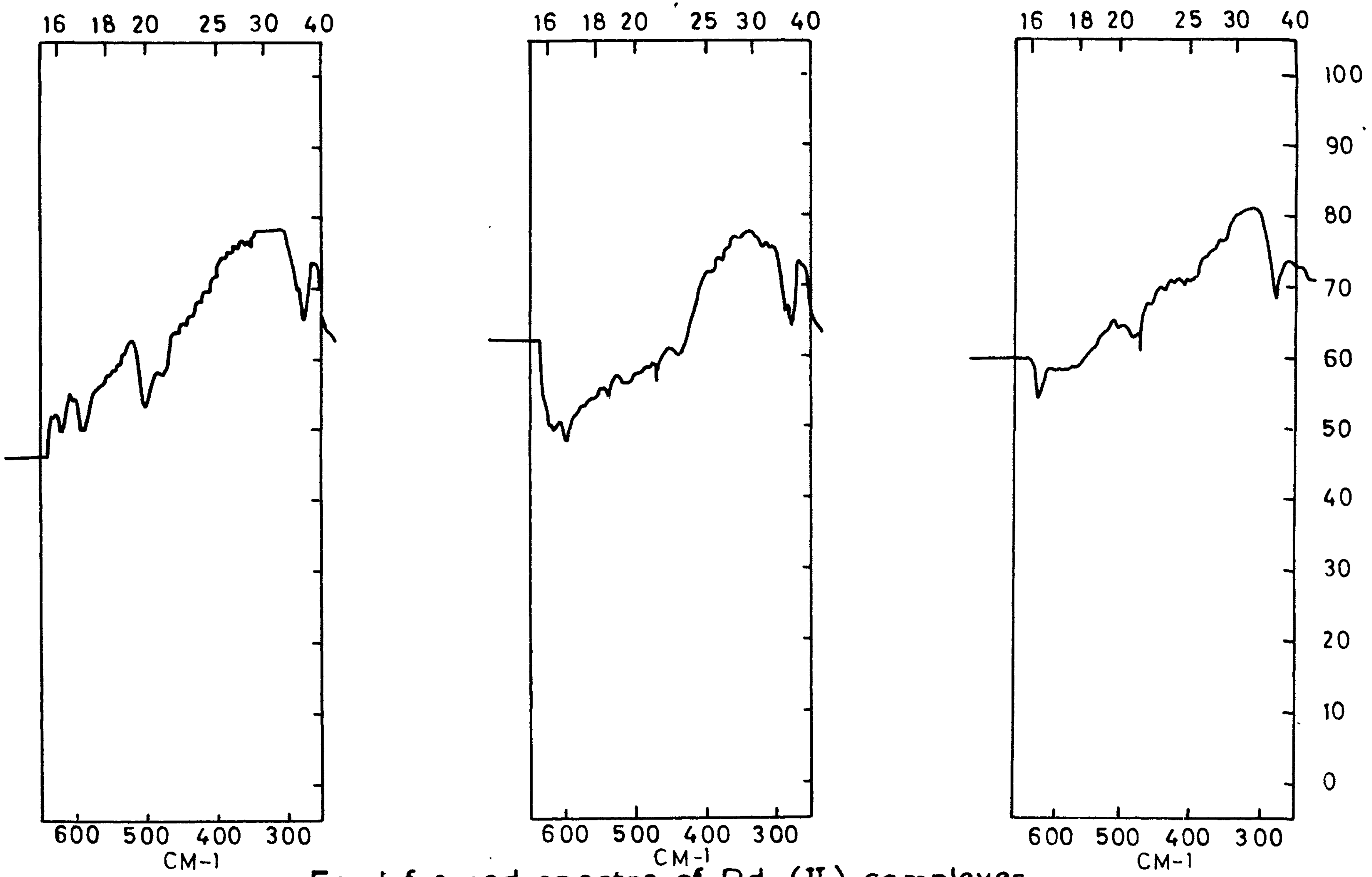
Following are the details of the spectral data of the various complexes:

1. $[Pd(NTU)_3Cl]Cl$: 280(s), 440(w), 540(w), 600(m), 620(m), 680(m), 775(s), 800(m), 825(m), 865(m), 920(w), 1020(m), 1100(b&m), 1275(s), 1390(s), 1420(b&m), 1540(b&m), 1600(m), 1620(s), 1690(m), 3020-3120(b&m), (Fig.17)

2. $[Pd(DIPTU)_3Cl]Cl$: 280(s), 430(w), 470(w), 575(m), 600(m), 650(m), 740(s), 850(m), 880(m), 950(m), 980(s), 1130(m), 1170(s), 1280(s), 1280(s), 1310(w), 1340(w), 1375(s), 1390(s), 1460(m&b), 1510(s), 1580(m&b), 1800(s), 3100(m), 3160(s). (Fig.18)

3. $[Pd(DPTU)_3Cl]Cl$: 280(s), 500(s), 590(s), 620(s), 630(m), 700(s), 760(s), 850(w), 920(w), 940(m), 1010(s), 1040(s), 1080(s), 1150(w), 1200(m), 1230(m), 1270(m&b), 1300(m), 1320(m), 1360(w), 1380(s), 1400(w), 1460(s), 1490(s), 1550(m), 1600(s), 2900(w), 3200(b&m) and 3200(s). (Fig.19A and 19B)

4. $[Pd(TTU)_3Cl]Cl$: 280(s), 440(w), 470(w), 540(w), 600(m), 620(m), 630(m), 680(m), 720(m), 770(s), 790 (s), 1020(m), 1100(m),



For Infra red spectra of Pd (II) complexes

Figures.19 B: $[Pd(D.P.T.U)_3Cl]Cl$, 20 B: $[Pd(T.T.U)_3Cl]Cl$ and 23 B: $[Pd(tu)_2o\text{-}phen]Cl_2$

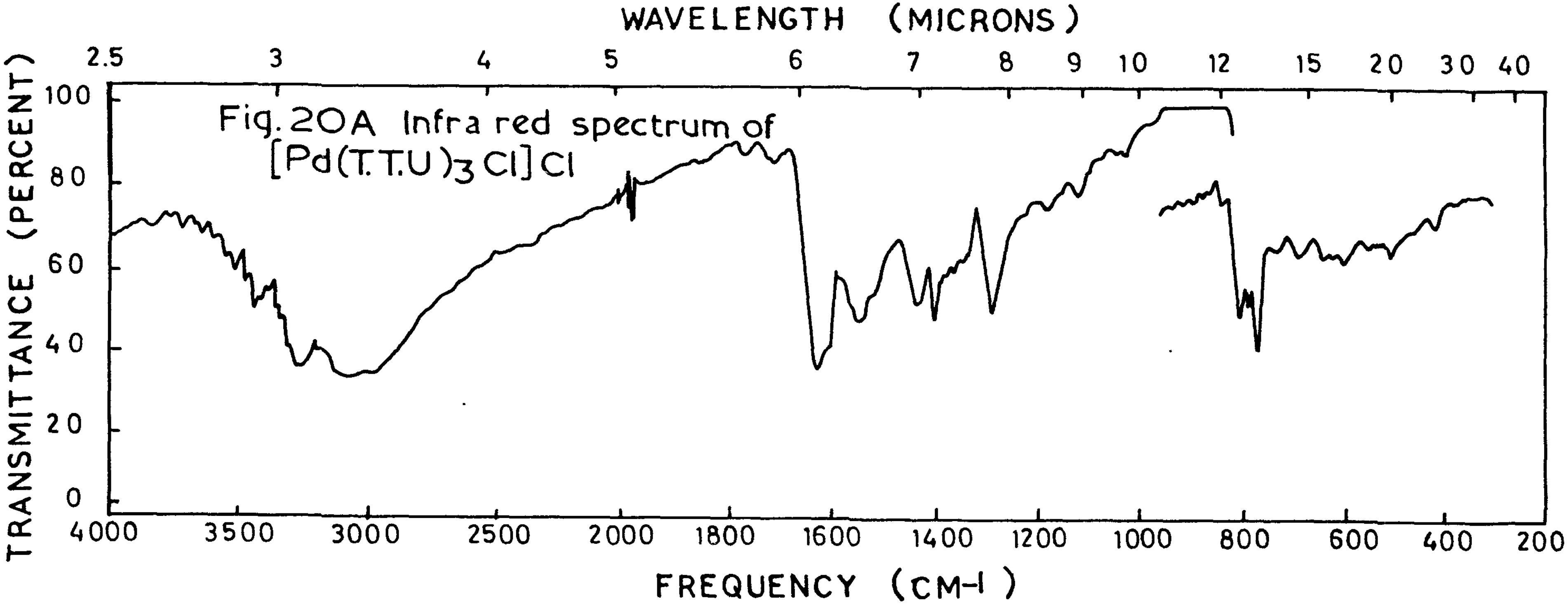


Fig. 20A Infra red spectrum of $[Pd(T.T.U)_3Cl]Cl$

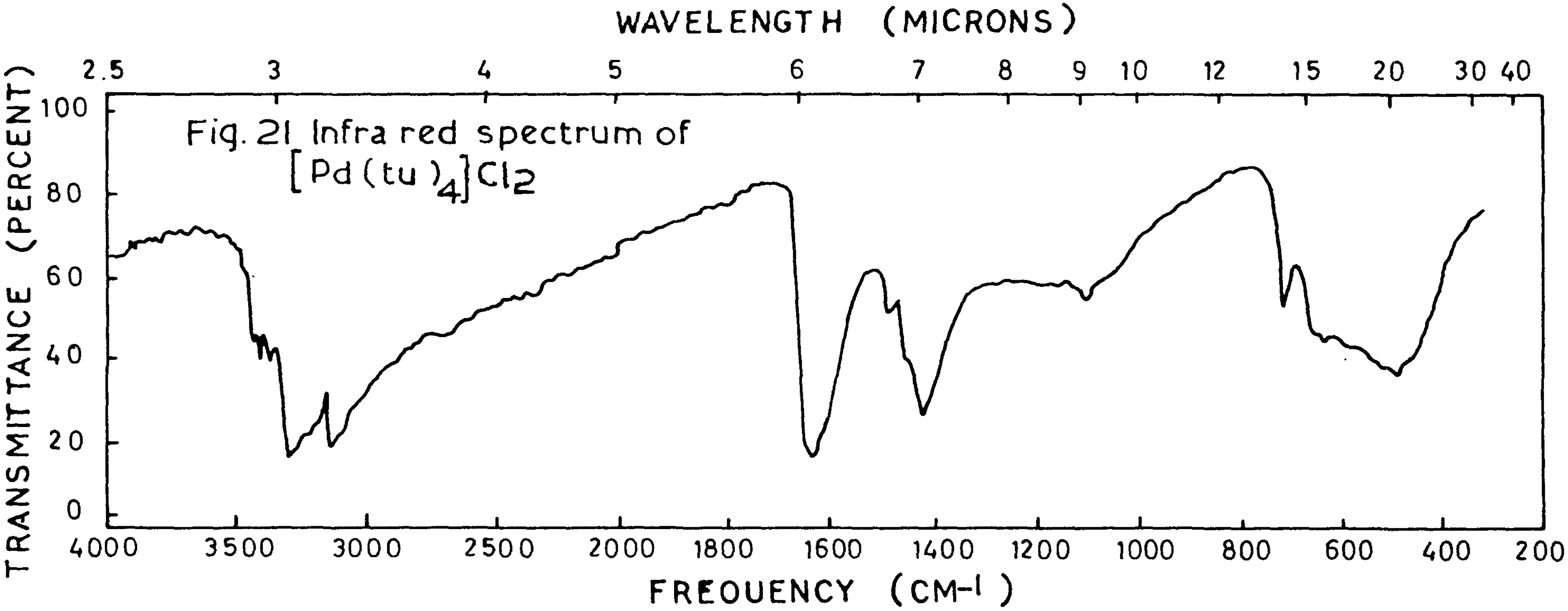


Fig. 21 Infra red spectrum of $[Pd(tu)_4]Cl_2$

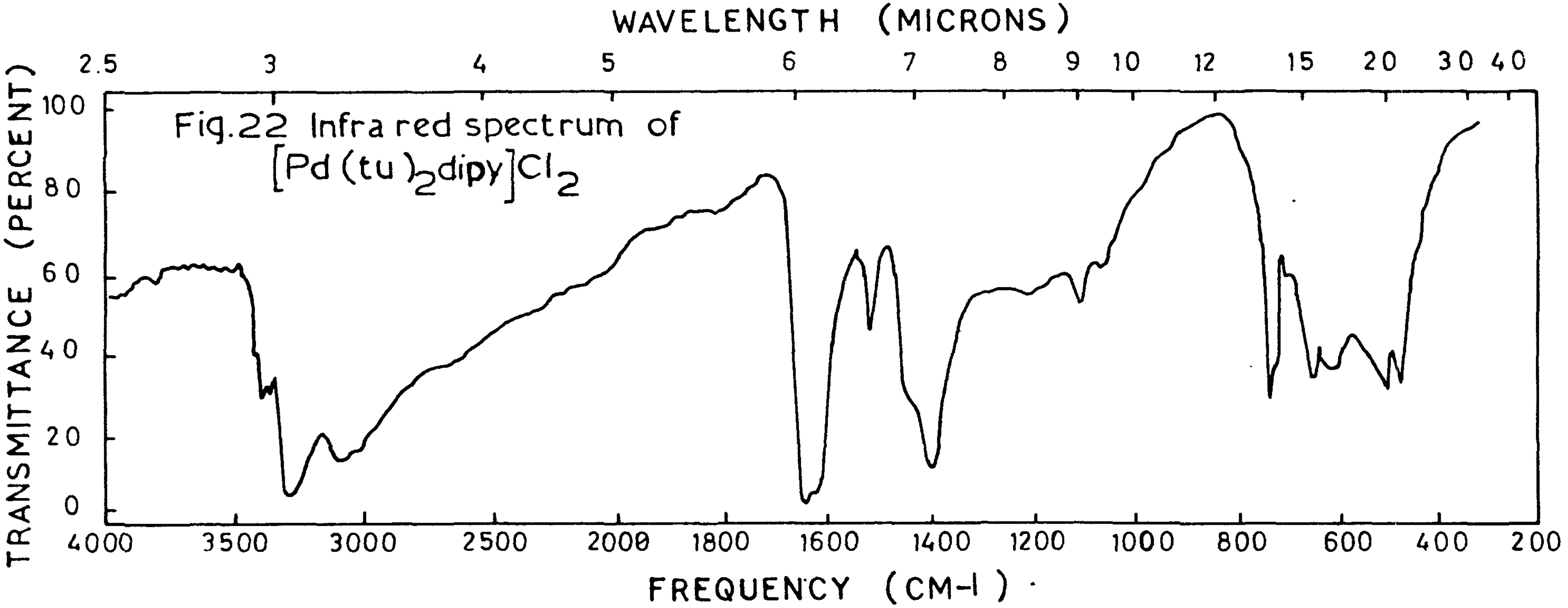


Fig.22 Infrared spectrum of $[Pd(tu)_2dipy]Cl_2$

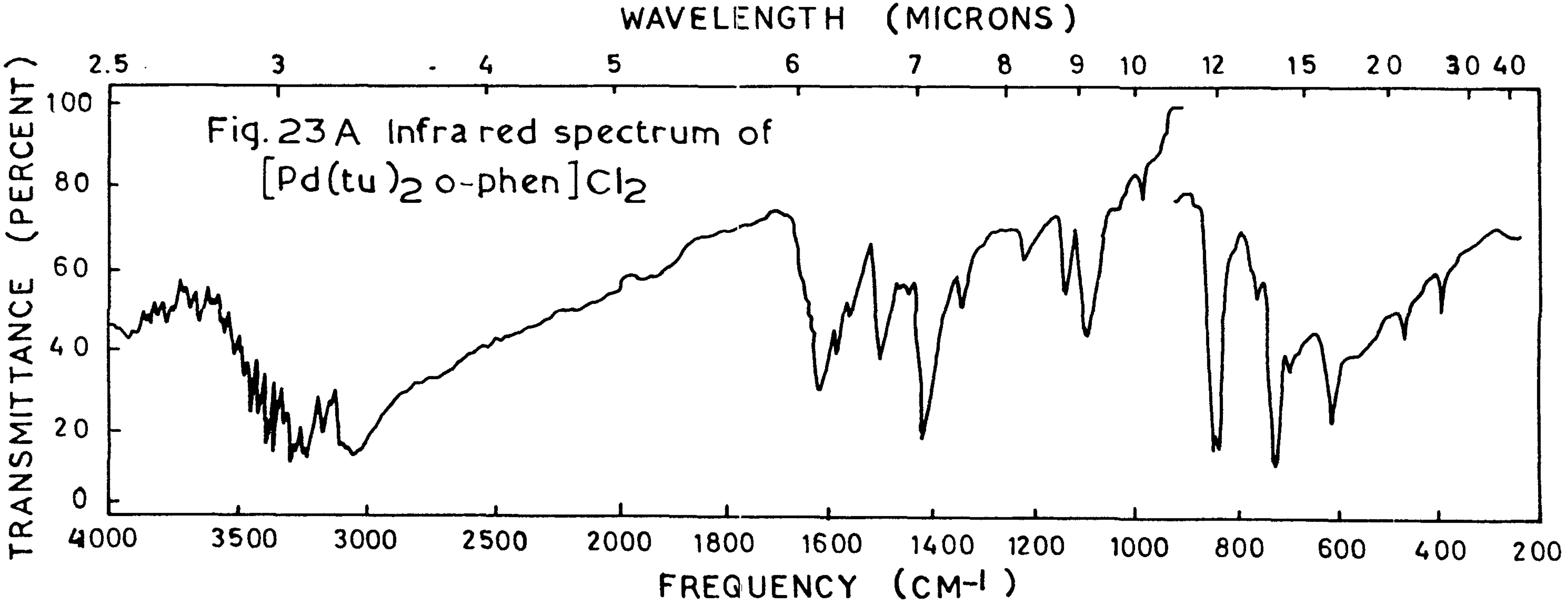


Fig. 23A Infrared spectrum of $[Pd(tu)_2\,o\text{-}phen]Cl_2$

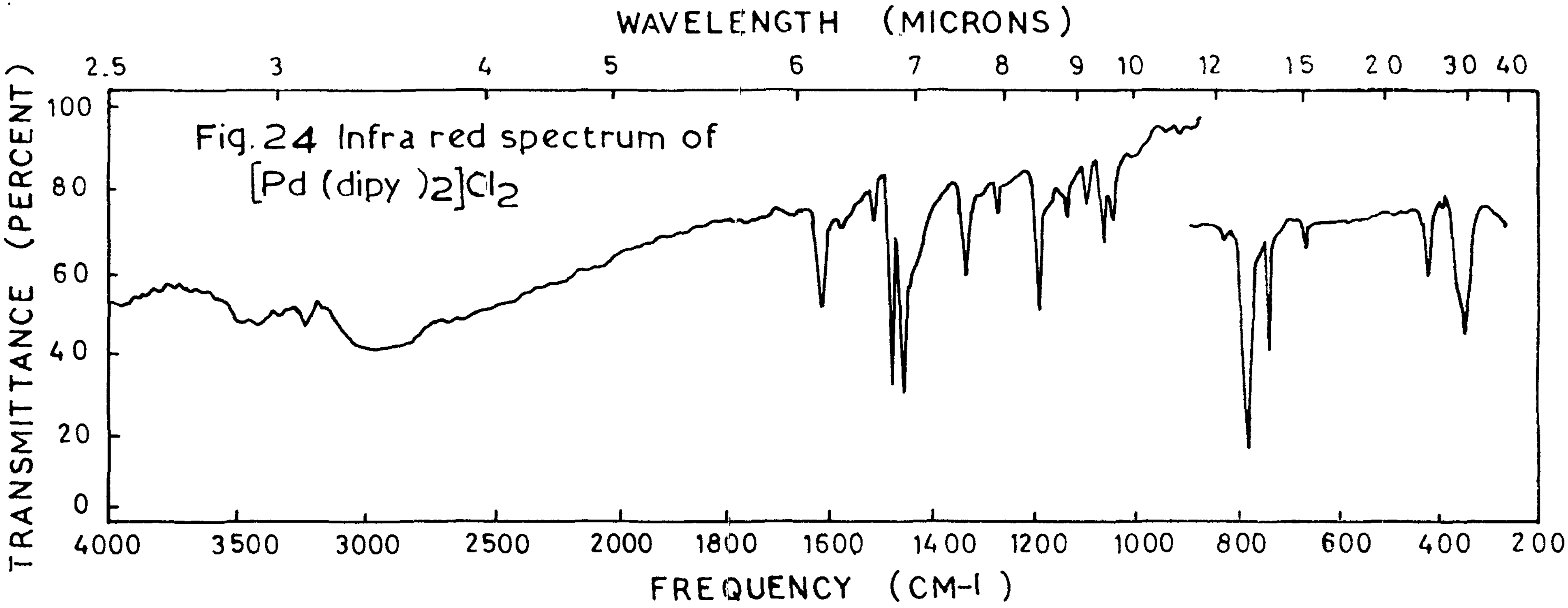


Fig. 24 Infra red spectrum of $[Pd(dipy)_2]Cl_2$

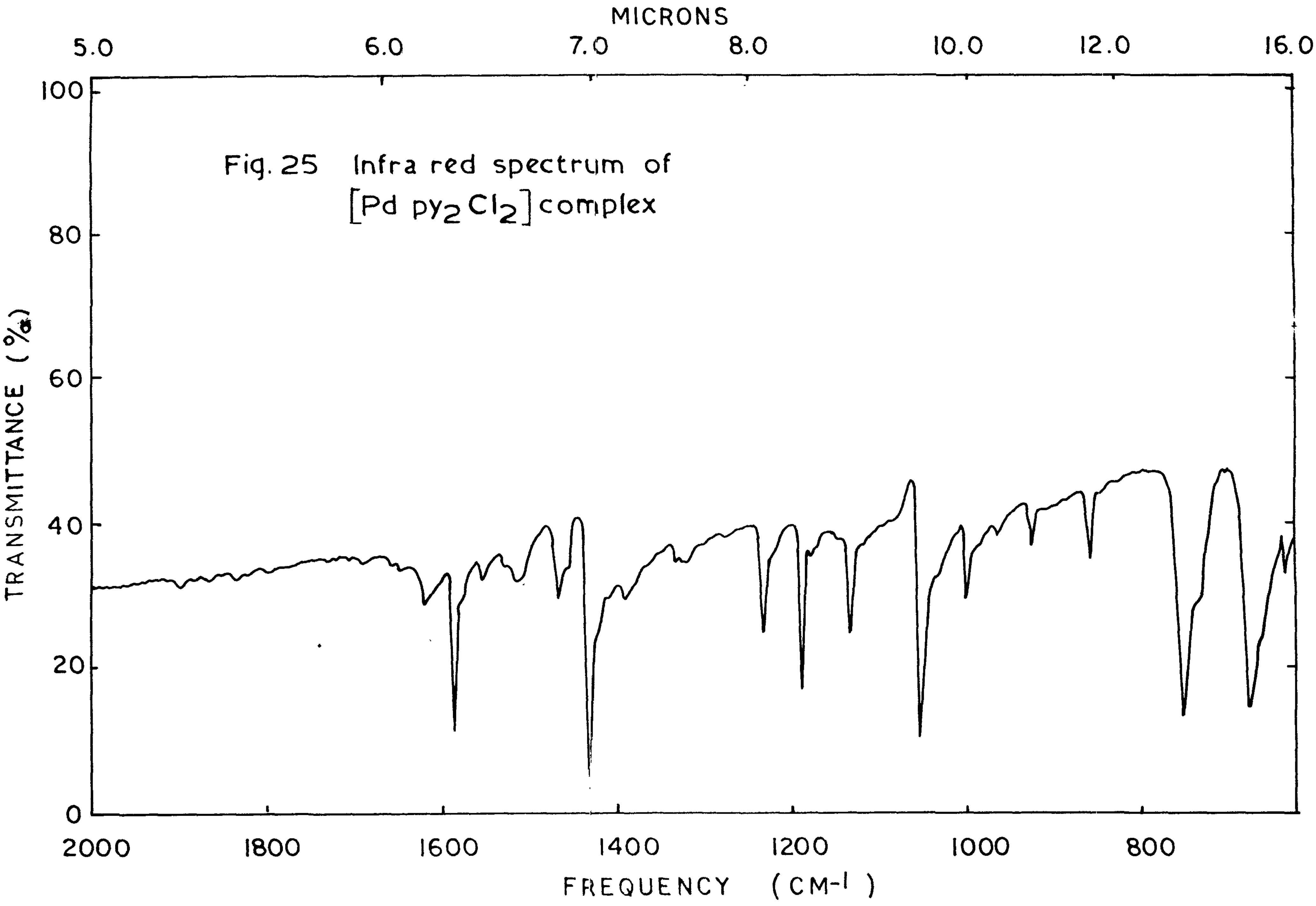


Fig. 25 Infra red spectrum of $[Pd\ py_2Cl_2]$ complex

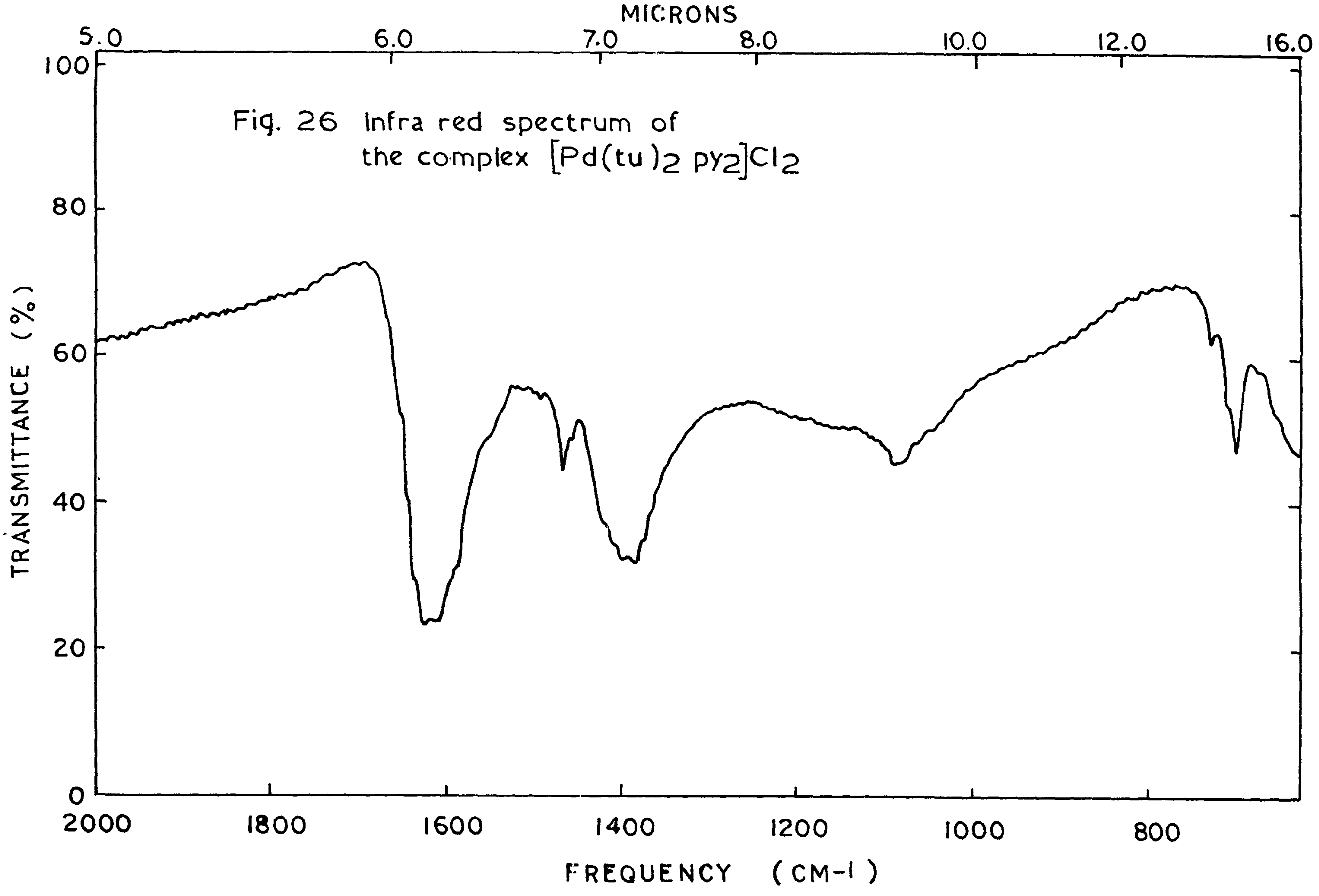


Fig. 26 Infra red spectrum of the complex $[Pd(tu)_2 py_2]Cl_2$

1170(m), 1270(s), 1390(s), 1430(b&m), 1530(s), 1610(s&b), 2920(m), 3030(b&m), 3220(m). (Fig.20A and 20B)

5. $[Pd(tu)_4]Cl_2$: 280(s), 480(s), 580(m), 670(m), 700(s), 1100(m), 1300(s), 1430(w), 1610(m&b), 1630(s), 3050(s), 3130(s). (Fig.21)

6. $[Pd\ py_2Cl_2]$: 660(m), 700(s), 880(s), 950(m), 990(w), 1030(m), 1075(s), 1260(m), 1335(w), 1350(w), 1405(w), 1450(s), 1485(m), 1530(m), 1570(m), 1605(s), 1635(m). (Fig.25)

7. $Pd(tu)_2py_2\ Cl_2$: 280(s), 470(sh), 610(s), 700(s), 730(w), 1085(w&b), 1380(m&b), 1470(s), 1630(s&b), 1720(m&b). (Fig.26)

8. $[Pd(tu)_2dipy]Cl_2$: 275(s), 490(s), 530(m), 600(m), 640(m), 730(v.s), 1060(w), 1100(m), 1390(s&b), 1510(s), 1610-1630(m&b). (Fig.22)

9. $[Pd(tu)_2(o\text{-}phen)]Cl_2$: 275(s), 430(m), 470(sh), 480(w), 500(w), 530(m), 645(m), 650(m), 730(m), 740(s), 790(m), 800(m), 870(s), 880(s), 990(m), 1050(w), 1110(s), 1150(s), 1240(m), 1360(m), 1430(s), 1445(w), 1465(w), 1500(s&b), 1560(m), 1580(m), 1620(s&b). (Fig.23A and 23B)

10. $[Pd(dipy)_2]Cl_2$: 360(s), 430(s), 670(w&b), 730(s), 890(w), 910(w), 1025(w), 1050(m), 1085(m), 1120(m), 1170(s), 1250(m), 1320(s), 1460(v.s), 1475(v.s), 1510(m), 1570(w), 1600(s). (Fig.24)

Infra red spectra of palladium(II) complexes:

The infra red spectra of the substituted thiourea and respective Pd(II) complexes were studied in the region 2.5 to 40 μ (Fig.17 to 20).

The spectra of the complexes generally show two strong bands associated with N-H stretching vibrations in the region, 3200-3500 cm.$^{-1}$ There is no significant shifting of these bands by coordination. Quagliano et al.[27] while studying i.r. spectra of metal-urea complexes found the splitting of these bands in nitrogen coordinated complexes but there were little changes in the spectra of oxygen coordinated complexes. By analogy, bonding through sulphur is inferred in Pd(II) complexes on the basis of non splitting of bands in this region (3200-3500 cm^{-1}).

The B_1, N-C-N stretching modes found near 1500 cm^{-1} in the substituted thioureas (1475 cm^{-1} in thiourea), show marked changes in the spectra usually with an increase of 10-35 cm^{-1}, because of the increased double bond character of C-N bond, this is illustrated by the following data;

tu 1475(1510), DIPTU 1520(1555), TTU 1520(1530)
NTU 1520(1530), DPTU(1510).

(The figures in brackets are given for the complexes).

The three strong bands (A_1modes) ca.1400 cm^{-1}, 1100 cm^{-1} and 700-750 cm^{-1} observed in substituted thioureas are attributed to NH_2 rocking, C-N, and C-S stretching modes. Coordination through sulphur will lead to decrease in C-S stretching and increase in C-N stretching frequencies. According to Oliff,[28] the experimental frequencies will result from 'hybrids of 3 modes' and the effect of coordination on the frequency will depend on their weighting in each hybrid. The bands ca.1100 cm^{-1} can rightly be assigned as the bands having major contributions from C-N stretching modes. The bands are slightly shifted to higher wave numbers in the complexes: tu 1090(1100), DIPTU 1120 (1130), TTU 1090(1100), NTU 1035(1100) and DPTU 1075(1080). The bands ca.700-750 cm^{-1} may be assigned to C-S stretching vibrations, there is a decrease in frequencies on coordination, e.g., tu 735 (700), DIPTU 750 (740), and TTU 760(720). However, the bands at 775 cm^{-1} and 760 cm^{-1} observed in NTU and DPTU respectively, remain unshifted by coordination. This may be explained on considering the order of nucleophilities of the substituted thioureas[29]

tu > DIPTU > TTU > NTU > DPTU

A glance on the data, given above for the various modes shows an interesting behaviour, a gradual decrease in

C-S stretching vibrations and increase in N-C-N stretching modes, an indication of lesser tendency to coordinate through sulphur as we move from tu to DPTU. Apparently, this factor would be responsible to produce either small changes or no changes in N-C-N stretching and C-S stretching modes of DPTU and NTU complexes. The data given in the following table clearly illustrate this point:

	tu	DIPTU	TTU	NTU	DPTU
N-C-N str. vibrations(B_1 modes):	+36cm^{-1}	+35	+10	+10	nil
C-S str. vibrations(A_1 modes):	-35cm^{-1}	-10	-40	nil	nil

The most conclusive evidence regarding coordination through sulphur is obtained on observing a strong band at 275-280 cm^{-1} in all the substituted thiourea complexes, this band may be rightly assigned to metal-sulphur bond.

<u>Infra red spectra of mixed ligand complexes of palladium(II):</u>

The infra red spectra of the mixed ligand complexes show some marked changes resulting by the introduction of heterocyclic amine in the coordination sphere of $[Pd(tu)_4]Cl_2$. The spectra of the complexes e.g., $[Pd(tu)_2py_2]Cl_2$, $[Pd(tu)_2dipy]Cl_2$ and $[Pd(tu)_2o\text{-}phen]Cl_2$ were studied by comparing with those of the substituent ligands (amines), thiourea, $[Pd(tu)_4]Cl_2$ and corresponding palladium (II)-amines complexes. In general, coordination through amines is indicated by the observed changes in the bands near 1600 cm^{-1} (ring CC, CN stretching vibrations) and near 800 cm^{-1} (CH out of plane deformation modes), whereas the coordinated thiourea bands are marked by the changes in B_1 (N-C-N stretchings) and A_1 (NH_2 rocking, C-N stretchings and C-S stretchings) modes. The infra red spectra of mixed sulphur and nitrogen ligated complexes are distinguished from the corresponding amine and thiourea complexes by their simplicities while retaining the characteristics bands due to the coordinated ~~amine and~~ thiourea.

In the complex, $[Pd(tu)_2\,py_2]Cl_2$, the absorption bands observed ca. 1600 cm^{-1}, corresponding to ring CC, CN stretching vibrations of free pyridine (1635, 1600, 1485 and 1440 cm^{-1}), are greatly reduced in number but shifted to higher frequencies (1720, 1630, 1470 cm^{-1}) but in contrast, the complex, $[Pdpy_2Cl_2]$ shows bands at 1635, 1605, 1570, 1530, 1485 cm^{-1}. This indicates the possibility of band splitting, and as well as shifting to higher frequencies in metal pyridine complex, however, the presence of thiourea in the coordination sphere largely reduced the number of bands. The bands at 1630 cm^{-1} and

1470 cm^{-1} in the complex, $[Pd(tu)_2py_2]Cl_2$, may also be atributed to NH_2 banding and N-C-N stretching modes of coordinated thiourea which are observed at 1630 cm^{-1} and 1475 cm^{-1} in free thiourea. This indicates the almost non shifting of the bands at 1475 cm^{-1} in the mixed ligand complex which otherwise shifted to higher frequency (1510 cm^{-1}) in the complex, $[Pd(tu)_4]Cl_2$. By these observations, it implies that due to the introduction of pyridine molecule, the C-N bond weakend and C-S bond strengthened in the substituted complex, $[Pd(tu)_2py_2]Cl_2$. The band observed at 1035 cm^{-1} in the complex, $[Pd(tu)_2py_2]Cl_2$, corresponds to C-N stretching vibrations of thiourea observed at 1090 cm^{-1} (1100 cm^{-1} in $[Pd(tu)_4]Cl_2$). The bands observed ca. 800 cm^{-1} are assigned to CH out of plane deformation vibrations of pyridine (700, 745, 810 cm^{-1}). In the complex, only two bands 730(w) and 700(s) are observed whereas in the complex, $[Pdpy_2Cl_2]$, these bands occur at 700, 775 and 830 cm^{-1} showing thereby the shifting of the bands to higher wave numbers on coordination through heterocyclic nitrogen. The presence of thiourea molecule reduced the number of bands in the substituted complex (cf. 1600 cm^{-1}) to two (730, 700 cm^{-1}), the weak band at 730 cm^{-1} may also be called a corresponding band of coordinated thiourea (obsd. at 735 in free tu and 700 cm^{-1} in $Pd(tu)_4Cl_2$) which is shifted only to 5 cm^{-1} to the lower side in the substituted complex whereas in $Pd(tu)_4Cl_2$, the observed decrease is about 35 cm^{-1} (Cf. 1600 cm^{-1}). These observations support the view that there is considerable strengthening of C=S bond and weakening of C-N double bond on substitution by pyridine in the complex, $[Pd(tu)_4]Cl_2$, which otherwise contains a Pd-S covalent bond of considerable strength.

T A B L E -17:

Effect of substitution on the i.r. frequencies of the spectra of Pd(II) complexes.

Thiourea: 1630^a, 1475^b, 1090^c, 735^d

$Pd(tu)_4Cl_2$: 1630^a, 1510^b, 1100^c, 700^d

pyridine: 1635^e, 1600^e, 1485^e, 810^f, 745^f, 700^f

$Pd(py)_2Cl_2$: 1635^e, 1605^e, 1670^e, 1630^e, 1485^e, 1450^e
880^f , 775^f , 700^f

$Pd(tu)_2py_2Cl_2$: 1720, 1630, 1470, 1035, 730, 700

a: NH_2 bending, b: N-C-N stretching, c: C-N stretching, d: C-S stretching, e: ring CC,CN stretching, f: CH out of plane deformation.

Like $[Pd(tu)_2py_2Cl_2]$, it is difficult to have a distinction between coordinated thiourea and dipyridyl in certain regions but the changes taking place due to the presence of coordinated thiourea are more obvious in $[Pd(dipy)(tu)_2]Cl_2$ than the corresponding pyridine complex. For example, the broad band (1610-1630 cm^{-1}) in the substituted complex must be a combination band arising from NH_2 bending vibrations (observed at 1630 cm^{-1} in tu and $Pd(tu)_4Cl_2$) and ring CC,CN stretching vibrations. The strong band at 1510 cm^{-1} observed in the complexes, $[Pd(dipy)(tu)_2]Cl_2$, $[Pd(dipy)_2]Cl_2$ and $[Pd(tu)_4]Cl_2$ may be assigned either to N-C-N band of coordinated thiourea or ~~ring (CC,CN) stretching vibrations of coordinated dipyridyl.~~ On coordination, dipyridyl bands split as observed from the i.r. spectrum of the complex, $[Pd(dipy)_2]Cl_2$ having bands at 1600, 1570, 1510, 1475, 1466 cm^{-1}/corresponding to 1580, 1470 and 1430 cm^{-1}/in free dipyridyl, in the region ca. 1600 cm^{-1}, with a marked increase in wave numbers- a characteristic of the coordinated dipyridyl. However, in the complex, $[Pd(dipy)(tu)_2]Cl_2$, the number of bands are greatly reduced, an observation also noted in case of corresponding pyridine complexes. A medium band at 1100 cm^{-1} is obviously corresponded to C-N stretching vibrations of coordinated thiourea (1090 cm^{-1} in free tu and 1100 cm^{-1} in $Pd(tu)_4Cl_2$). Similarly, the bands in the region ca. 800cm^{-1} are attributed to CH out of plane deformation vibrations of dipyridyl (730, 760, 890) cm^{-1} which split on coordination as observed in the spectrum of the complex, $[Pd(dipy)_2]Cl_2$, however, in the complex $[Pd(tu)_2(dipy)]^{++}$, only one band at 730 cm^{-1} is noted (Cf. $Pd(tu)_2py_2\ Cl_2$), the latter may also be assigned to the band arises from coordinated thiourea (observed at 700 cm^{-1} in $[Pd(tu)_4]Cl_2$) which is shifted slightly to the lower frequency by 5 cm^{-1} (free tu: 735 cm^{-1}). These observations lead to the conclusion that there is considerable strengthening of C=S bond and weakening of C=N bond on dipyridyl substitution in tetrakis thiourea palladium(II) chloride complex.

The spectrum of bis(thiourea) mono(o-phen) palladium(II) chloride is marked by a number of bands in the region ca. 800 cm^{-1}, a situation not observed in case of corresponding pyridine and dipyridyl complexes. The bands observed at 730, 740, 790, 800, 870, 880 cm^{-1} are obviously the splitted bands of coordinated o-phenanthroline (observed at 740, 775, 860 cm^{-1} in the free ligand). The bands at 1600, 1590, 1540, 1470 cm^{-1} observed in o-phenanthroline are shifted to higher frequencies e.g., 1620, 1580, 1560 1500 cm^{-1} and are of greater intensities in the substituted complex. The bands at 1620, 1500, 1110 and

730 cm^{-1} may also be assigned to coordinated thiourea bands of NH_2 bending, N-C-N str., C-N str., and C-S str. vibrations respectively, observed at 1630, 1475, 1090 and 735 cm^{-1} in free thiourea and at 1630, 1510, 1100 and 700 cm^{-1} in the complex, $[Pd(tu)_4]Cl_2$.

An examination of the results obtained from i.r. spectrum of $[Pd(o\text{-}phen)(tu)_2]Cl_2$ complex indicates the possibility of strong coordination by heterocyclic nitrogens of o-phenanthroline to the metal as well as a weak bonding through sulphur of thiourea which results in the strengthening of C=N bond but weakening of C=S bond.

The far infra red spectra of the complexes studied in the range 16 to 40 μ exhibit a strong band at 275 cm^{-1} in all the three complexes besides the bands at 610(s), 500(w), 480(w), 470 cm^{-1}(sh). The strong band at 275 cm^{-1} can undoubtly be assigned to that arising from metal-sulphur stretches.

The following conclusions may be drawn from the results obtained by the study of the infra red spectra of the complexes:

(i) It is difficult to make distinction between coordinated thiourea and coordinated amines bands particularly in the regions: ca.1500 cm^{-1} and ca.800 cm^{-1}.

ii) In the substituted complexes, $[Pd(tu)_2py_2]Cl_2$ and $[Pd(tu)_2dipy]Cl_2$, the coordination through amines is indicated by the increase in frequencies and decrease in the number of bands whereas in Pd(II) amines complexes, e.g., $[Pd(py)_2Cl_2]$ and $[Pd(dipy)_2]Cl_2$, splitting of the bands take place together with shifting to higher wave numbers.

(iii) In the substituted complex, $[Pd(tu)_2\ o\text{-}phen]Cl_2$, there is splitting of bands similar to that observed in $[Pd(o\text{-}phen)_2]Cl_2$ complex together with increase in frequencies.

(iv) Chifting of frequencies (increase in N-C-N str. and C-N str. vibrations and decrease in C-S str. vibrations) is less obvious in substituted complexes in comparison to the tetrakis (thiourea) palladium(II) chloride complex. This is an indication of relative strengthening of C=S bond and weakening of C=N, bond.

(v) The observed splitting in o-phenanthroline complex, $[Pd(tu)_2o\text{-}phen]Cl_2$, may be attributed to the stronger coordination of the metal to the ligand (o-phenanthroline) in comparison to the corresponding pyridine and dipyridyl complexes.

(vi) The strong band at 275-280 cm^{-1} in all the substituted complexes iS an indication of the presence of a Pd-S bond.

RESULTS AND DISCUSSION

Palladium(II) chloride forms 1:3 complexes with substituted thioureas, e.g., naphthyl thiourea (dark orange), o-tolyl thiourea (brownish red), diisopropyl thiourea(orange) and diphenyl thiourea (dark orange). The complexes are insoluble in water, soluble in alcohol but highly soluble in acetone and chloroform. The analysis of the complexes indicates the presence of one ionizable chloride ion thus giving evidence of the formation of tetracoordinated species, $[Pd(L)_3Cl]^+$, where L = substituted thiourea. The presence of three substituted thiourea molecules in the coordination sphere, however, may be explained on considering the large size of the ligand which is a hindering factor for accomodating more than 3 molecules of the substituted thiourea, however, to achieve its tetracovalency one chloride ion is attached to the central metal ion (Pd^{2+}). The enterance of Cl^- ion in the coordination sphere is entirely nucleophilic, this is enhanced by the d orbital contraction as a result of increased positive charge on the complex.

All attempts to prepare allyl thiourea complex failed as the end product was an oily mass which was difficult to be dried.

The infra red spectra of the complexes give some interesting information regarding the coordinating tendencies of various substituted thioureas. A gradual increase in N-C-N stretchings and decrease in C-S stretchings are observed as we move from thiourea to diphenyl thiourea which is in conformity with the nucleophilic order[29] of substituted thioureas, viz., tu > DIPTU > TTU > NTU > DPTU. These observations led to the conclusion that there is decreasing tendency to coordinate through sulphur with decreasing nucleophilities of substituted thioureas. The presence of a strong band at 275-230 cm^{-1} in all the complexes is indicative of the presence of a metal-sulphur bond in the substituted thioureas complexes.

The syntheses of the following mixed ligand complexes were achieved: $[Pd(tu)_2py_2]Cl_2$ (brown crystals); $[Pd(tu)_2dipy]Cl_2$ (pink crystals), and $[Pd(tu)_2o\text{-}phen]Cl_2$, (orange crystals). The complex, $[Pd(tu)_2py_2]Cl_2$, was prepared by the action of pyridine on the complex, $[Pd(tu)_4]Cl_2$. The complex, $[Pd(tu)_2py_2]Cl_2$, should undoubtly be a cis-isomer as tu has a greater trans directing influence than does py, substitution of py into $[Pd(tu)_3\ py]^{++}$ is least likely to occur in position trans to py already present and thus cis isomer is favoured.

The formation of dipyridyl and o-phenanthroline substituted Pd(II) thiourea complexes may be discussed on considering two important characteristics of these reagents. Firstly, their effectiveness to form strong metal to π bonds, ($d_\pi - p_\pi$) due to the availability of partially empty p orbitals and secondly, perhaps more important are their strong nucleophilic characters which enable them (dipyridyl and o-phenanthroline) to enter into the coordination sphere by a nucleophilic substitution.

The spectrophotometric method was applied to determine the composition of the complex formed by the interaction of pyridine with $Pd(tu)_4Cl_2$. From the plots of Job's method of continuous variation (Table 1A Fig. 1A), a combining ratio of 1 ($Pd(tu)_4Cl_2$): 2(pyridine) is obtained indicating thereby the formation of the substituted complex, $[Pd(tu)_2py_2]Cl_2$.

The plots of log $\frac{A_a - A_0}{A_\infty - A_a}$ versus log X, for the pyridine system using the equation, log $\frac{A_a - A_0}{A_\infty - A_a}$ = log K_f + n log X, for an equlibrium mixture involving two complexes: $Pd(L)_4^{2+} + n\ X \rightleftharpoons Pd(L)_4\ X_n$ (for details see experimental part), gave straight lines with unity slopes and the values of the formation constants, K_f, for the equilibrium:

$[Pd(tu)_4]Cl_2 + py$ —— $[Pd(tu)_4py]^{++}$ were found to be 2.917 and 2.818 at 20°C and 25°C, respectively (table and Fig. 7A and 7B).

The main characteristics of the infra red spectrum of the complex, $[\mathrm{Pd\ tu_2py_2}]\mathrm{Cl_2}$, discussed in details earlier, are namely the reduction in the number of bands and shifting to higher frequencies in the regions: ca. 1600 $\mathrm{cm^{-1}}$ (ring CC, CN str. vibrations of free pyridine, $\mathrm{NH_2}$ bending and N-C-N str. vibrations of thiourea), ca. 1100 $\mathrm{cm^{-1}}$ (C-N str. vibrations of thiourea), and ca. 800 $\mathrm{cm^{-1}}$ (CH out of plane deformation vibrations of pyridine and C-S str. of thiourea). The presence of the fewer bands in the substituted complex may be explained on considering the spectrum of coordinated pyridine, e.g., $[\mathrm{Pd\ py_2Cl_2}]$, where splitting of bands and shifting to higher frequencies take place. However, due to the presence of thiourea, the splitting of bands is checked but the bands are remain shifted to higher frequencies resulting in the considerable strengthening of C=S bond and weakening of C=N bond, the point can be best illustrated by the presence of a weak band observed at 730 $\mathrm{cm^{-1}}$ in the complex, $[\mathrm{Pd(tu)_2py_2}]\mathrm{Cl_2}$, corresponding to 700 $\mathrm{cm^{-1}}$ in the complex, $[\mathrm{Pd(tu)_4}]\mathrm{Cl_2}$, and 735 $\mathrm{cm^{-1}}$ in free thiourea, assigned to C-S stretching modes.

The infra red spectra of substituted 2,2'dipyridyl and o-phenanthroline complexes show more or less the same behaviour as observed in case of substituted pyridine complex with the difference that in o-phenanthroline complex there is splitting of bands (not observed in substituted pyridine and dipyridyl complexes) which is an indication of stronger metal to ligand (o-phenanthroline) coordination in comparison to corresponding pyridine and dipyridyl complexes.

All the substituted complexes show a strong band at 275-230 cm^{-1} corresponding to metal - sulphur bond.

The kinetics of the substitution reactions of tetrakis (thiourea) palladium(II) chloride with substituted amines were studied spectrophotometrically and potentiometrically.

The e.m.f. measurements were carried out with the assumption that there could exist a linear relationship between the concentration of thiourea and the potential while working with in the pH range of 4-8 and utilising $Ag-Ag_2S$ as an indicator electrode (see experimental part for details). The first order rate of reaction was determined by plotting log $\frac{E_t}{E_{\infty} - E_t}$ vs. time, t. The plots were found to be linear (vide fig.8A to 15D) and the K_{obs} values are summarised in table 16A. A comparison of the K_{obs} values (vide tables 6A, 6B and 16A) evaluated from the spectrophotometric as well as the potentiometric plots for the various heterocyclic amines reveals the following order:

2 pic > 2,6L > py > 2,4L > 4 pic (spectrophotometric)
o-phen > 2,6L > 2 pic > py > 2,4L(potentiometric)

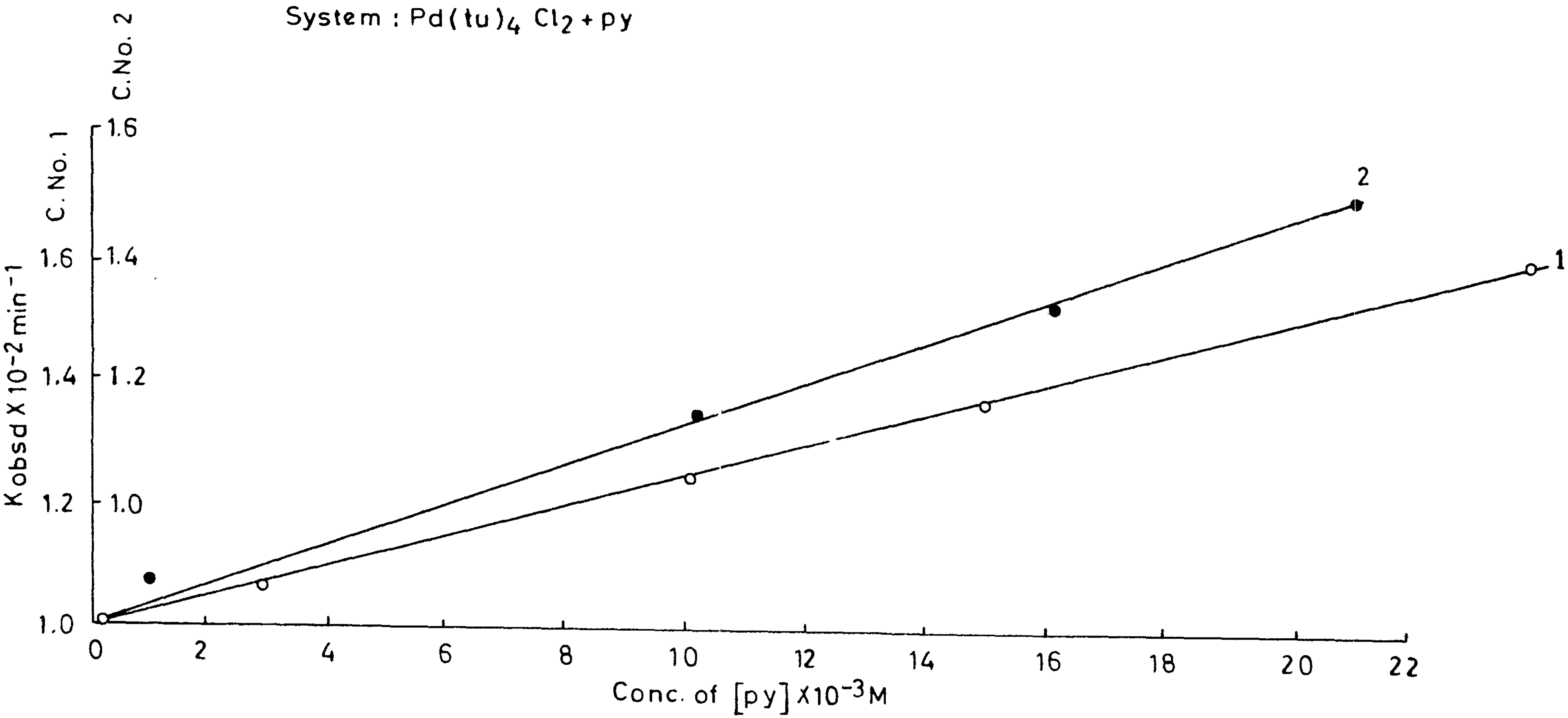


Fig. 6A & 6B Plot Of K_{obsd} Vs $[py]$ At 25°C (C.No.1) & 20°C (C.No.2)

It is not possible to correlate the $K_{obs.}$ values, with those of the pK_a's of the substituent ligands, which follow the following order.[31]

o-phen > 2,4L > 2,6L > 4 pic > 2 pic > 3 pic > py

However, it must be emphasised that the basicity[32] would be of little importance in such reactions and polarizability plays a determine role in the reactivity of nucleophiles. On the basis of present studies it is also not possible to make a quantitative correlation between K_{obs} values and nucleophilic reactivities, however, in alkyl pyridines under study, the nucleophilities are reported to be almost of the same order.

The kinetic studies based upon spectrophotometric measurements (data given in Table 2A to 5E) can be best described by the equation:

$$K_{obs} = K_1 + K_2 [Y] \qquad (I)$$

The equation(I) is equivalent to the general rate law equation for ligand substitution in square planar metal complexes

$$\text{Rate} = K_1 + K_2 [Y] [\text{Complex}] \qquad (II)$$

where K_1 and K_2 are the first and secomd order rate constants, respectively, and $[Y]$ is the entering group.

The equation (I) is valid for the present reaction of $[Pd(tu)_4]Cl_2$ with pyridine and related compounds. The reactions involve the displacement of one or more thiourea molecules in the complex, $[Pd(tu)_4]Cl_2$, by heterocylic molecules.

The values of K_{obs} are given in tables 6A and 6B for pyridine, 2-picoline, 3-picoline, 4-picoline, 2,4 lutidine and 2,6 lutidine.

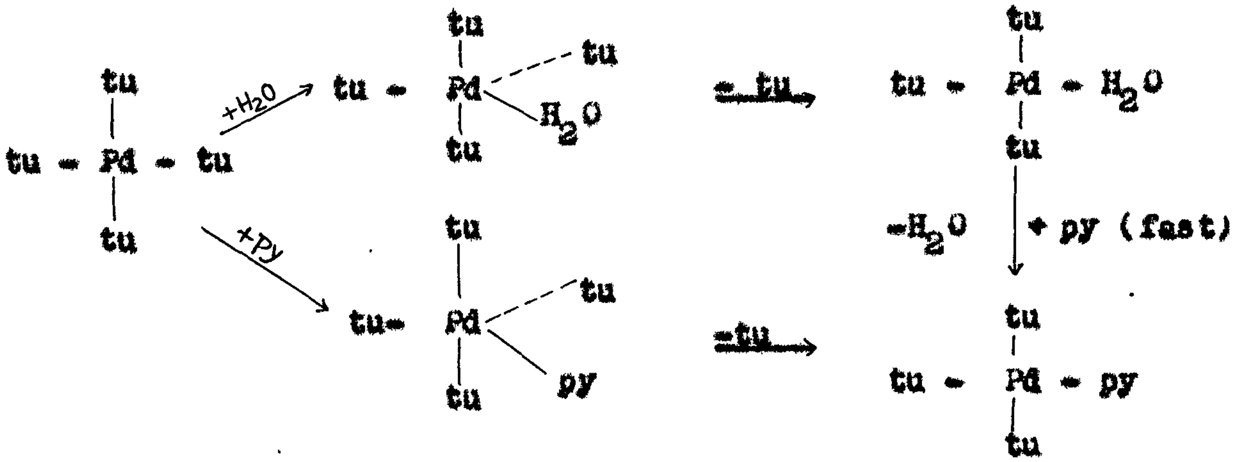
The plots of K_{obs} vs. [Y] for pyridine at two different temperatures, 20°C and 25°C are given in fig. 6A and 6B. The plots are straight lines with slopes equal to K_2 and intercepts equal to K_1 (table 17).

TABLE -17:

K_1 and K_2 values from Fig. 6A and 6B for the system: $[Pd(tu)_4]Cl_2$ + py

$Pd(tu)_4^{++}$ + py	K_1 $min.^{-1}$	$K_2 mol^{-1}$ $min.^{-1}$
at 20°C	$8x10^{-3}$	$3.47x10^{-1}$
at 25°C	$1.0x10^{-2}$	$2.6x10^{-1}$

The two term rate law applicable in this case requires two step mechanisms which have been proposed for ligand substitution square planar complex.



The rate constant K_1 is due to the slow displacement of thiourea by the solvent which then readily replaced by pyridine. A direct nucleophilic replacement of tu by py is responsible for K_2 or in other words, the second order rate law is simply due to a direct bimolecular (S_N2) reactions between the incoming ligand (py) and the complex, $[Pd(tu)_4]Cl_2$, involving bond making and bond breaking.

The S_N2 mechanism suggested above can be very well explained by taking into consideration firstly, the nature of leaving group (tu) and secondly, the well known energy reaction profile described by Basolo and Pearson.[30] Two types of leaving groups may be considered (i) ligand which are replaced readily and the rate of replacement is almost independent of the leaving group (ii) ligands which are difficult to be displaced and the rate of replacement depends upon the leaving group.

In the present studies, the leaving ligand (tu) belongs to the second type, forming strong metal to ligand π bond, here activation energy will be determined by the transition state (B') since B' involves primarily a breaking of Pd-S bond and rate of its displacement will depend on the nature of X(tu). It means the addition of nucleophile (py) is reversible and rate step is the loss of leaving group, accompanied by rearrangement. The role of pyridine as an effective reagent for Pd(II) and Pt(II) square planar substitution reactions is well known, although classified amongst the weak trans activator (weak σ and π bonding) and good cis activator but keeping in mind the important point that such effect is generally small in Pd(II) systems, the effectiveness of pyridine as an incoming ligand is explained on the basis of its capacity to form metal to ligand bond (d_π - p_π) and thus it is possible to stabilise the transition state by the formation of π bonds using electrons in the 4d orbitals (of Pd^{++}) and empty or partially empty ligand orbital (p_π in pyridine). For the above reaction, the configuration of the transition state is most likely to be a trigonal bipyramid since this allows more orbitals for π bonding in the trigonal plane.

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CHAPTER - VIII:

STUDIES ON SOME SUBSTITUTION REACTIONS OF SQUARE PLANAR $Ni(tu)_4Cl_2$ COMPLEX.

Studies on Some Substitution Reactions of Square Planar $Ni(tu)_4Cl_2$ Complex.

Amongst the transition metals, nickel occupies a unique place due to its property of exhibiting a number of oxidation states e.g., - 1, 0, + 1, +2, +3 and +4. These oxidation states are stabilised through complex formation giving away a variety of complexes, having different coordination numbers and structures.[1] The fact that the stereochemistry of a metal is sensitive to steric and inductive properties of the ligand can be very well illustrated by studying of the coordination chemistry of Ni(II).[2] Nickel(II), belonging to d^8 system, forms complexes with coordination numbers 4, 5 and 6. Six coordinated high spin complexes of the type, $Ni(H_2O)_6^{2+}$ are very common and the typical complexes, $Ni(dipy)_3^{2+}$, $Ni(o\text{-}phen)_3^{2+}$ etc., belong to this group.[3,4] Pentacoordinated complexes having trigonal pyramidal structure[5,6] such as $[Ni(QAS)\ Br]Br$ (low spin) and $[Ni\ N(C_2H_4\ N(CH_3)_2)_3Cl]Cl$ (high spin) are not very common (QAS stands for tris(o-diphenyl arsino phenyl) arsine) whereas complexes with distorted tetragonal bipyramidal structures[7,8] such as $NiCH_3AsC_3H_6\ As(CH_3)_2Br_2$ (low spin) or high spin, Ni-Schiff base complexes are rare. The tetra coordinated Nickel(II) complexes are either tetrahedral e.g., $NiBr_4^{2-}$ (paramagnetic) or square planar e.g., $Ni(CN)_4^{2-}$ (diamagnetic).[9,10]

One of the important formulations drawn from the ligand field theory is the criterion for the distinction between the 4-coordinated tetrahedral(I) and square planar(II) complexes of the divalent nickel. Four coordinated complexes surrounded with ligands of high field strength and ligand-ligand repulsion have a square planar structure(II), whereas ligands of low field and high repulsion interactions tend to give tetrahedral complexes(I).[11,12] The complexes where ligand field strengths and ligand-ligand repulsions are in between the two extreme categories (I and II), exhibit what is called conformational isomerism in which the energy difference in the two structures (I and II) is small and one form of the same complex may be found as square planar and the other as tetrahedral. One of the best examples of the above phenomenon cited in literature is that of the complexes of the type $Ni(PR_3)_2X_2$[13,14]. Halogeno complexes, $Ni(PEt_3)_2X_2$ and $Ni(Ph_3P)_3X_2$ are planar and tetrahedral, respectively in solid state as well as in solution. Intermediate compounds of the type $Ni(PRPh)_2)_2X_2$ where X = Br (R=n-Pr, i-Pr, n-But) and X= Cl(R=n-But) show intermediate behaviour and it is possible to isolate both forms (conformational isomers) of the particular compounds. Thus, these examples support the presence of the following equilibria in solution:

Planar
II

tetrahedral
I

Studies carried out independently by Sacconi[15] and Holmes[16] on certain Ni(II)-N substituted salicyladimines and by Cotton[17] on certain β-diketone complexes showed that, depending on the system, the observed paramagnetism is responded either due to the presence of tetrahedral speceis or axial interaction sufficient to produce a triplet ground state, or combination of both. The fact that the production of a triplet ground state is the result of the imposition carried on an axial component through the solvent or solute agency so as to reduce the tetragonality of the field is demonstrated by the molecular weight and absorption studies on the above mentioned complexes where paramagnetism is attributed to molecular association and the magnetic effects in good and non-coordinating solvents are explained on the basis of solute-solvent and solute-solute interactions, respectively.[18]

The kinetics of the substitution reactions of Ni(II) have been extensively investigated, however, the greater part of the work is limited to the studies on the high spin octahedral complexes and only relatively a few references are available for the kinetic investigations on square planar complexes. Amongst the substitution reactions of octahedral Ni(II) complexes which are not of much interest here, $Ni(o\text{-}phen)_3^{2+}$ and $Ni(dipy)_3^{2+}$ systems[19,20,21,22] have been investigated in very much details. For example, $(+)\text{-}Ni(o\text{-}phen)_3$ and $(+)\text{-}Ni(dipy)_3^{2+}$

racemise by an intermolecular process as revealed by the C^{14}-labeled ligand exchange studies with the coordinating ligand.

The earliest kinetic work carried out on square planar complexes of Ni(II) dealt with $Ni(CN)_4^{--}$ complex.[23] The rapid exchange with $C^{14}N$(30 secs.) was explained on the basis of low energy bimolecular displacement process. Kinetic studies are reported on the mechanism of the substitution reactions between pyridine and square planar complexes of Ni(II) containing unidentate ligands.[24]

$$\text{Trans } Ni(PEt_3)_2(o\text{-tolyl})Cl + py \longrightarrow$$

$$\text{Trans } Ni(PEt_3)_2(o\text{-tolyl})\,py^+ + Cl^-$$

The rate of reaction increases with increasing py concentration and follows the typical two term rate law. Comparative study with corresponding Pd(II) and Pt(II) systems show that the rate of reaction decreases in the order:

$$\begin{array}{ccccc} Ni(II) & > & Pd(II) & > & Pt(II) \\ 5\times10^6 & & 10^5 & & 1 \end{array}$$

relative rates

indicating thereby the decrease in reaction rates with increase in stability of the complex. A study of the effect of steric environment on the rate of replacement reaction shows that for trans $[Ni(PEt_3)_2]Cl_2$, there is a marked steric retardation found in going from L = o-tolyl to L = mesityl(K_{obs}, sec^{-1}; for o-tolyl = 3.3×10^{-1}, mesityl = 2.0×10^{-2}).

Murmann[25] carried out an interesting study of the substitution reactions in planar Ni(II) chelates, consisting of the exchange of C^{14} labeled α aminoximes (AO) with their Ni(II) complexes, as well as the reaction of complexes with E.D.T.A. At constant pH and ionic strength, the familiar two term rate law is followed. That the rate of reaction of $Ni(AO)_2-H^+$ is approximately 100 times faster than that of $Ni(MeAO)_2-H^+$, is believed to be due to the steric shielding by the methyl group and the slower reactivity of $Ni(bn\ AO)_2-H^+$ attributed to its greater stability.

In general, low spin Ni(II) complexes react by a bimolecular displacement process typical of square planar complexes and it is probable that the substitution in such cases proceeds by an associative (A) mechanism, considering the numerous examples of stable 5 coordinated complexes of Ni(II) ion.[26]

The work described in the preceding pages concerns with the studies on some aspects of the solution chemistry of square planar Ni(tu)$_4$Cl$_2$ complex. The studies consist of the potentiometric titrations performed to determine the composition of the complex species (present in the solution) formed by the interaction of heterocyclic amines and Ni(tu)$_4$Cl$_2$. Kinetic studies on the substitution reactions of Ni(tu)$_4$Cl$_2$ with pyridine, o-phenanthroline and 2,2 dipyridyl are discribed and the possible mechanisms of the reactions are suggested. The synthesis of some mixed ligand complexes formed by the interaction of pyridine, 2,2'dipyridyl and o-phenanthroline with Ni(tu)$_4$Cl$_2$ has also been carried out and the bonding is discussed on the basis of their infra red spectra.

EXPERIMENTAL:

The reagents: thiourea, pyridine, 2,2'dipyridyl, o-phenanthroline, and potassium chloride were all of analytical grades. Thiourea was estimated potentiometrically, using Ag-Ag_2S electrode as described previously (vide chapters II and III). Amines were estimated pH-metrically using standard HNO_3 as a titrant.

Preparation of the complexes:

1. Nickel(II) chloride-thiourea complex:

60 ml of an alcoholic solution of thiourea(0.1M) was added to 100 ml. of 1% aqueous solution of Nickel(II) chloride containing a small quantity of HCl (2-3 drops of conc. HCl). The mixture was heated over a water bath for about half an hour and then filtered. The filtrate was kept for 1-2 hours when the crystals of the complex appeared. The latter were separated from the main liquor, washed with acetone and dried in air.

Tetrakis(thiourea) nickel(II) chloride.

$[Ni(tu)_4]Cl_2$. Yellowish green crystals, highly soluble in water and organic solvents such as acetone, alcohol, dimethyl formamide etc., m.p. 225°C. Molar conductance: 524 $ohm^{-1}cm^2$ (1.0^{-3}M, dimethyl formamide as solvent), diamagnetic.

Analytical data: Calc. for $C_4H_{16}N_8S_4NiCl_2$: C-11.1, H-3.7, Ni-13.5, Cl-16.4. Found: C-10.9, H-3.7, N-13.4, Cl-16.4.

2. $Ni(tu)_4Cl_2$-pyridine complex.

To an aqueous solution of 10 ml of 1% $Ni(tu)_4Cl_2$, was added 5 ml. of pyridine followed by the addition of 50 ml. of acetone. The whole mixture was heated over a water bath for about 5 mts. and then filtered. The filtrate was refluxed for over two hours. The refluxed solution was diluted with water, warmed for about 15 mts. and allowed to stand for about 48 hours when crystals of the complex appeared. The crystals were separated from the main bulk and dried in a vacuum desiccator over CaO.

Bis(thiourea) bis (pyridine) nickel(II) chloride.

$[Ni(tu)_2py_2]Cl_2$— Bluish green crystals, soluble in water and very slightly soluble in alcohol and acetone, m.p. above 360°C. Molar conductance: 253 ohm^{-1} cm^{2} (10^{-3}M soln. in water), diamagnetic. Analytical data: Calc. for $C_{12}H_{18}N_6S_2NiCl_2$: C-32.75, H-4.1, Ni-13.35, Cl-16.15. Found: C-30.9, H-3.8, Ni-13.3, Cl-16.1.

3. $Ni(tu)_4Cl_2$-2,2'dipyridyl complex.

About 50 ml. of 2% alcoholic solution was mixed with 100 ml. of an aqueous solution of 1% $Ni(tu)_4Cl_2$ complex. The mixture was boiled over a water bath for about half an hour, cooled and filtered. The filtrate was kept in an ice bath for 1-2 hours when the complex crystallised, separated and washed with acetone and dried with ether. The complex was recrystallised from 80% ethanol.

Bis(thiourea) mono(dipyridyl) nickel(II) chloride.

$[Ni(tu)_2(dipy)]Cl_2$ - Pink crystals, highly soluble in water, soluble in alcohol, dimethyl formamide and nitromethane but sparingly soluble in acetone, m.p. 210°C. Molar conductance : 101.40 ohm^{-1} cm^2 at 35°C (10^{-3}M in nitromethane), diamagnetic. Analytical data: Calc. for $C_{12}H_{16}N_6S_2NiCl_2$: C-32.9, H-3.7, Ni-13.4, Cl-16.2. Found: C-32.3, H-3.7, Ni-13.3, Cl-16.3.

4. $Ni(tu)_4Cl_2$ - o-phenanthroline complex.

The preparation of the complex was carried out by the same procedure as described above for $[Ni(tu)_2(dipy)]Cl_2$ complex.

Bis(thiourea) mono(o-phenanthroline) nickel(II) chloride.

$[Ni(tu)_2(o\text{-}phen)]Cl_2$ - Dark pink crystals, highly soluble in water and alcohol, soluble in dimethyl formamide and nitromethane but insoluble in acetone, m.p. 319-320°C. Molar conductance: 98.6 ohm^{-1} cm^2 (10^{-3}M in nitromethane), diamagnetic. Analytical data: Calc. for $C_{14}H_{16}N_6S_2NiCl_2$: C-36.4, H-3.5, Ni-12.7, Cl-15.4. Found: C-35.8, H-3.7, Ni-12.6, Cl-15.4.

5. $Ni(tu)_4Cl_2$ - phenyl arsonic acid complex.

A hot soln. of phenyl arsonic acid (2%) was prepared in alcohol (70%) and was added drop by drop to a 50 ml. solution of $Ni(tu)_4Cl_2$ with constant shaking. On heating the mixture over a water bath for about half an hour or more, a yellow product was separated from the mixture. The yellow solid was separated by filtration through a sintered glass funnel, washed several times with alcohol and then with acetone, and dried in air.

Mono(thiourea) bis (phenyl arsonic acid) nickel(II) mono chloride.

$[Ni(phOAs)_2tu]Cl$ - Canary yellow product, sparingly soluble in water, insoluble in acetone, alcohol, dimethyl formamide, and nitromethane but very slightly soluble in tetrahydrofurane, m.p. 211°C, diamagnetic. Analytical data: Calc. for $C_{13}H_{17}N_2O_6As_2SNiCl$: C-27.2, H-3.0, Ni-10.2, Cl-6.2. Found: C-27.1, H-3.4, Ni-10.4, Cl-6.0.

<u>Spectrophotometric studies</u>: All the spectrophotometric measurements were carried out with a Unicam spectrophotometer, model SP 600, using 1 cm diameter cuvettes.

The λ_{max} of the complexes was determined by applying Vosburgh and Cooper's method. The λ_{max} of the various complexes are given in table 1.

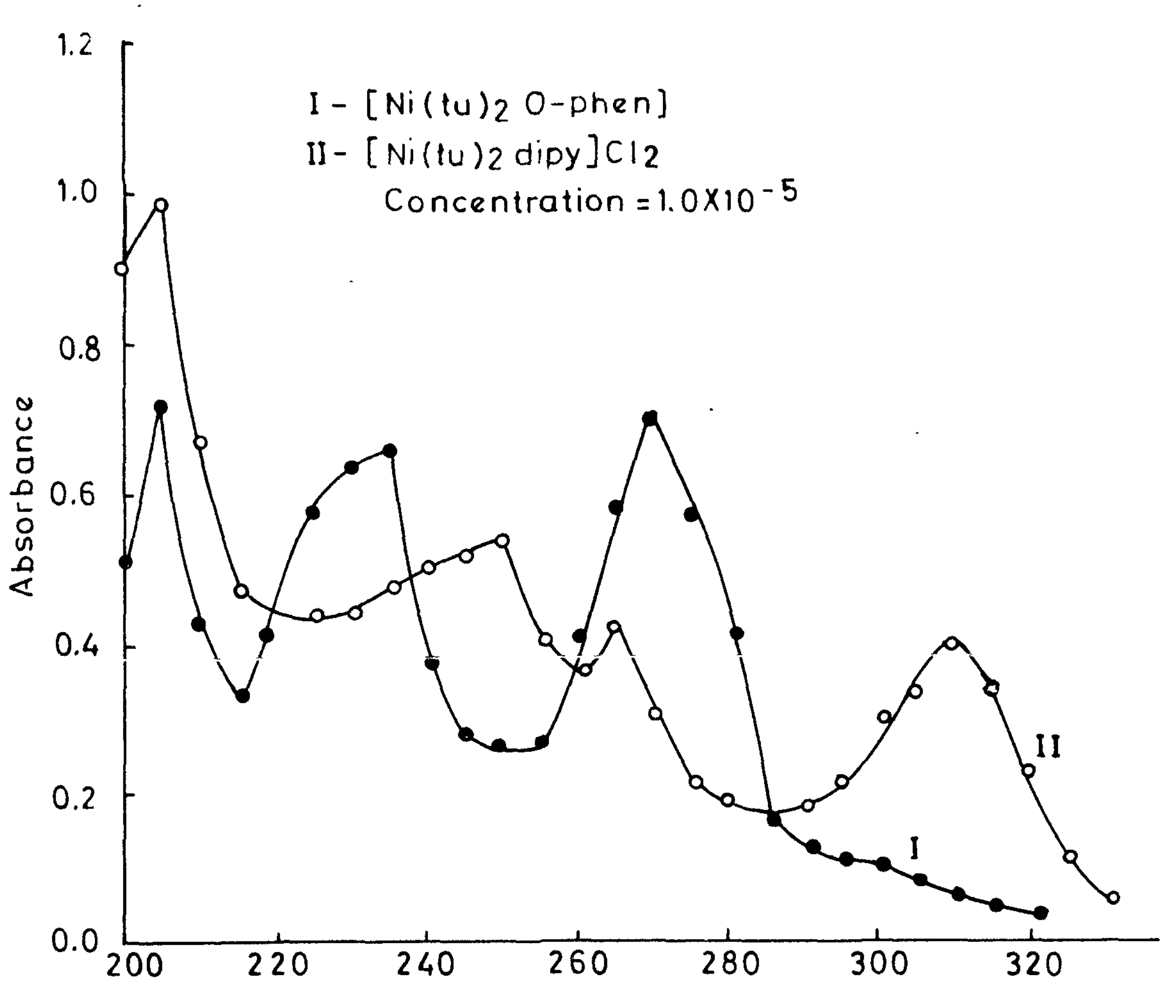


Fig. 1A U.V. Spectra Of Ni (II) Complexes

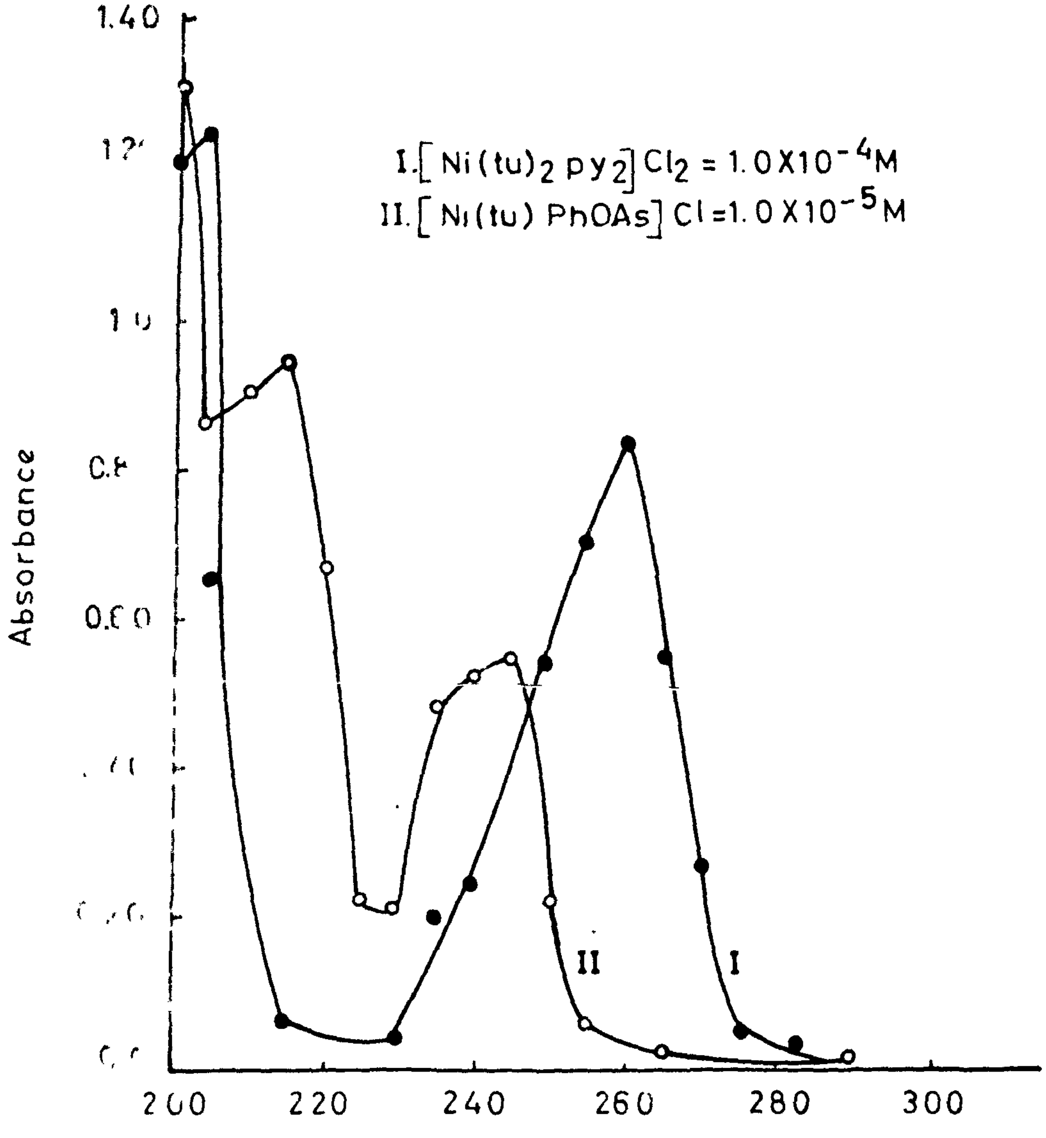


Fig. 1B U V. Spectra Of Ni(II) Complexes

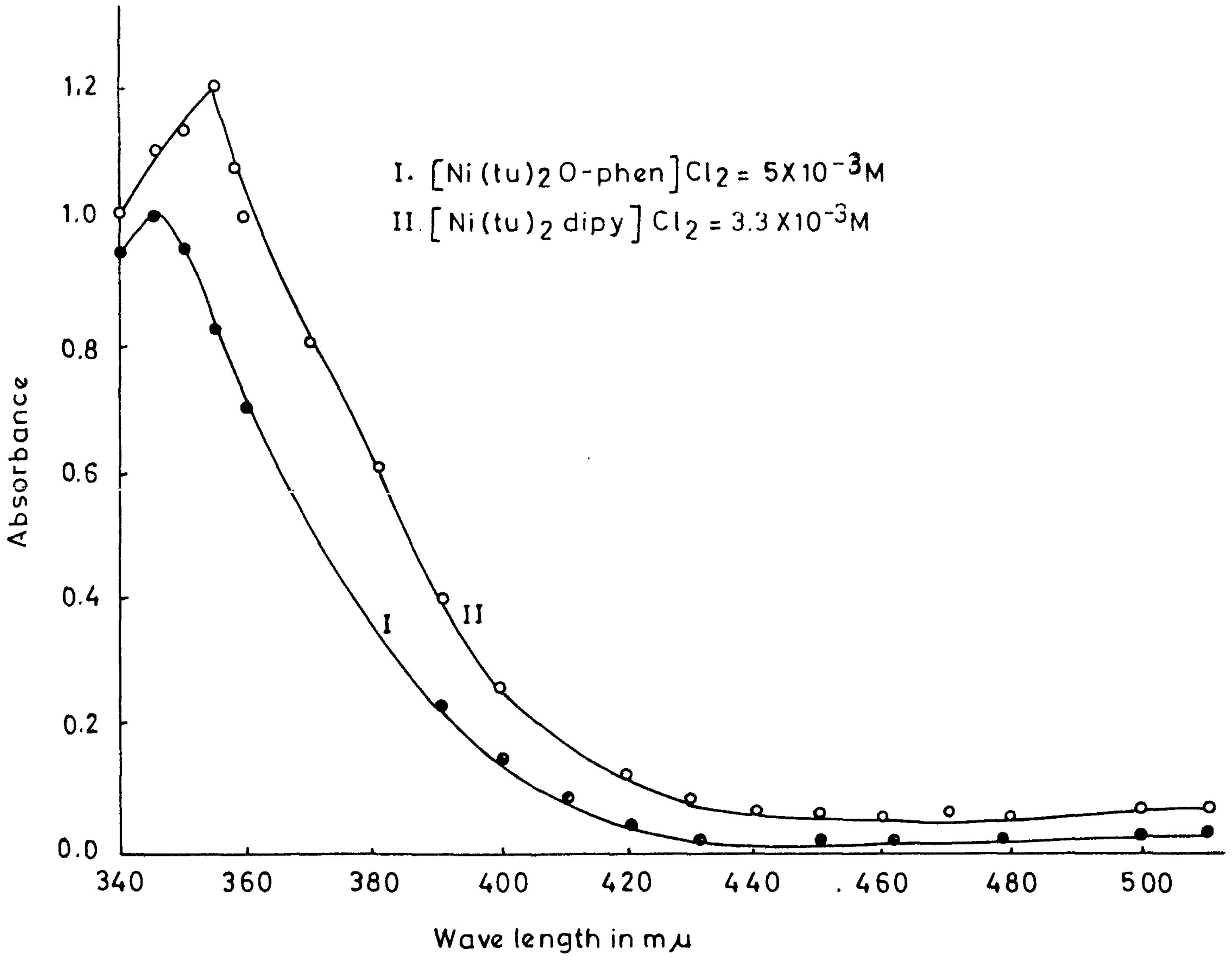


Fig. 1C Visible Spectra Of Ni(II) Complexes

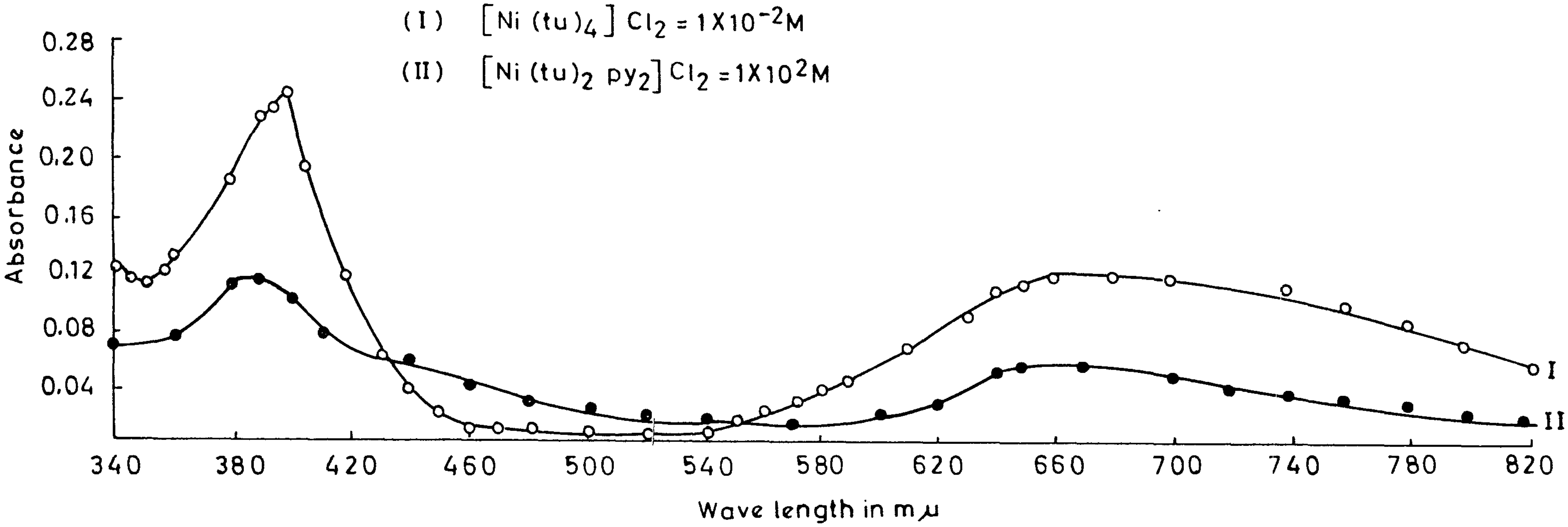


Fig. 1d Visible Spectra Of Ni (II) Complexes

TABLE -1:

Compound	Concentration in mole	λ max (m µ)	Wave number (cm^{-1})	State	ε max
$[Ni(tu)_4]Cl_2$	$1x10^{-2}$	400	25,000	D.M.F.	24
		680	14,705		11
	$1x10^{-2}$	400	25,000	H_2O	-
		680	14,705		
$[Ni(tu)_4]Cl_2$ + py	*	390	25,640	H_2O	-
		520	19,230		-
		660	15,160		-
$[Ni(tu)_2py_2]Cl_2$	$1x10^{-4}$	205	48,770	H_2O	$1.3x10^4$
		260	38,460		$8.4x10^3$
	$1x10^{-2}$	390	25,640	H_2O	11.5
		520	19,305		5
$[Ni(tu)_2$ dipy$]Cl_2$	$1x10^{-5}$	205	48,770	H_2O	1x10
		250	40,000		$5.4x10^4$
		265	37,730		$4.2x10^4$
		310	32,250		$4x10^4$
	$3.3x10^{-3}$	355	28,140	nitromethane	303
		520	19,230		3
$[Ni(tu)_2$ o-phen$]Cl_2$	$1x10^{-5}$	205	48,770	H_2O	$7.2x10^4$
		235	42,550		$6.5x10^4$
		270	37,040		$7.0x10^4$
	$5x10^{-3}$	350	28,570	nitromethane	19
		520	19,230		8
$[Ni(phOAs)_2$ tu$]Cl$	$1x10^{-5}$	215	46,510	H_2O	$9.4x10^4$
		245	40,810		$8.4x10^4$

(Vide Fig. 1A to 1D)

* Conc. of the complex, $Ni(tu)_4Cl_2$ = $1x10^{-2}M$, py = $1x10^{-1}M$

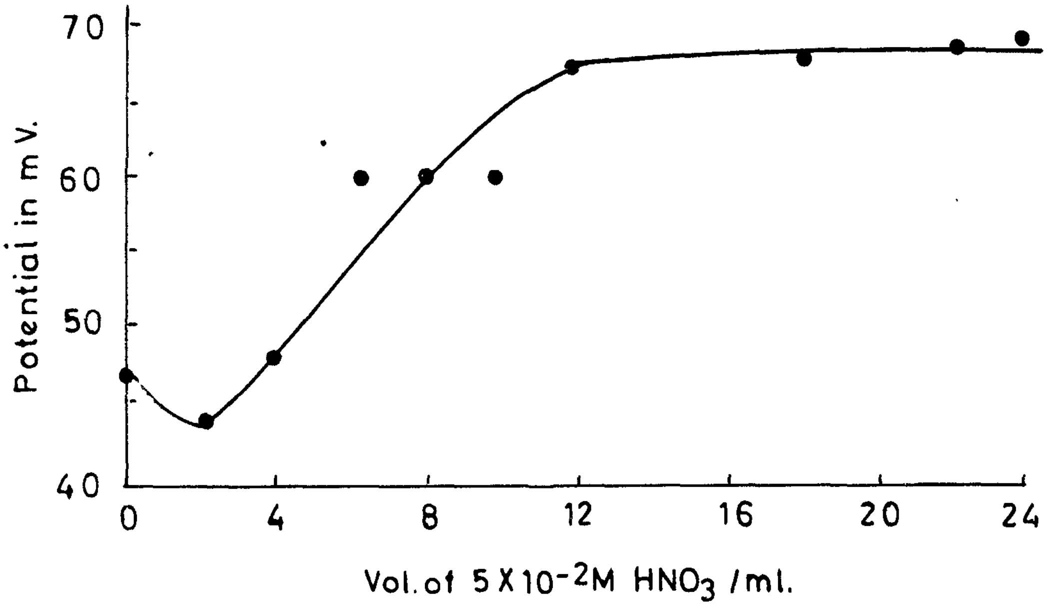


Fig. 2 (III) Potentiometric Titrations Of $NiCl_2$ & tu

10 ml Of $\frac{M}{20}$ $NiCl_2$ + 50 ml Of $\frac{M}{20}$ tu

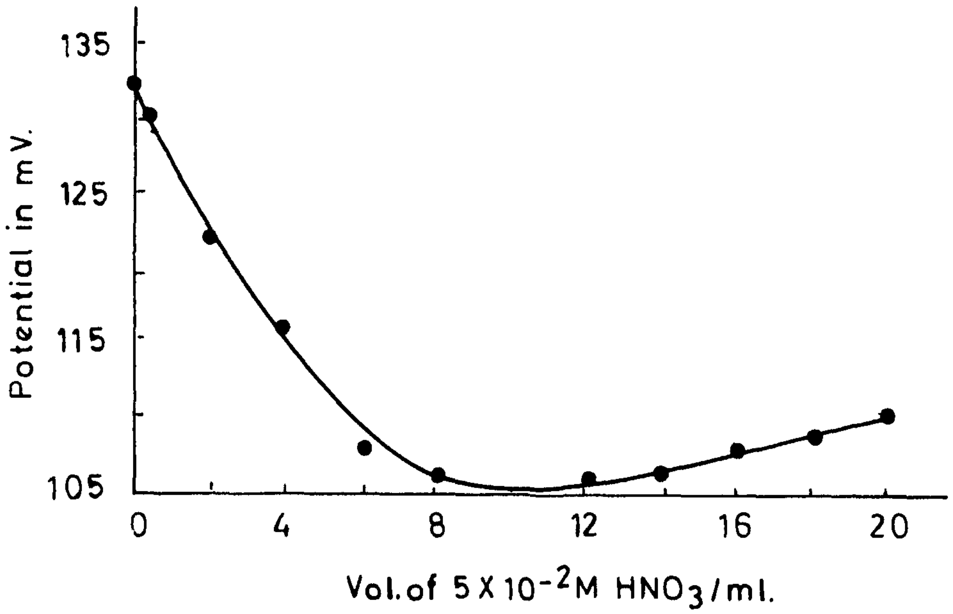


Fig. 2 (I) Potentiometric Titrations Of $NiCl_2$ & tu

10 ml Of $\frac{M}{20}$ $NiCl_2$ + 20 ml Of $\frac{M}{20}$ tu

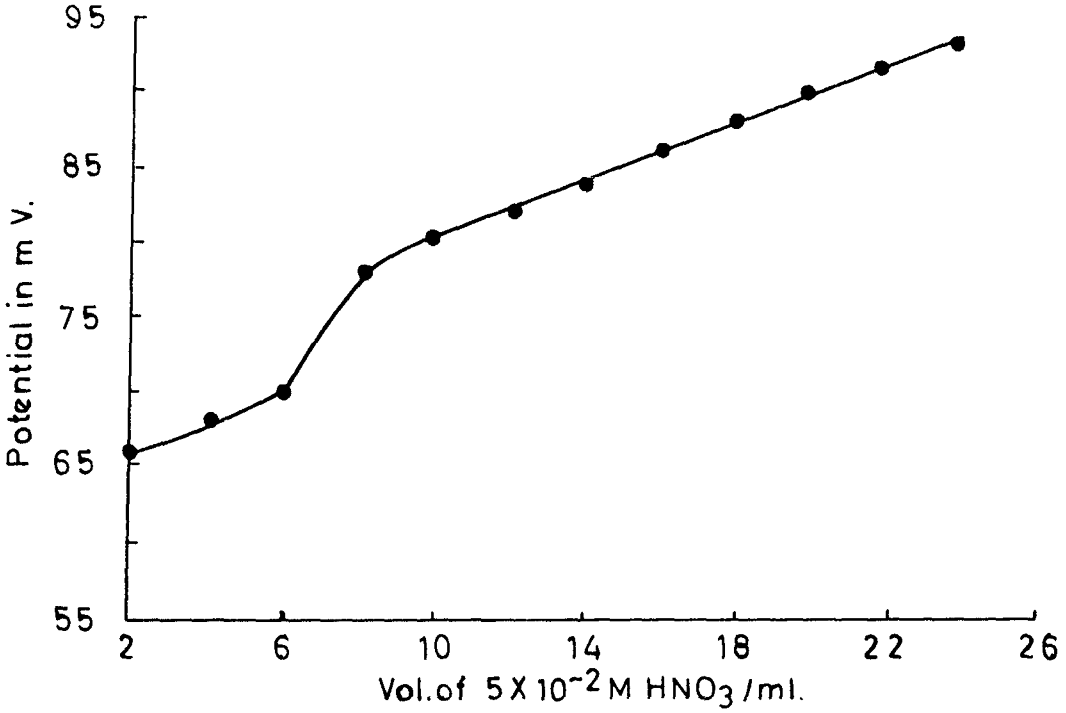


Fig. 2 (II) Potentiometric Titrations Of $NiCl_2$ & tu
10 ml Of $\frac{M}{20}$ $NiCl_2$ + 40 ml Of $\frac{M}{20}$ tu

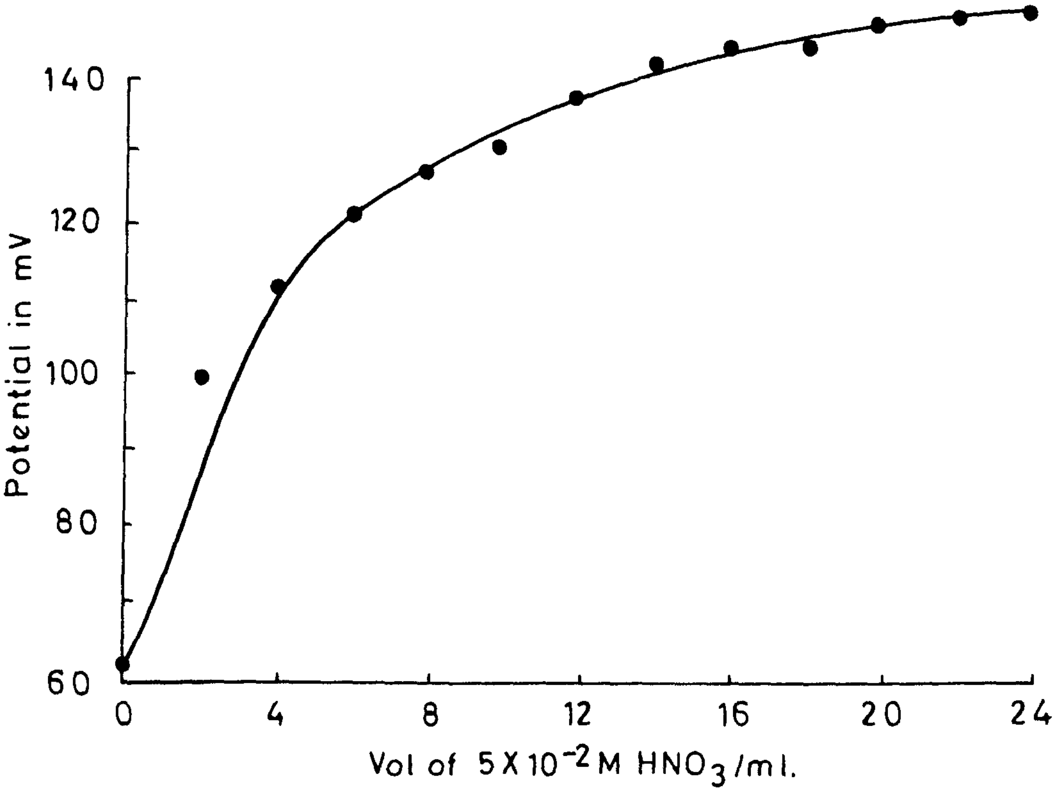


Fig. 2 (IV) Potentiometric Titrations Of $NiCl_2$ & O-phen
10 ml Of $\frac{M}{20}$ $NiCl_2$ + 40 ml Of $\frac{M}{20}$ O-phen

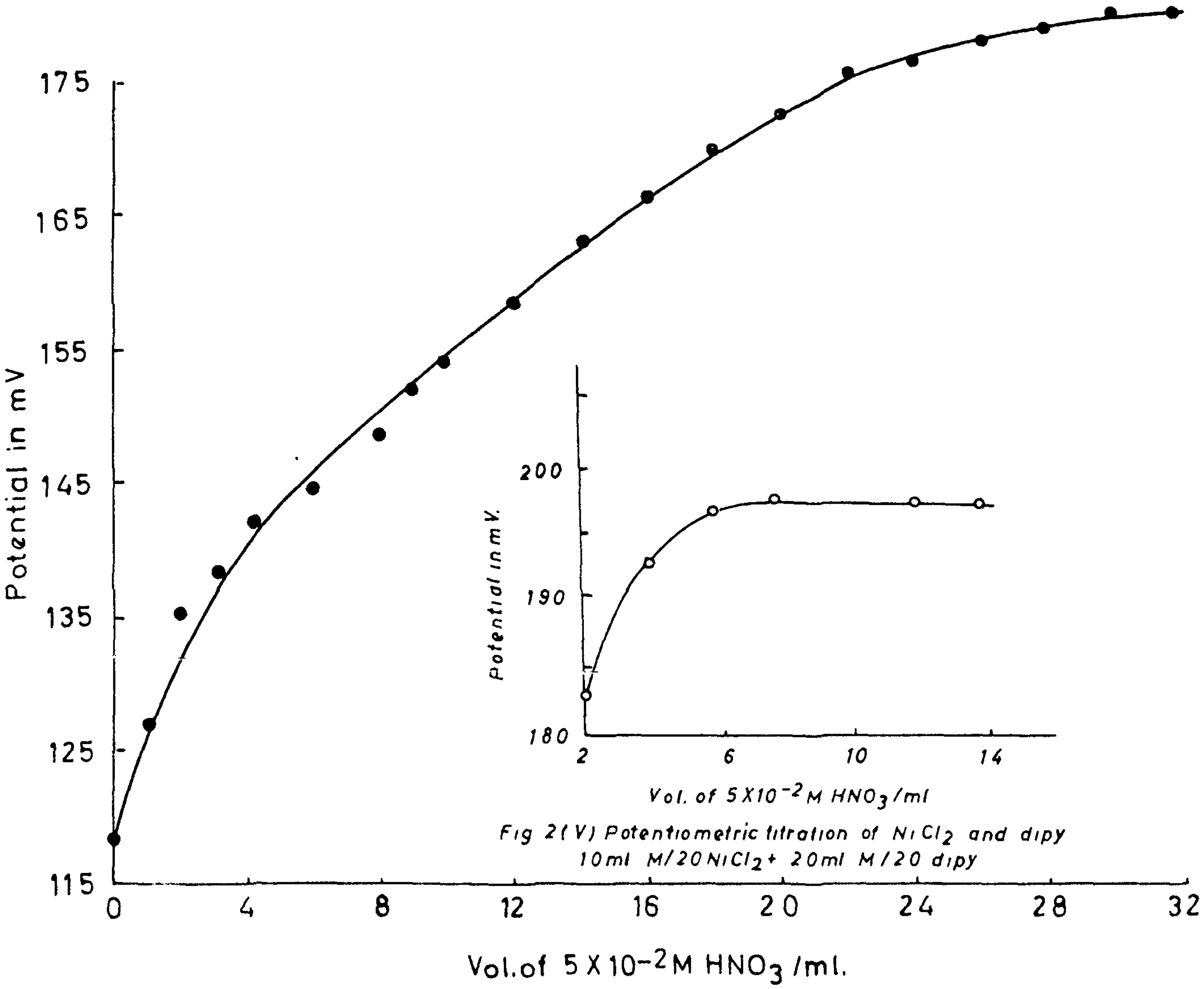


Fig 2(V) Potentiometric titration of $NiCl_2$ and dipy
10ml M/20 $NiCl_2$ + 20ml M/20 dipy

Fig 2 (VI) Potentiometric Titrations Of $NiCl_2$ And Dipy
10 ml Of M/20 $NiCl_2$ + 40 ml Of M/20 Dipy

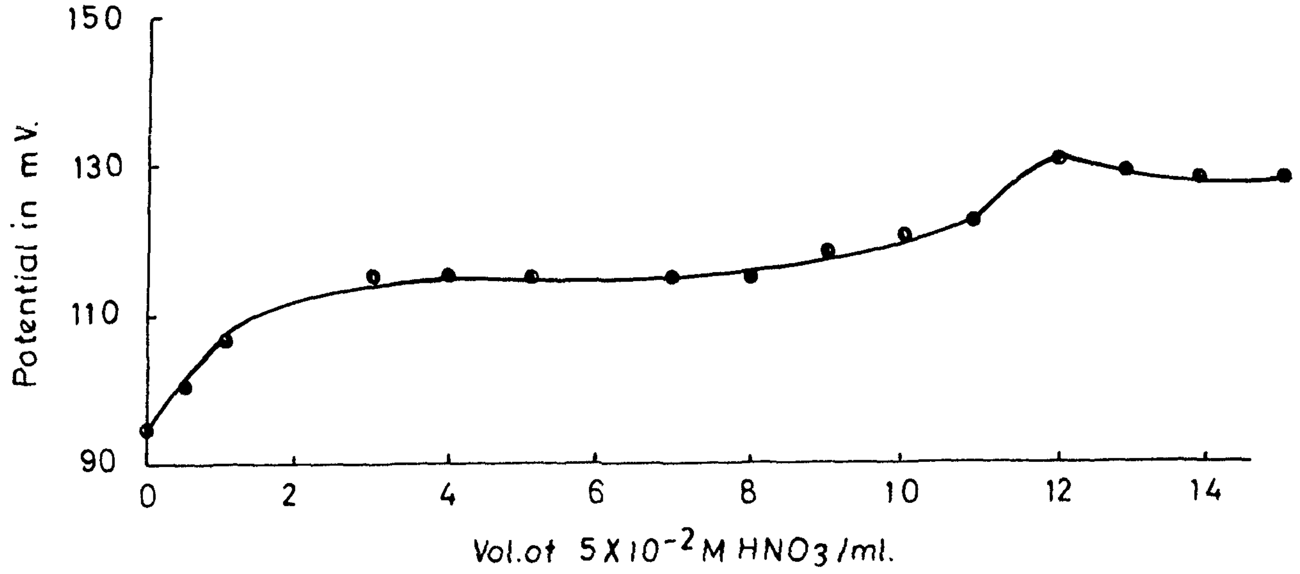


Fig.2 (XI) Potentiometric Titrations
10 ml Of $\frac{M}{20}$ NiCl$_2$ + 20 ml Of $\frac{M}{20}$ tu + 10 ml $\frac{M}{20}$ PhoAs

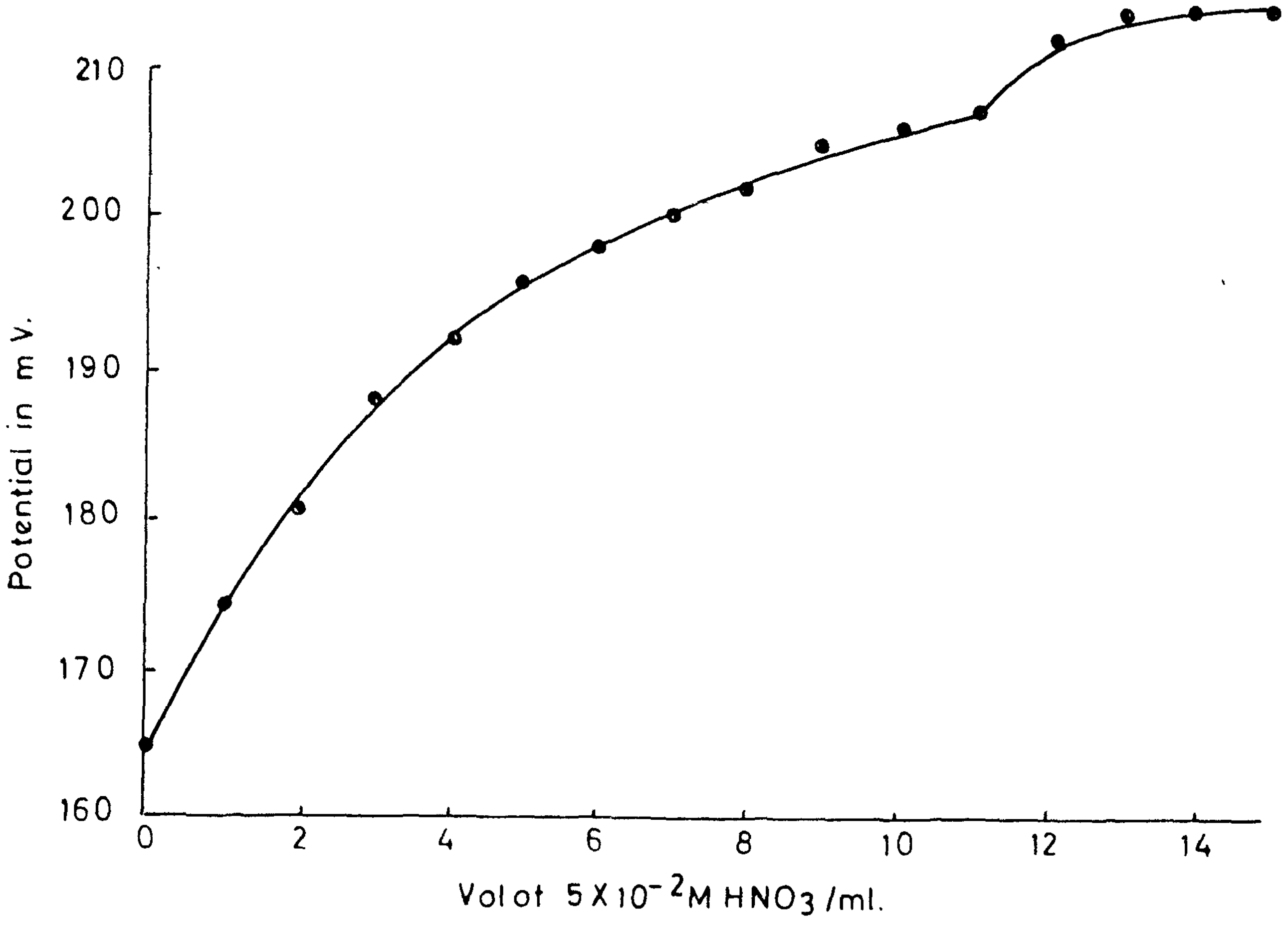


Fig.2 (VII) Potentiometric Titrations
10 ml $\frac{M}{20}$ NiCl$_2$ + 50 ml $\frac{M}{20}$ py

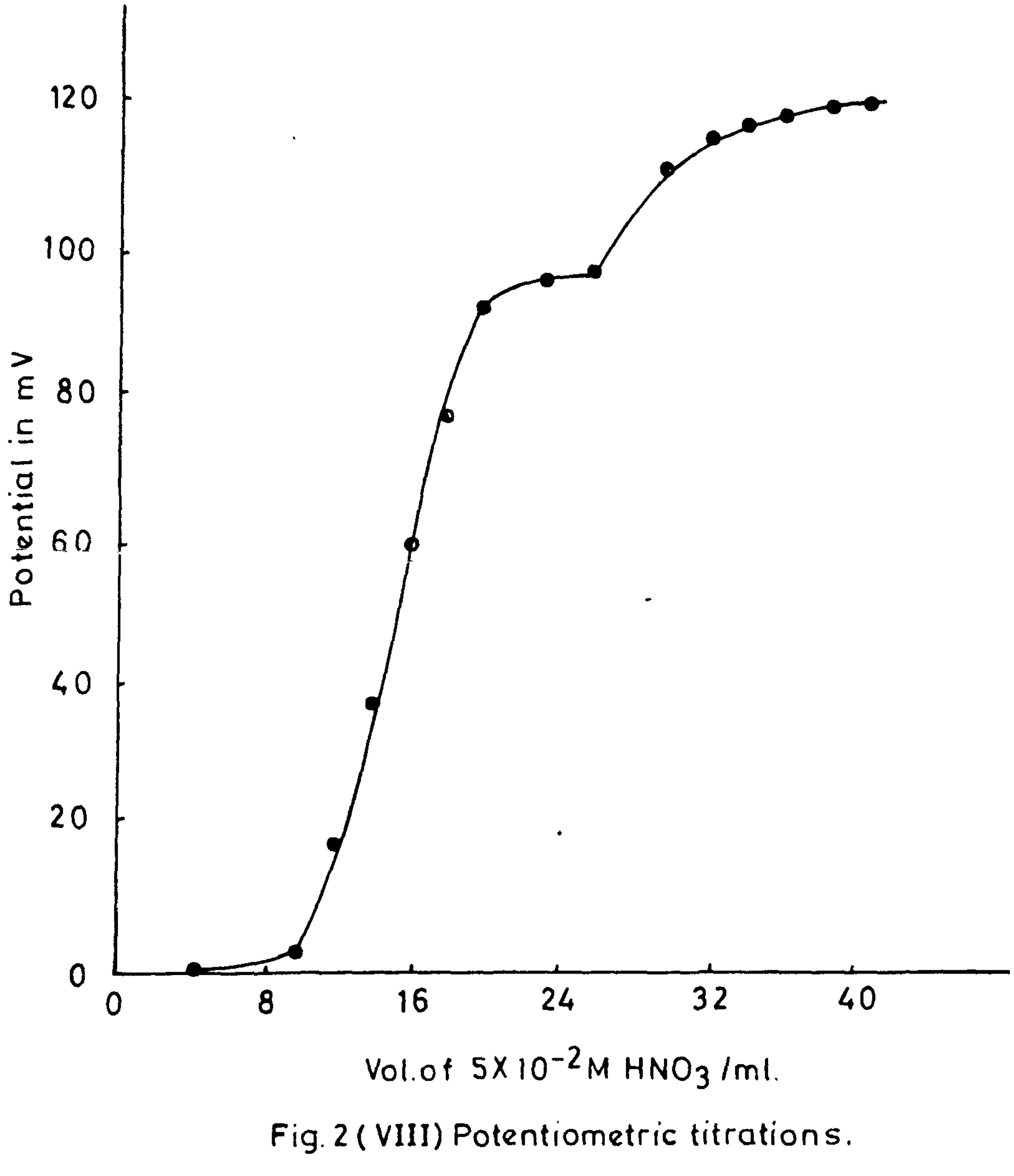


Fig. 2 (VIII) Potentiometric titrations.

10 ml $\frac{M}{20}$ $NiCl_2$ + 40 ml. $\frac{M}{20}$ tu + 40 ml $\frac{M}{20}$ py

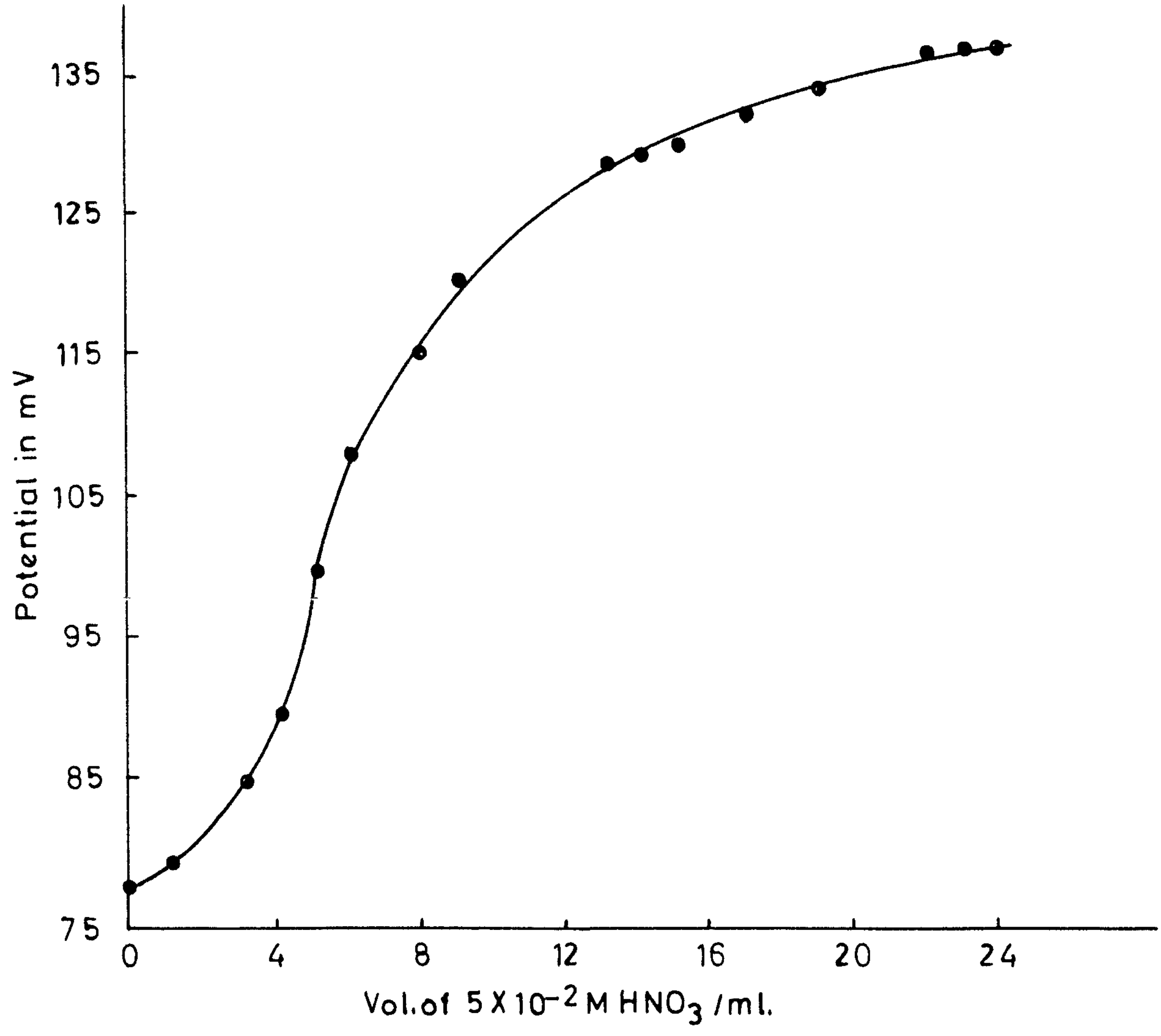


Fig.2 (IX) Potentiometric Titrations

10 ml $\frac{M}{20}$ NiCl$_2$ + 40 ml. $\frac{M}{20}$ tu + 20 ml $\frac{M}{20}$ Dipy

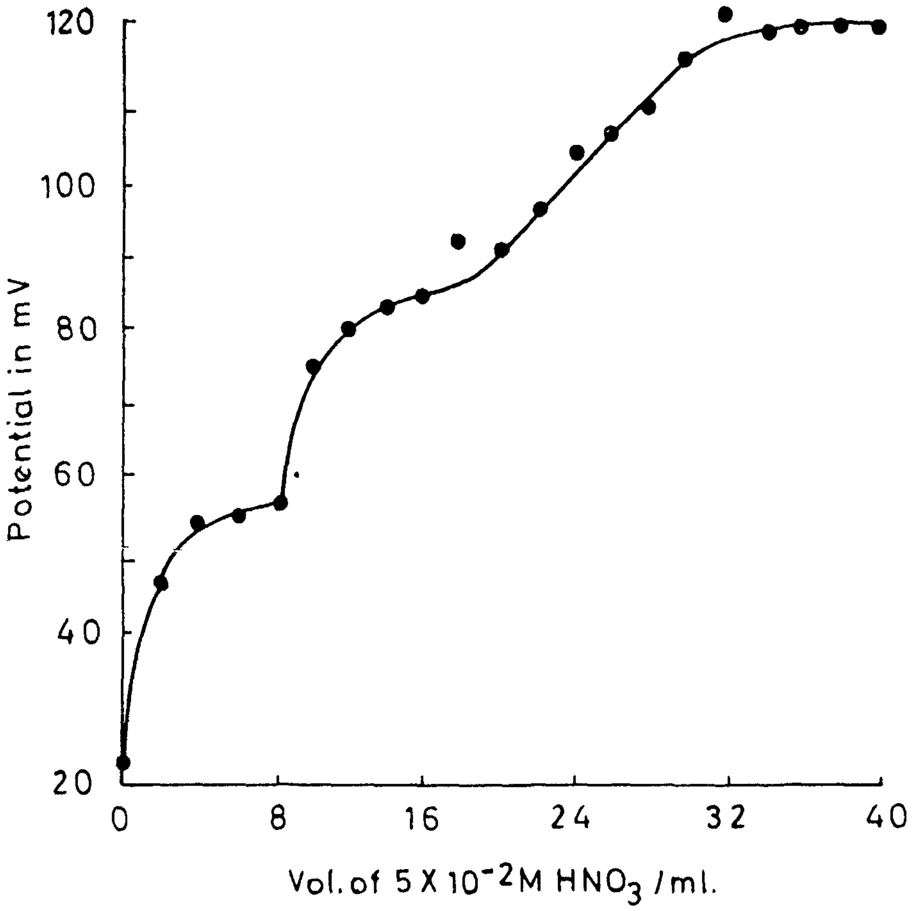


Fig. 2 (X) Potentiometric Titrations

10 ml Of $\frac{M}{20}$ $NiCl_2$ + 40ml Of $\frac{M}{20}$ tu + 20 ml O-phen

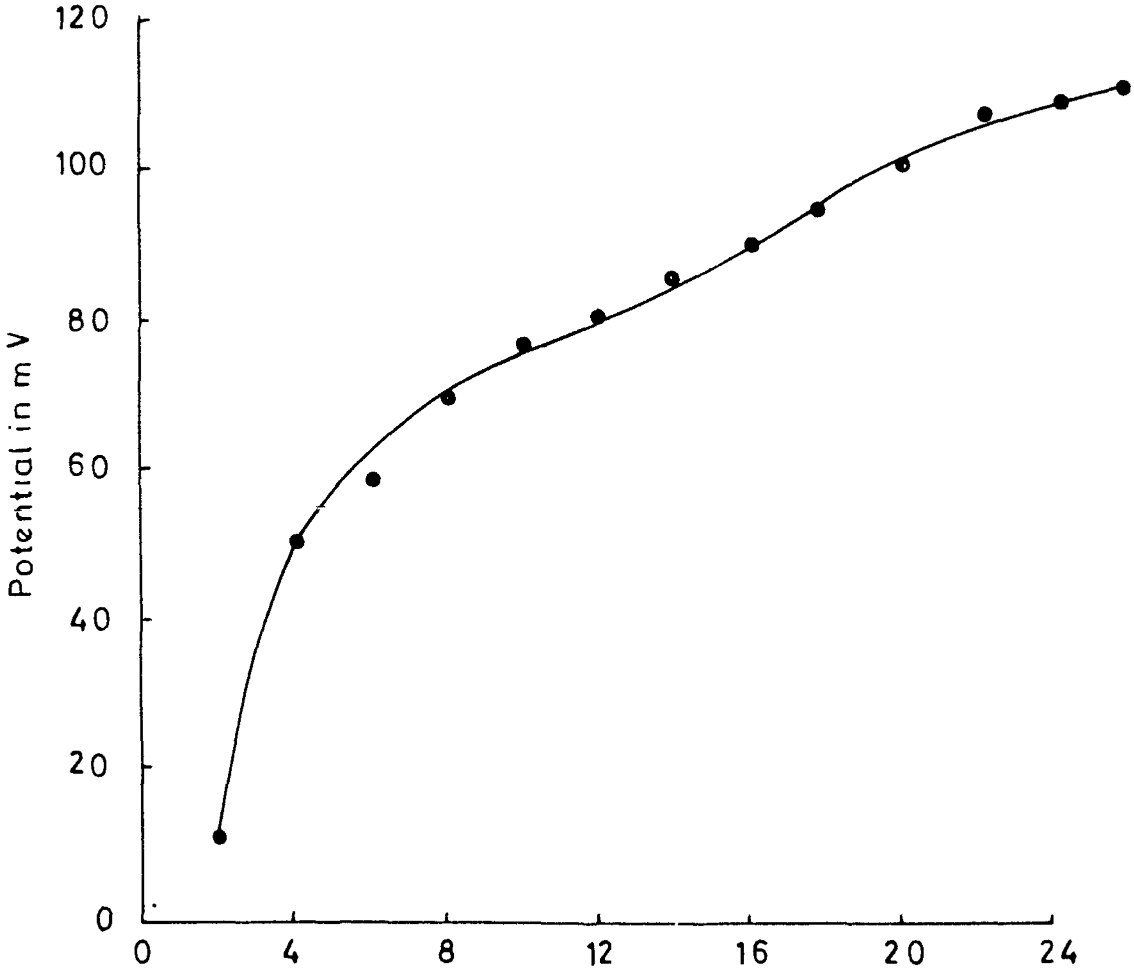


Fig 2(XIII) Potentiometric titrations

10ml($\frac{M}{20}$)Ni(tu)$_4$ Cl_2 + 20 ml ($\frac{M}{20}$)Pyridine

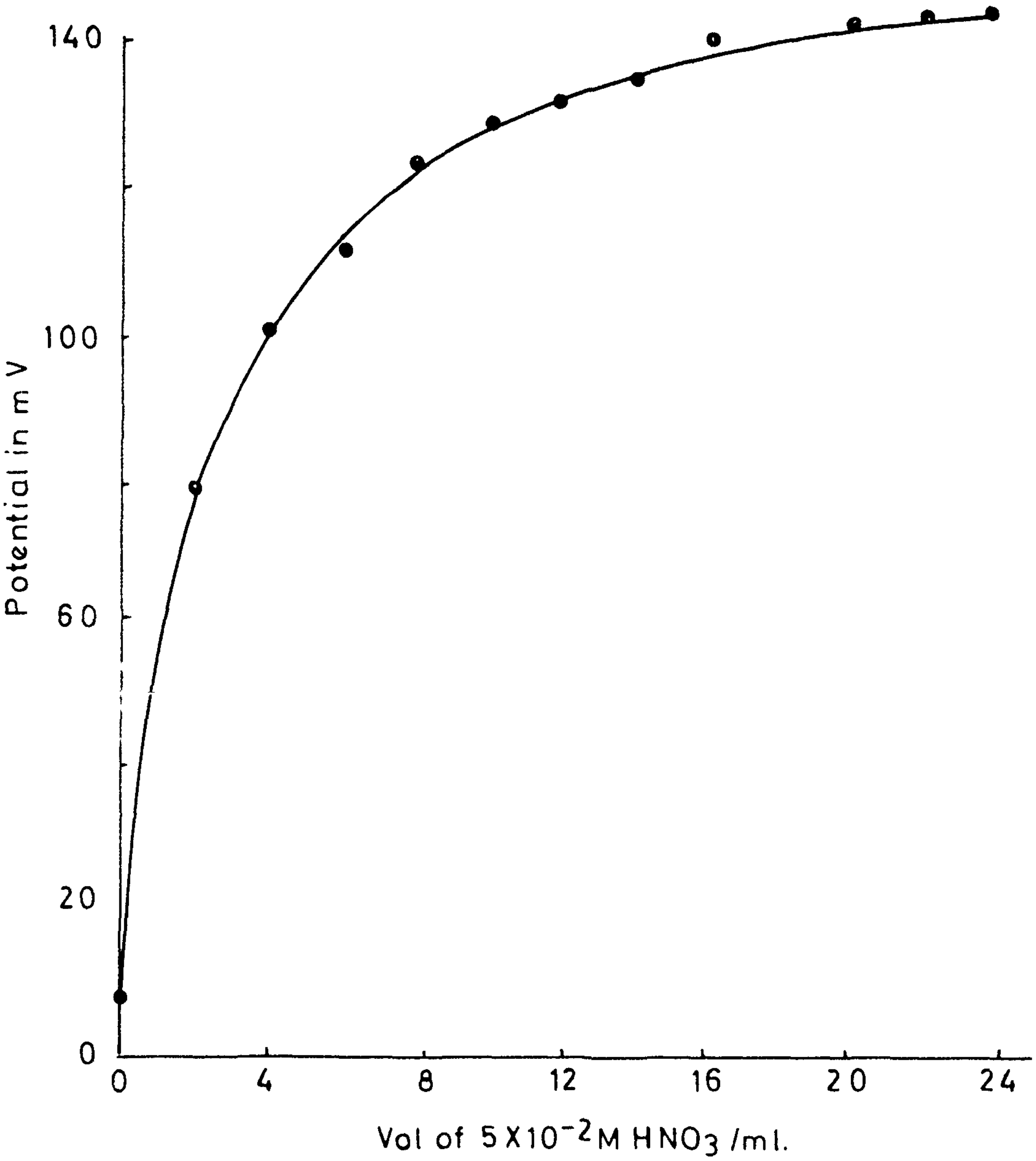


Fig. 2 (XIV) Potentiometric Titrations

10ml $(\frac{M}{20})$ $Ni(tu)_4Cl_2$ + 40 ml $(\frac{M}{20})$ Dipy

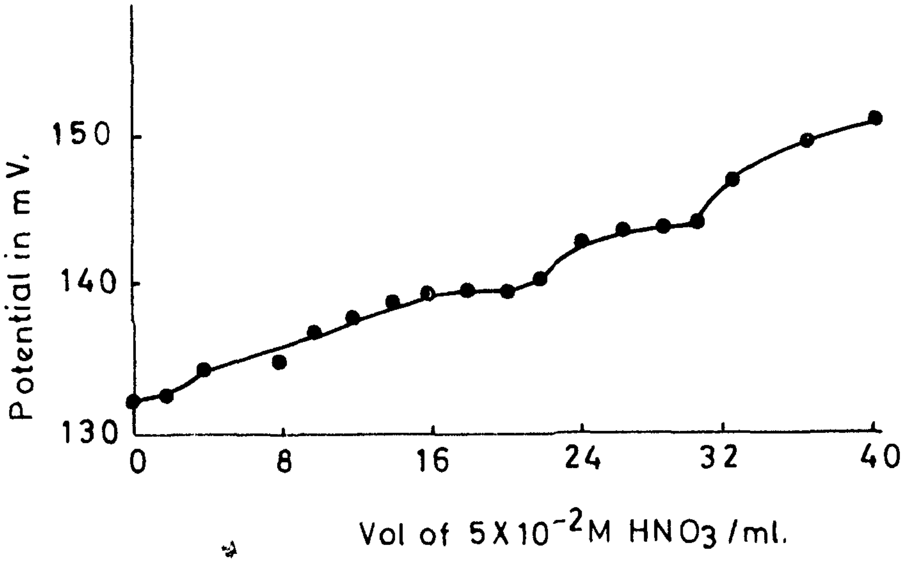


Fig. 2 (XVI) Potentiometric Titration Of $Ni(tu)_4Cl_2$ + Ph OAs

10 ml $\frac{M}{20}$ $Ni(tu)_4Cl_2$ + 40 ml $\frac{M}{20}$ PhOAs

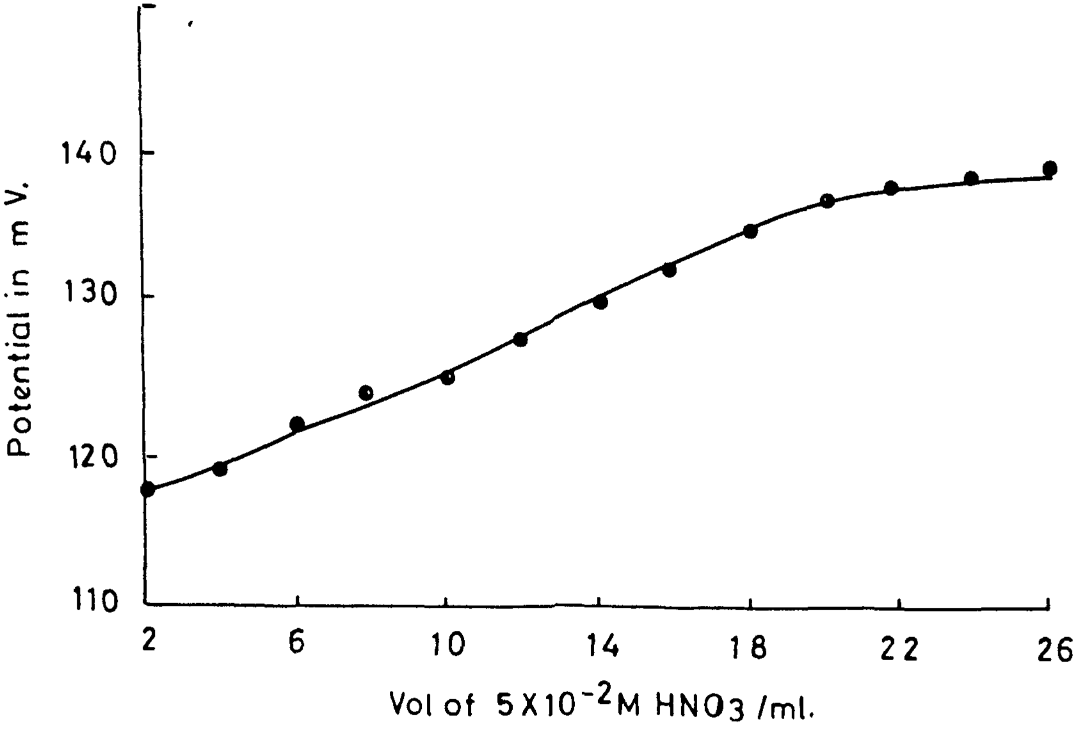


Fig. 2 (XV) Potentiometric Titration Of $Ni(tu)_4Cl_2$ + PhOAs

10 ml (5×10^{-2}M) $Ni(tu)_4Cl_2$ + 20 ml $\frac{M}{20}$ PhOAs

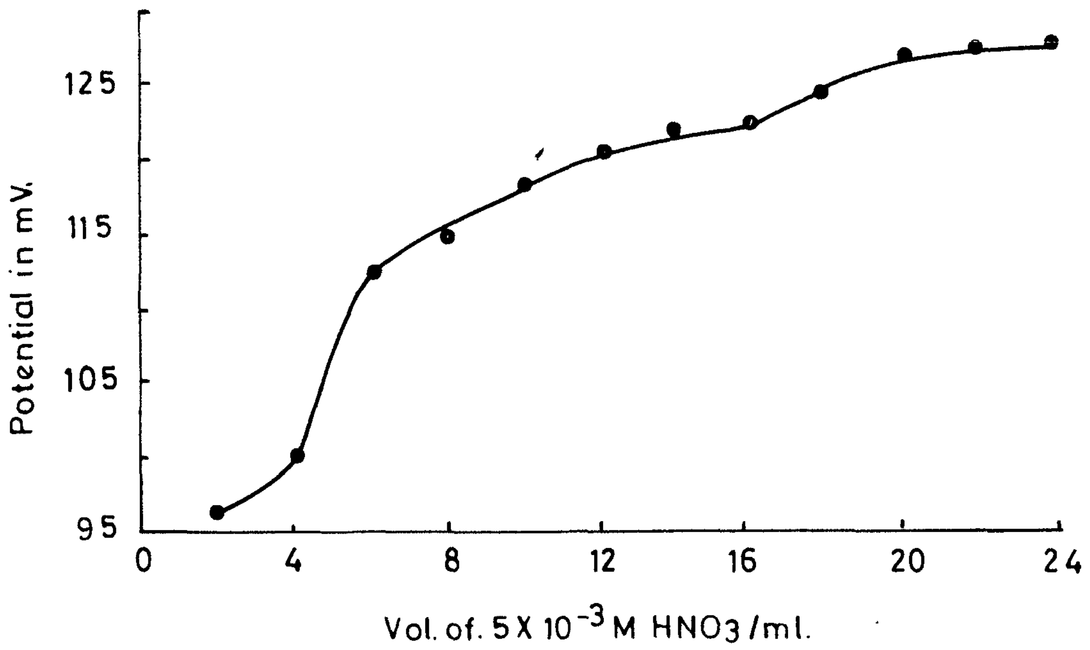


Fig. 2 (XVIII) Potentiometric Titrations

10ml ($\frac{M}{20}$) $Ni(tu)_4Cl_2$ + 20 ml ($\frac{M}{20}$) O-phen

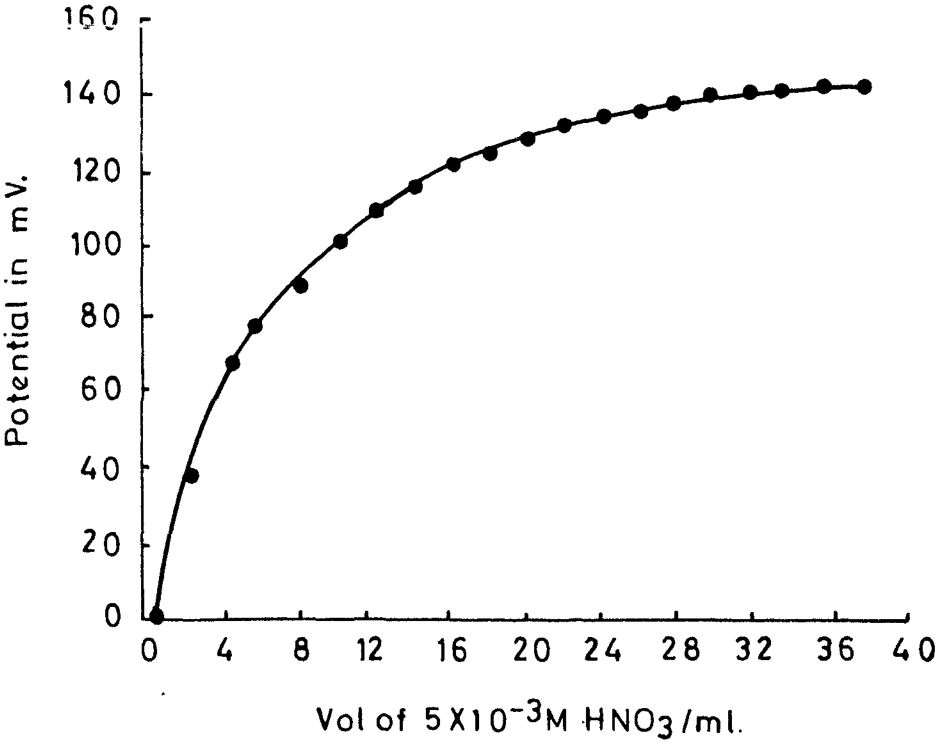


Fig. 2 (XVII) Potentiometric Titrations

10ml ($\frac{M}{20}$) $Ni(tu)_4Cl_2$ + 40ml ($\frac{M}{20}$) O-phen

Conductometric measurements: The conductivity of the solutions was measured with a Philips Conductivity bridge (type PR 9500, using a dip type conductivity cell (cell constant = 1.525).

Magnetic susceptibility measurements: The magnetic susceptibility measurements were made with a Gouy magnetic balance, attached with temperature control adjustments.

Potentiometric measurements: The potentiometric titrations were performed with a Toshniwal potentiometer type CL06 using platinum and saturated calomel as indicator and reference electrodes, respectively. The titrations were carried out with a series of solutions containing mixtures of: (i) $NiCl_2$ + tu (ii) $NiCl_2$ + py (iii) $NiCl_2$ + tu + py (iv) $NiCl_2$ + tu + dipy (v) $NiCl_2$ + tu + o-phen (vi) $Ni(tu)_4Cl_2$ + py (vii) $Ni(tu)_4Cl_2$ + dipy (viii) $Ni(tu)_4Cl_2$ + o-phen etc., with varied concentrations of the reagents, using standard $.5\times10^{-2}$M HNO_3 as the titrant. The results are summarised in table 2 and the curves are given in figures 2(I) to 2(XVIII).

Kinetic measurements: The kinetic studies were carried out by the potentiometric measurements using $Ag-Ag_2S$ as an indicator electrode (discussed in detail in case of Cu(I) and palladium(II) complexes, Vide Chapter III and VII). The application of potentiometric method in such systems

T A B L E -2:

Summarised results of the potentiometric titrations of Ni(II) complexes.

S.No.	Conc.of the species present	Ionic strength	Titrant value (in ml. of $5x10^{-2}$) HNO_3	$\bar{n}$	Curve No.	Complex formed
1.	10 ml($5x10^{-2}$M) $NiCl_2$ +20 ml ($5x10^{-2}$M) tu	0.166	7.0	1.3	2(I)	Ni(tu) Cl_2
2.	10 ml($5x10^{-2}$M) $NiCl_2$ +40 ml ($5x10^{-2}$M) tu	-	8.0	3.2	2(II)	$Ni(tu)_3Cl_2$
3.	10 ml($5x10^{-2}$M) $NiCl_2$ +60 ml ($5x10^{-2}$M) tu	-	12.0	3.8	2(III)	$Ni(tu)_4Cl_2$
4.	10 ml($5x10^{-2}$M) $NiCl_2$ +40 ml ($5x10^{-2}$M) o-phen.	-	17.0	2.3	2(IV)	$Ni(o\text{-}phen)_2Cl_2$
5.	10 ml($5x10^{-2}$M) $NiCl_2$ +20 ml ($5x10^{-2}$M) dipyridyl	-	7.0	1.3	2(V)	Ni(dipy)Cl
6.	10 ml($5x10^{-2}$M) $NiCl_2$ +40 ml ($5x10^{-2}$M) dipy	-	22.0	1.8	2(VI)	$Ni(dipy)_2Cl_2$
7.	10 ml($5x10^{-2}$M) $NiCl_2$ +60 ml ($5x10^{-2}$M) py	-	10.0	4.0	2(VII)	$Ni(py)_4Cl_2$
8.	10 ml($5x10^{-2}$M) $NiCl_2$ +40 ml ($5x10^{-2}$M) tu + 40 ml ($5x10^{-2}$M) py	-	20.0 and 25.0	2.0(py) 3.0(tu)	2(VIII)	$Ni(py)_2(tu)_3Cl_2$
9.	10 ml($5x10^{-2}$M) $NiCl_2$ +40 ml ($5x10^{-2}$M) tu + 20 ml ($5x10^{-2}$M) dipy	-	10.0	1.0(dipy)	2(IX)	$Ni(tu)_4dipy\ Cl_2$

TABLE -2: (Contd.)

S.No.	Conc. of the species present	Ionic strength	Titrant value (in ml. of $5x10^{-2}M$) HNO_3	$\bar{n}$	Curve No.	Complex formed
10.	10 ml($5x10^{-2}M$) $NiCl_2$ + 40 ml ($5x10^{-2}M$) tu + 20 ml ($5x10^{-2}M$) o-phen.	0.186	10.0 and 16.0	1(o-phen)	2(X)	$Ni(tu)_4$o-phen Cl_2
11.	10 ml($5x10^{-2}M$) $NiCl_2$ + 20 ml ($5x10^{-2}M$) tu + 10 ml ($5x10^{-2}M$) phOAs	-	22	1(phOAs)	2(XI)	$Ni(phOAs)^{+}$
12.	10 ml($5x10^{-2}M$) $NiCl_2$ + 40 ml ($5x10^{-2}M$) tu + 20 ml ($5x10^{-2}M$) phOAs	-	40	2(phOAs)		$Ni(phOAs)_2$
13.	10 ml($5x10^{-2}M$) $Ni(tu)_4$ Cl_2 + 20 ml($5x10^{-2}M$) py	-	10	1(py)	2(XIII)	$Ni(tu)_3py^{++}$
14.	10 ml($5x10^{-2}M$) $Ni(tu)_4$ Cl_2 + 40 ml($5x10^{-2}M$) dipy	-	20	2(dipy)	2(XIV)	$Ni(dipy)_2Cl_2$
15.	10 ml($5x10^{-2}M$) $Ni(tu)_4$ Cl_2 + 20 ml($5x10^{-2}M$) phOAs	-	20	2(phOAs)	2(XV)	Ni $(phOAs)_2tu_2$
16.	10 ml($5x10^{-2}M$) $Ni(tu)_4$ Cl_2 + 40 ml($5x10^{-2}M$) phOAs	-	20(tu) 36(phOAs)	2(tu) 2(phOAs)	2(XVI)	Ni $(phOAs)_2tu_2$
17.	10 ml($5x10^{-2}M$) $Ni(tu)_4$ Cl_2 + 40 ml($5x10^{-2}M$) o-phen	-	20	2(o-phen)	2(XVII)	Ni o-$phen_2$ Cl_2
18.	10 ml($5x10^{-2}M$) $Ni(tu)_4$ Cl_2 + 20 ml($5x10^{-2}M$) o-phen	-	10(o-phen) 20(tu)	1(o-phen) 3(tu)	2(XVIII)	Ni tu_3o-phen Cl_2

depends upon the fact that there existed a linear relationship between logarithm of thiourea concentration and e.m.f. at reaction mixture's pH (5-8) while using $Ag-Ag_2S$ as an indicator electrode. In other words, with the decrease or increase in concentration of thiourea, there will be corresponding decrease or increase in potential. Taking advantage of this additive property, first order reaction was found to follow a linear relationship between log $\frac{E_t}{E_\alpha - E_t}$ and time, t where E is the maximum potential attained by the system.

In the following pages are given the data of some of the potentiometric measurements obtained for the systems: (i) $Ni(tu)_4Cl_2$ + dipy and (ii) $Ni(tu)_4Cl_2$ + o-phen. (tables 3A to 3C, 4A, 4B). The plots of $\frac{E_t}{E_\alpha - E_t}$ vs. time, t are given in figures 3A, 3B, 3C, 4A and 4B. The K_{obs} values are computed from the slopes of the straight lines and multiplying the latter by a factor 2.3.

The results are summarised in table 4.

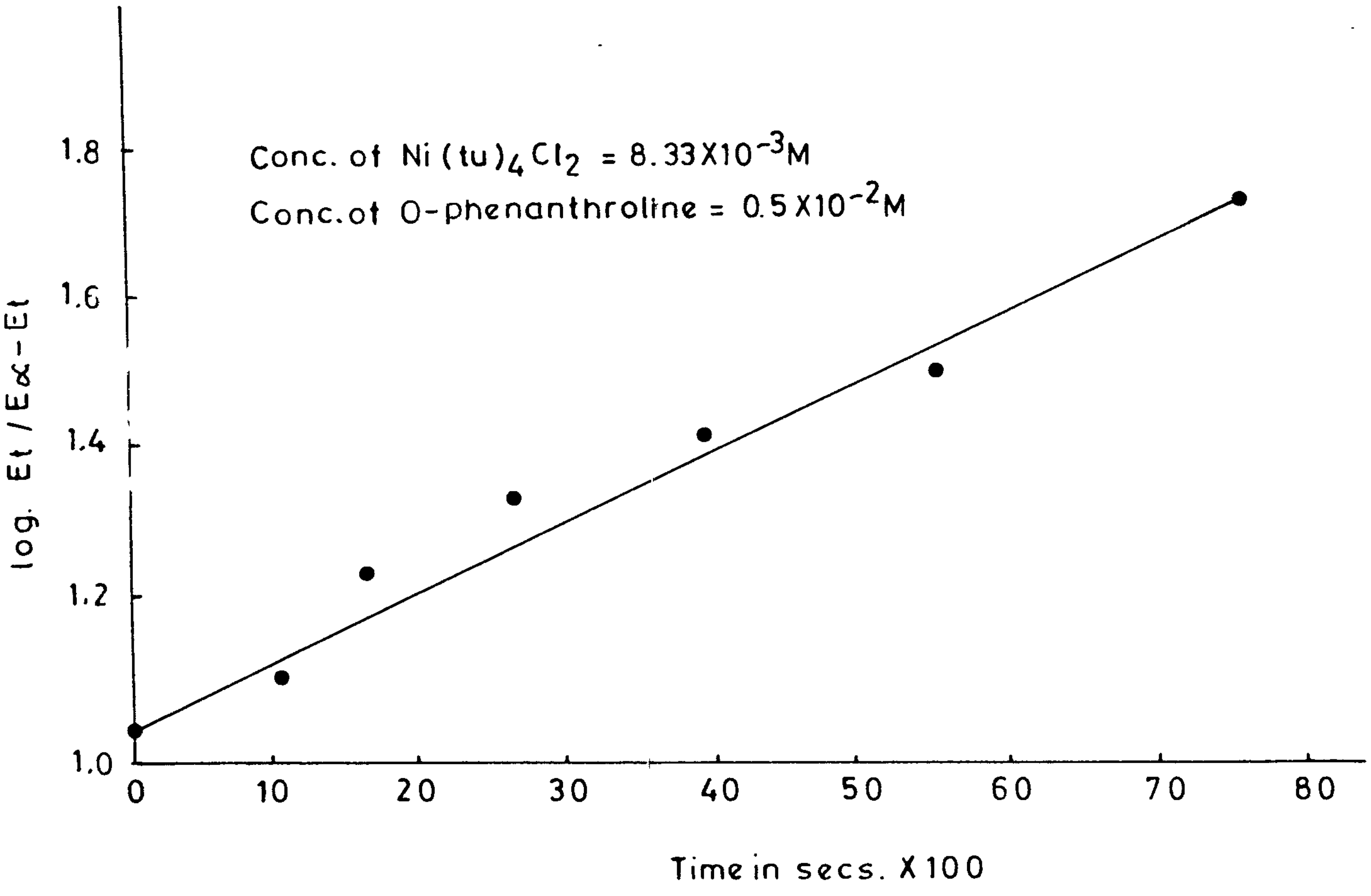


Fig. 3 A Plot $Et / E_{\alpha} - Et$ Vs. (t)

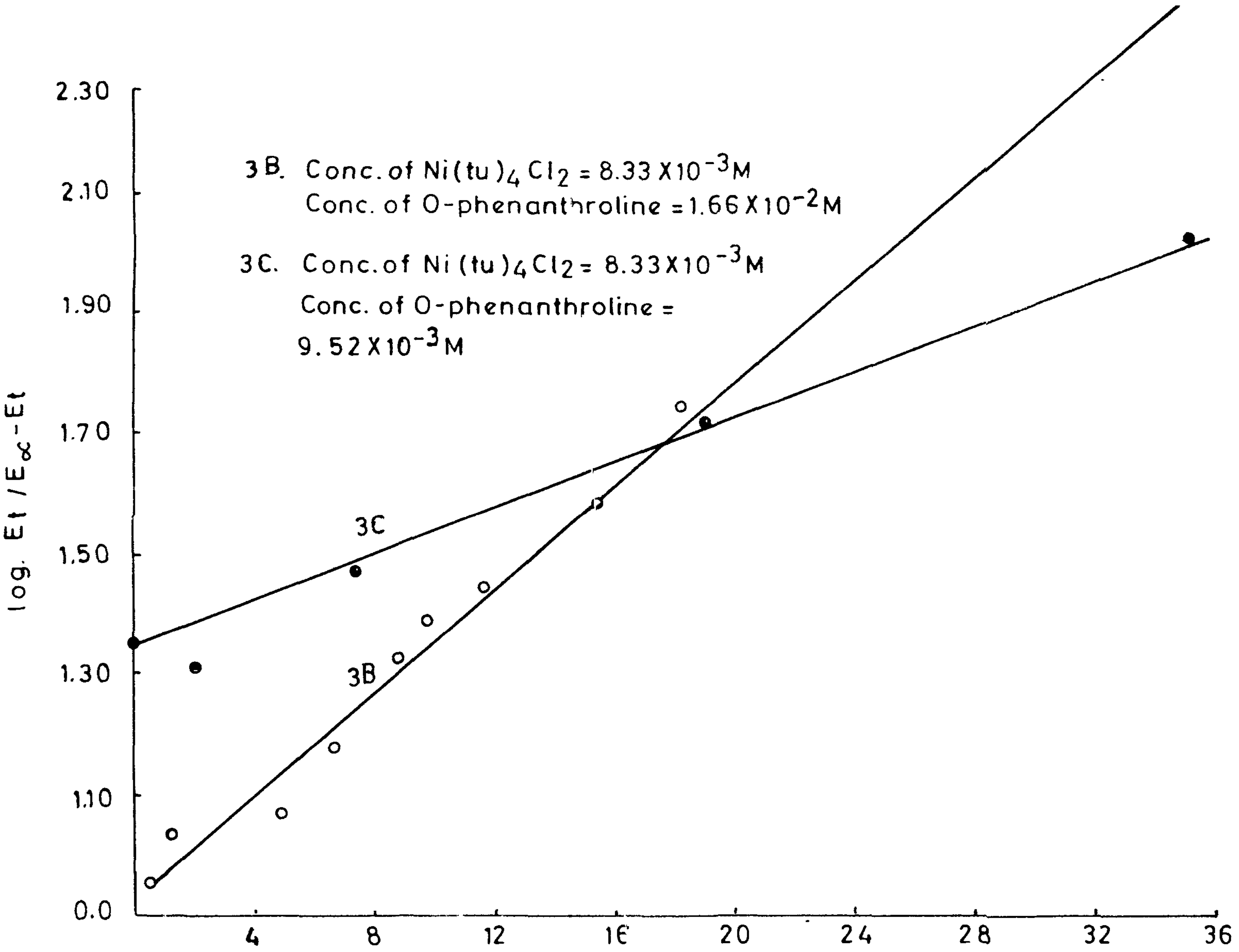


Fig.3B &3C Plot Et/E$_\propto$ −Et Vs. (t)

T A B L E -3A.

Potentiometric data for the first order rate law.

System: $[Ni(tu)_4]Cl_2$ - o-phen
Conc. of $Ni(tu)_4Cl_2$ = $8.33\times10^{-3}M$
Conc. of o-phen. = $0.5\times10^{-2}M$
Temp. = 35°C.

Time in (second)	Potential, E in m.V.	$\log\frac{E_t}{E_\infty - E_t}$	K_{obs} $sec.^{-1}$
0	250	1.017	
1020	253	1.079	
1620	259	1.237	
2580	262	1.339	
3900	264	1.421	
5460	266	1.509	
7560	268	1.650	2.07×10^{-4}
10080	274	-	

(Vide Fig.3A)

T A B L E -3B.

Potentiometric data for the first order rate law.

System: $[Ni(tu)_4]Cl_2$ - o-phen.
Conc. of $Ni(tu)_4Cl_2$ = $8.33\times10^{-3}M$
Conc. of o-phen = $1.66\times10^{-2}M$
Temp. = 35°C.

Time in (second)	Potential, E in m.V.	$\log\frac{E_t}{E_\infty - E_t}$	$K_{obs} sec^{-1}$
0	210	1.176	
30	205	1.033	
60	202	0.963	
120	204	1.029	
480	206	1.058	
660	210	1.176	
870	214	1.320	9.775×10^{-4}
960	215	1.380	
1140	216	1.431	
1530	218	1.560	
1830	220	1.740	
2640	221	1.867	
3540	222	2.045	
4620	223	2.348	
5880	224	-	

(Vide Fig.3B)

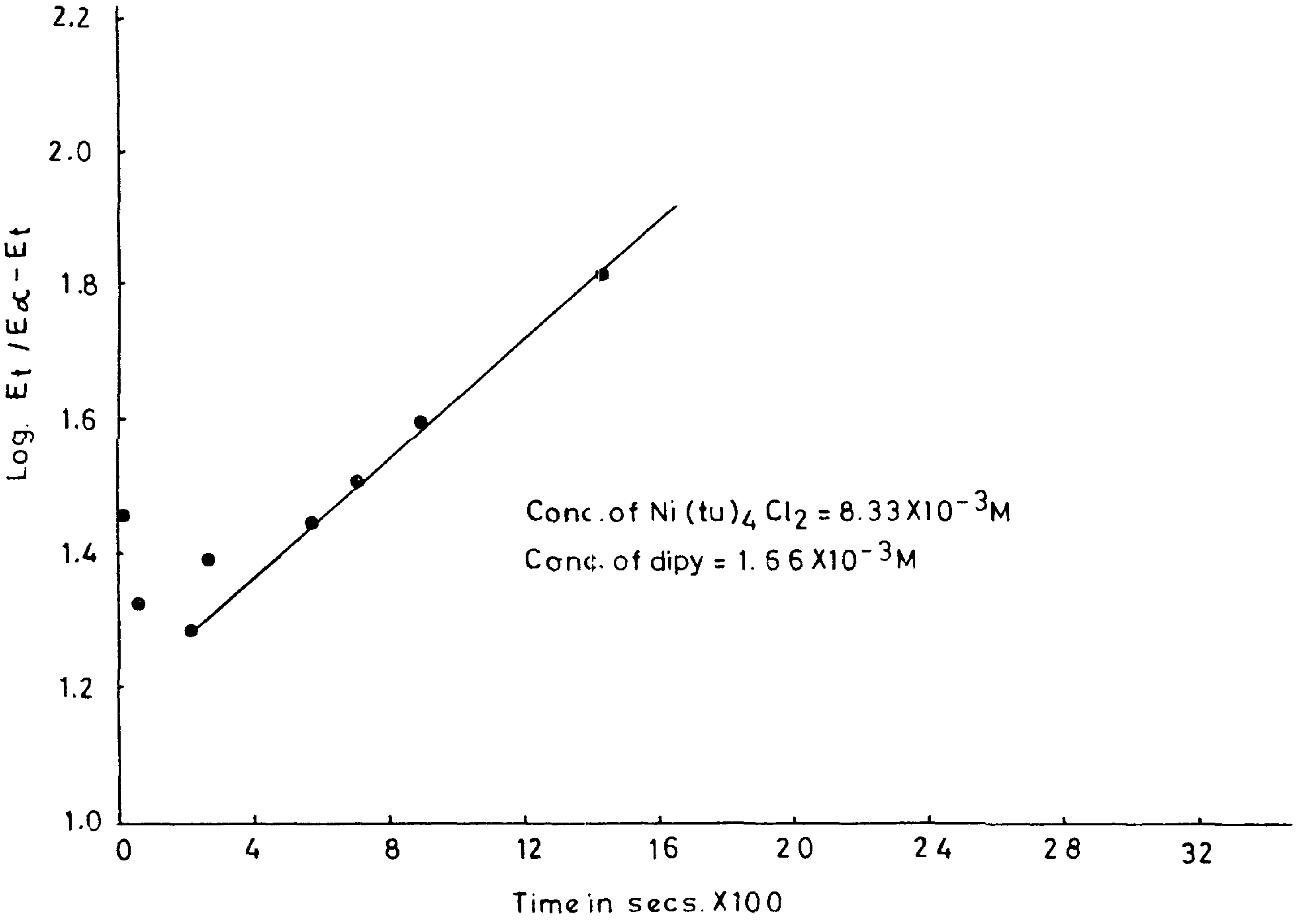


Fig. 4A Plot $E_t / E_\alpha - E_t$ Vs. (t)

TABLE -3C:

Potentiometric data for the first order rate law.

System: [$Ni(tu)_4$]Cl_2- o-phen.

Conc. of $Ni(tu)_4Cl_2$ = $8.33x10^{-3}M$

Conc. of o-phen = $9.52x10^{-3}M$

Temp. = 35°C.

Time in (second)	Potential, E in m.V.	$\log \frac{E_t}{E_\infty - E_t}$	K_{obs} sec^{-1}
0	203	1.353	
20	204	1.406	
740	205	1.467	$4.60x10^{-4}$
1880	208	1.716	
3600	210	2.021	
6200	212	-	

(Vide Fig.3C)

TABLE -4A:

~~Potentiometric data for the first~~ order rate law.

System: [$Ni(tu)_4$] Cl_2-dipy

Conc. of $Ni(tu)_4Cl_2$ = $8.33x10^{-3}M$

Conc. of dipy = $1.66x10^{-2}M$

Temp. = 35°C.

Time in (second)	Potential, E in m.V.	$\log \frac{E_t}{E_\infty - E_t}$	K_{obs} sec^{-1}
0	196	1.447	
60	194	1.333	
210	193	1.286	
270	195	1.387	$9.775x10^{-4}$
670	196	1.447	
690	197	1.516	
870	198	1.597	
1410	200	1.823	
2130	202	2.305	
2970	203	-	

(Vide Fig.4A)

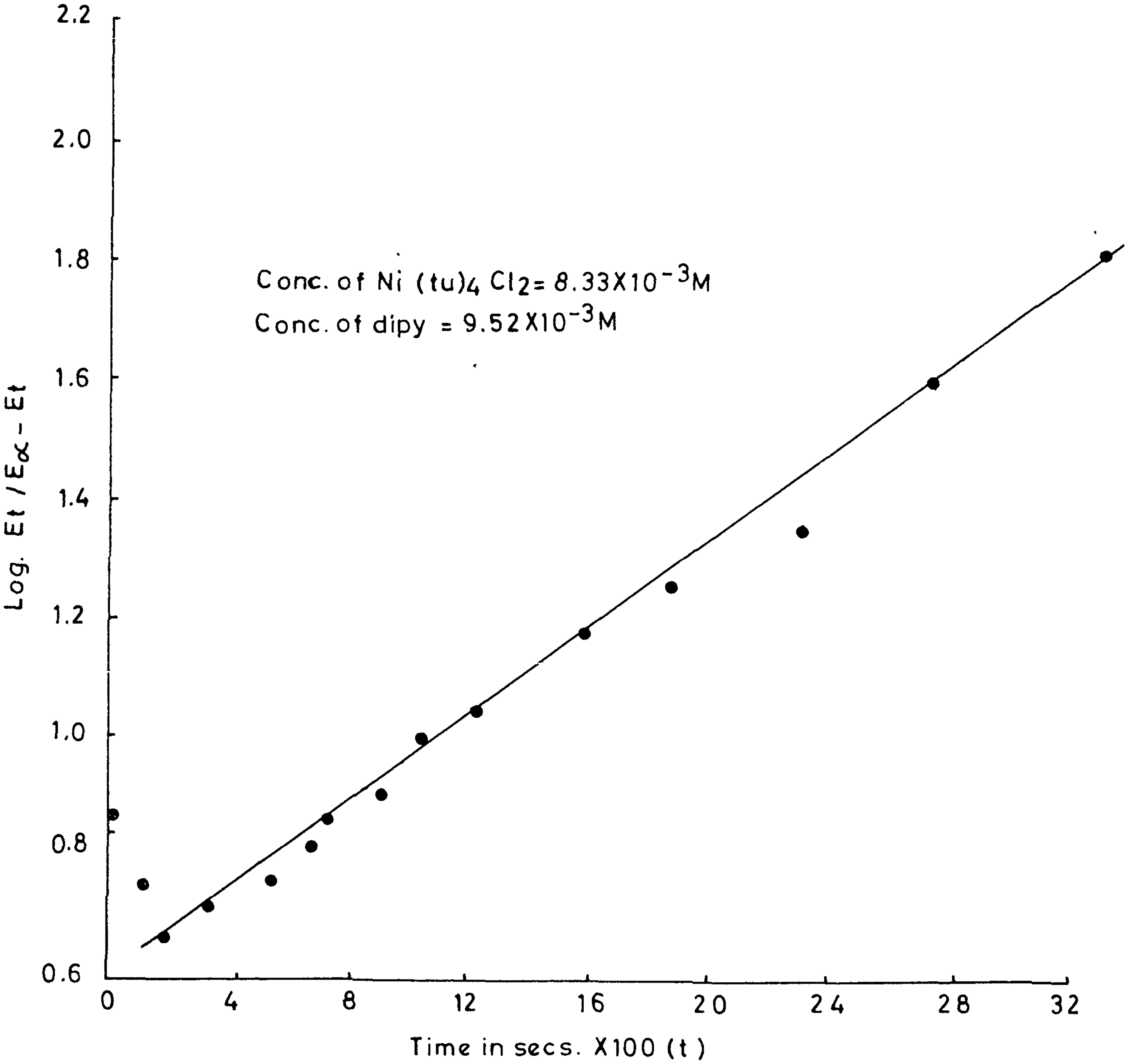


Fig. 4 B Plot $E_t/E_\infty - E_t$ Vs. (t)

TABLE -4B:

Potentiometric data for the first order rate law.

System: $[Ni(tu)_4]Cl_2$ - dipy

Conc. of $Ni(tu)_4Cl_2$ = 8.33×10^{-3}M
Conc. of dipy = 9.52×10^{-3}M
Temp. = 35°C.

Time in (Second)	Potential, E in m.V.	$\log \frac{E_t}{E_\infty - E_t}$	K_{obs} sec^{-1}
0	182	0.862	
105	175	.738	
195	170	.662	
315	173	.707	
555	176	.748	8.05×10^{-4}
675	180	.819	
735	182	.862	
915	184	.903	
~~1035~~	~~188~~	~~.925~~	
1245	190	1.048	
1575	194	1.176	
1875	196	1.250	
2295	199	1.344	
2745	202	1.606	
3315	204	1.832	
3975	206	1.314	
4695	207		

(Vide Fig.4B)

T A B L E -4:

Summarised results* of the kinetic measurements for the systems: (i) $[Ni(tu)_4]Cl_2$ + o-phen. (ii) $[Ni(tu)_4]Cl_2$ + dipy.

Conc. of the complex, $Ni(tu)_4 Cl_2$ = $8.33x10^{-3}M$

Conc. of the reagent		K_{obs} sec^{-1}
$0.5x10^{-2}M$	(o-phen)	$2.0x10^{-4}$
$.95x10^{-2}M$	"	$4.60x10^{-4}$
$1.66x10^{-2}M$	"	$9.775x10^{-4}$
$2.01x10^{-2}M$	"	$7.31x10^{-4}$
$2.53x10^{-2}M$	"	$8.65x10^{-4}$

(Vide Fig. 3A to 3C)

$0.4x10^{-2}M$	(dipy)	$6.98x10^{-4}$
$.95x10^{-2}M$	"	$8.06x10^{-4}$
$1.66x10^{-2}M$	"	$9.77x10^{-4}$
$2.33x10^{-2}M$	"	$11.05x10^{-4}$
$3.0x10^{-2}M$	"	$11.98x10^{-4}$

(Vide Fig. 4A, 4B)

* No data are given for the $Ni(tu)_4Cl_2$- *py* and $Ni(tu)_4 Cl_2$ + ph₃As systems, as the reactions are too fast to be measured.

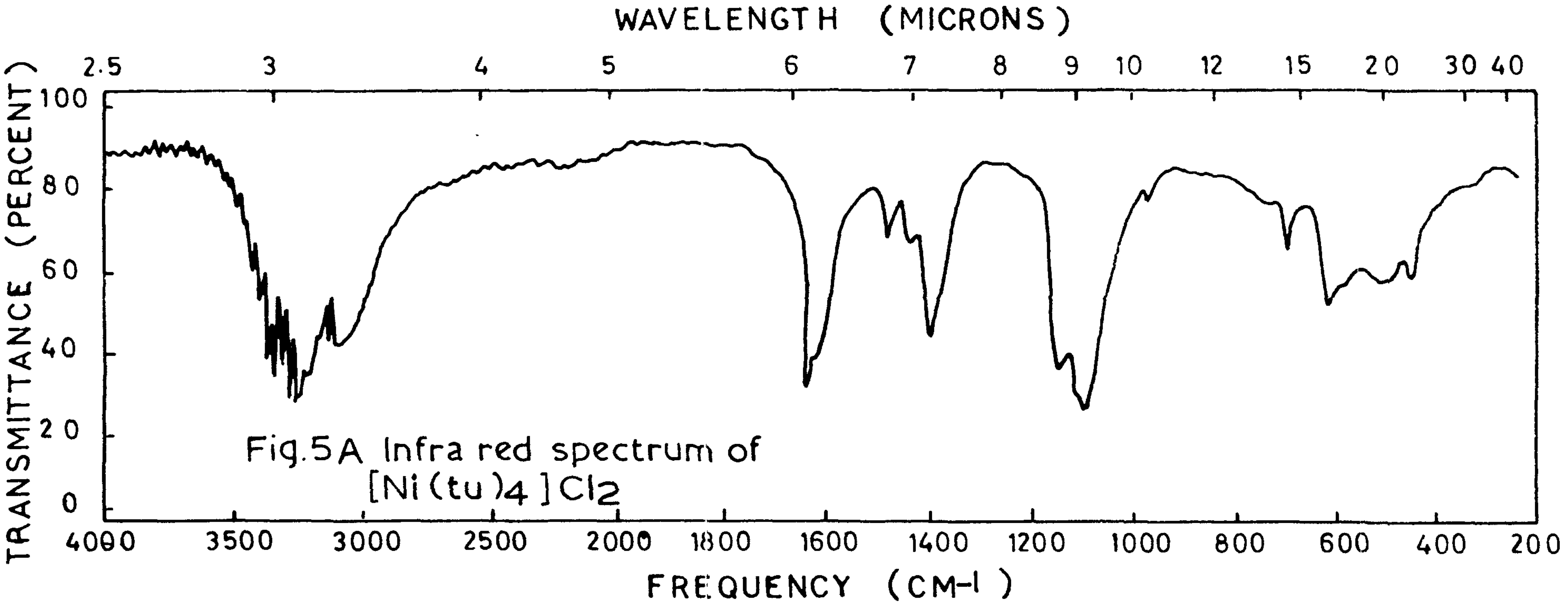


Fig.5A Infra red spectrum of $[Ni(tu)_4]Cl_2$

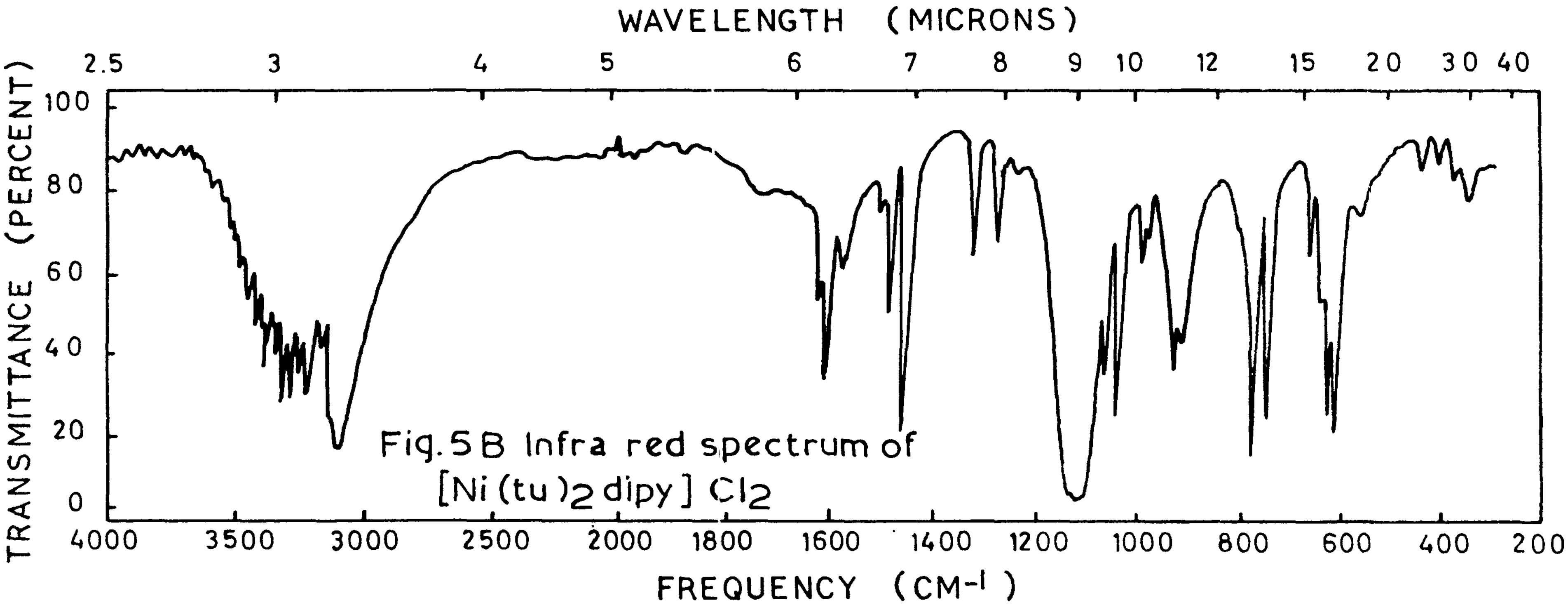


Fig. 5B Infra red spectrum of $[Ni(tu)_2 dipy]Cl_2$

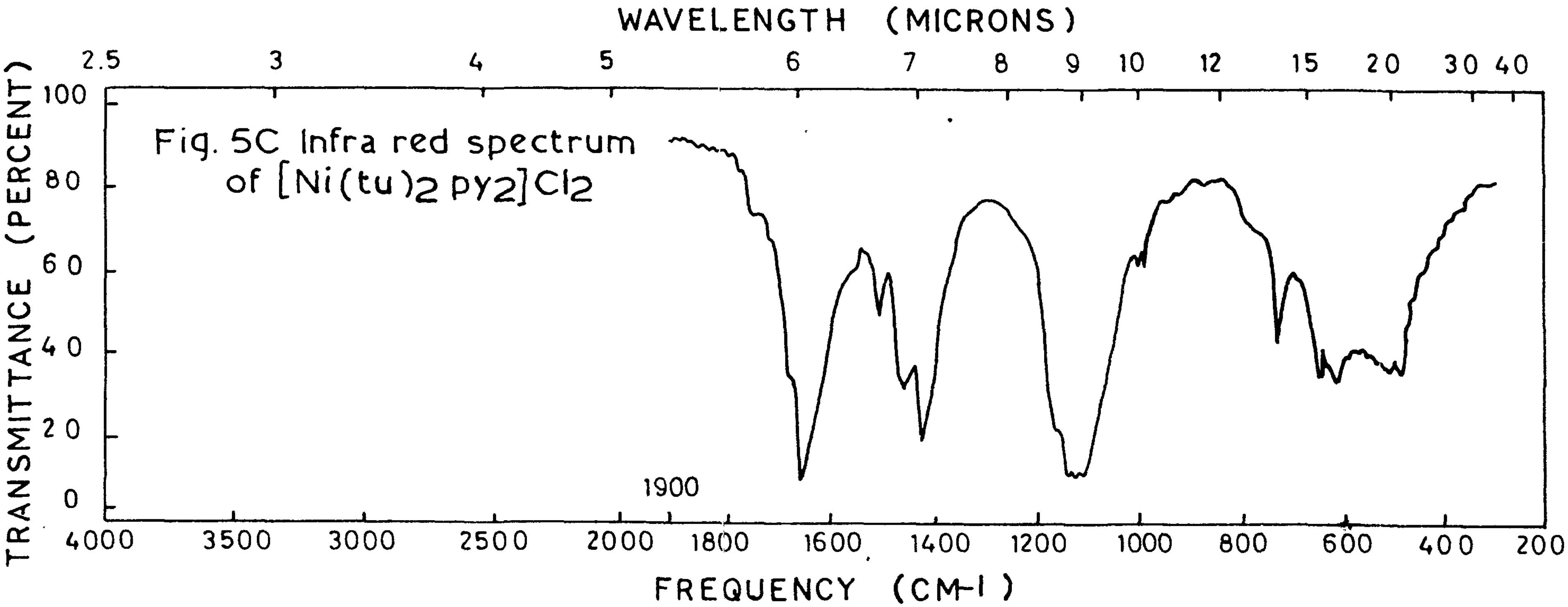


Fig. 5C Infra red spectrum of $[Ni(tu)_2py_2]Cl_2$

Infra red spectra of Ni(II) Complexes:

The infra red spectra of the complexes were recorded with a Perkin Elmer 237 spectrometer, in the region 2.5 to 15 μ, employing standard KBr technique. The far infra red spectra (16 to 40 μ) were taken with a Perkin Elmer IR-10 spectrometer, using nujol mull and CsI prism. The spectra of Ni(II) complexes are given in figures 5A to 5C, and the positions of the various bands present in the spectra are stated as follows:

1. $[Ni(tu)_4]Cl_2$: 1620(s), 1495(m), 1390(s), 1130(m), 1090(s&b), 985(w), 710(s), 640(s), 585(s), 470(s), 280(s).
2. $[Ni(tu)_2py_2]Cl_2$: 1620(v.s), 1480(s), 1435(m), 1390(s), 1030-1100(m&b), 880(w), 870(w), 715(s), 630-640(w&b), 590(m), 400(m), 275(s).
3. $[Ni(tu)_2dipy]Cl_2$: 1610(m), 1600(v.s), 1565(m), 1495(m), 1480(s), 1450(v.s), 1440(m), 1310(s), 1260(s), 1230(m), 1080-1070(s&b), 1055(m), 1030(v.s), 1020(m), 980(s), 970(m), 915(s), 910(m), 865(v.s), 735(v.s), 665(m), 620(s), 610(s), 600(s), 565(m), 440(s), 410(s), 380(m), 355(s), 265(s).
4. $[Ni(tu)_2o\text{-}phen.]Cl_2$: 1620(s), 1580(m), 1540(m), 1500(s), 1460(w), 1440(m), 1430(s), 1360(m), 1240(m), 1120(s), 1080(s), 990(m), 880(s), 870(s), 830(m), 800(m), 730(s), 725(m), 650(m), 630(m), 530(m), 480(s), 470(m), 430(m), 270(s).

The infra red spectrum of the complex, $[Ni(tu)_4]Cl_2$ has been discussed by Cliff[27] in detail and more or less same changes are being observed here as reported by the author. For example, the band at 1475 cm^{-1} assigned to N-C-N stretching modes (B_1) of thiourea is shifted to higher frequency e.g., 1495 cm^{-1} on coordination. The thiourea bands at 1090 cm^{-1} and 735 cm^{-1} are appeared at 1130 cm^{-1} and 710 cm^{-1}, respectively in the complex. The spectra of the complexes, $[Ni(tu)_2py_2]Cl_2$, $[Ni(tu)_2dipy]Cl_2$ and $[Ni(tu)_2o\text{-}phen]Cl_2$ are studied, taking into considerations (i) the changes brought about on coordination with amines and thiourea, and (ii) the conclusions already drawn from the studies of the spectra of mixed ligand complexes of Cu(I) and Pd(II) (Chapter III and VII). As expected it is difficult to make a distinction between the bands arising from ring CC,CN stretches and CH out of plane deformations of amines in one band and the NH bending, N-C-N stretching and A_1 modes (composite bands of C-S str., C-N str. and NH_2 rocking) of thiourea on the other band, but the presence of a relatively few bands in the spectrum of $[Ni(tu)_2py_2]Cl_2$ is an indication of the absence of any major change brought by the coordinated pyridine. Considering the changes occured due to the coordination through sulphur (of thiourea) it is revealed that the shifting of the bands was not so obvious as in case of $Ni(tu)_4Cl_2$ complex (Cf. $[Cu(tu)_3py]I$, chapter III). These observations are not in parallel with those of $[Pd(tu)_4]Cl_2$ (chapter VII) where the bands due to coordinated pyridine are more obvious. One satisfactory conclusion from this study is the presence of a relatively loose bonding of pyridine with Ni(II) in the coordination sphere, $[Ni(tu)_2py_2]^{2+}$.

The spectra of $[Ni(tu)_2dipy]Cl_2$ and $[Ni(tu)_2o\text{-}phen]Cl_2$ are characterised by the appearance of a number of bands. These bands are typical of coordinated dipyridyl and o-phenanthroline. Peaks in the regions ca.1600 cm^{-1} and 700-800 cm^{-1} resulting from CC,CN ring stretchings and CH out of plane deformations, respectively are splitted and shifted slightly to higher wave numbers in the spectra of the complexes. The splitting is more pronounced in the 700-800 cm^{-1} region whereas shifting to higher frequences is more marked in the ca.1600 cm^{-1} region. In case of o-phenanthroline complex, the CH out of plane absorptions at 850 and 740 cm^{-1} are slightly lowered. Due to complexity of the spectra it is difficult to assign completely the bands arising from coordinated thiourea, however, it is not unreasonable to assign bands at 1480(1500), 1080-1070(1120) and 735 (725) cm^{-1} to those arising from coordinated thiourea (frequencies in brackets are given for o-phenanthroline complex).

An interesting aspect of the i.r. spectra of the substituted dipyridyl and o-phenanthroline complexes is that the shiftings of the frequencies arising from coordinated thiourea were less pronounced in comparison to that observed in thiourea complex, $Ni(tu)_4Cl_2$ - a conclusion also arrived in case of palladium(II) substituted complexes (Chapter-VII). Qualitatively, this is an indication of stronger bonding through heterocyclic nitrogens of bidentate ligand in comparison to sulphur (of thiourea) in $[Ni(tu)_2o\text{-}phen]Cl_2$ and $[Ni(tu)_2dipy]Cl_2$ complexes, wherease there is weaker nitrogen bonding in case of $[Ni(tu)_2py_2]Cl_2$ complex.

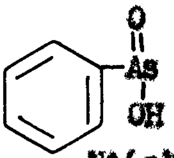
The strong bands at 280 cm^{-1} in $[Ni(tu)_4]Cl_2$, 275 cm^{-1} in $[Ni(tu)_2py_2]Cl_2$, 265 cm^{-1} in $[Ni(tu)_2dipy]Cl_2$ and 270 cm^{-1} in $[Ni(tu)_2o\text{-}phen]Cl_2$ may be assigned to metal - sulphur stretches.

RESULTS AND DISCUSSION

The substitution reactions of square planar $[Ni(tu)_4]Cl_2$ with heterocyclic amines and phenyl arsonic acid, $C_6H_5AsO-(OH)_2$, were investigated mainly to study the effect of substitution on the stereochemistry of Ni(II), and to suggest some mechanism for the changes taking place during the course of reaction.

With pyridine, 2,2'bipyridyl and o-phenanthroline, mixed ligands complexes of the types $[Ni(tu)_2py_2]Cl_2$ (bluish green), $[Ni(tu)_2dipy]Cl_2$ (pink) and $[Ni(tu)_2\ (o\text{-}phen)]Cl_2$ (pink) were isolated and characterised. All the complexes were found to be diamagnetic at room temperature indicating thereby no apparent stereochemical change on substitution. The magnetic studies were further extended to solutions. Two types of experiment were performed one in which the magnetic susceptibility measurements were made with solutions obtained by dissolving the complexes in water and solvents like dimethyl formamide, tetrahydrofuran and nitromethane, and the other in which yellowish green complex, $[Ni(tu)_4]Cl_2$, was dissolved in the solvents (water, acetone, alcohol, tetrahydrofurane and dimethyl formamide) in presence of excess of the ligands. Unfortunately, these studies indicate the absence of any magnetic change over and thus it was concluded that during substitution no major stereochemical shift takes place and therefore, no mechanism is required for substitution involving stereochemical change in such systems.

The substitution product with phenyl arsonic acid



$- OH$ (phOAs), on isolation gave an interesting product, Ni(phOAs)$_2$tu Cl (canary yellow, diamagnetic), indicating thereby the replacement of three thiourea molecules by two phenyl arsonic acid molecules with the elimination of one proton. The formation of such a compound may take place only when out of the two arsine ligands one acts as a monodentate group and the other as a bidentate.

Considering the electronic absorption spectra of square planar complexes,[28] three types of electronic transition can be anticipated from spectral absorption bands namely "d-d", ligand to metal ($L \rightarrow M$), and metal to ligand ($M \longrightarrow L$) charge transfers. For the d^8 diamagnetic complexes, there are the possibilities of three spin-allowed d-d transitions, $d_{xy} \longrightarrow d_{x^2-y^2}$, $d_{z^2} \rightarrow d_{x^2-y^2}$, and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$. We also expect intramolecular $L \longrightarrow M$ charge transfer bands from all the allowed transitions described generally as $\sigma \longrightarrow x^2-y^2$. For complexes containing π acceptor ligands such as CN^-, one may expect $M \longrightarrow L$ transitions from the three filled 'metal' levels to the lowest energy 'ligand orbitals'.

The spectrum of Ni(tu)$_4^{2-}$ (fig.ID) gives a low energy intense band at 14,705 cm^{-1}. However, in the substituted complexes, $[Ni(tu)_2dipy]Cl_2$, $[Ni(tu)_2\ o\text{-}phen]Cl_2$ and $[Ni(tu)_2py_2]Cl_2$ (Fig. IA to ID), we assign the bands at 19230 cm^{-1}, 19230 cm^{-1} and 19305 cm^{-1}, respectively, due to d-d transitions ($1_{A_{1g}} \longrightarrow 1_{A_{2g}}$).

The bands at 25,000 cm^{-1} $[Ni(tu)_4]^{++}$; 28140 cm^{-1} $[Ni(tu)_2dipy]^{++}$, 28570 cm^{-1} $[Ni(tu)_2\ o\text{-}phen]^{++}$, and 25640 cm^{-1} $[Ni(tu)_2(py)_2]^{++}$, are assigned as charge transfer bands arising from $M \longrightarrow L$ transitions, whereas the bands at still higher energies, viz., 32250, 37730, and 40,000 cm^{-1} $[Ni(tu)_2dipy]^{++}$; 37040 and 42550 cm^{-1} $[Ni(tu)_2o\text{-}phen]^{++}$ 38460 cm^{-1} $[Ni(tu)_2py_2]^{++}$ are $L \longrightarrow M$ charge transfer bands. The assignments are summarised in table 5.

TABLE -5.

Assignments to the Electronic Absorption Spectra of Ni(II) Complexes

Complex	cm^{-1}	(ε)	Assignments
$Ni(tu)_4Cl_2^a$	14705	(11)	d — d
$Ni(tu)_2dipy\ Cl_2^c$	19230	(3)	"
$Ni(tu)_2o\text{-}phen\ Cl_2^c$	19230	(8)	"
$Ni(tu)_2py_2\ Cl_2^b$	19305	(5)	"

(Contd.)

TABLE -5: (Contd.)

Assignments to the Electronic Absorption Spectra of Ni(II) Complexes

Complex	cm^{-1}	($\mathcal{E}$)	Assignments
Ni(tu)$_4$Cl$_2^a$	25,000	(24)	M → L
Ni(tu)$_2$dipy Cl$_2^c$	28,140	(303)	"
Ni(tu)$_2$o-phen Cl$_2^c$	28,570	(19)	"
Ni(tu)$_2$py$_2$ Cl$_2^b$	25,640	(11.5)	"
Ni(tu)$_2$dipy Cl$_2^b$	32,250	(4.0x10^4)	"
	37,730	(4.2x10^4)	"
	40,000	(5.4x10^4)	L → M
Ni(tu)$_2$o-phen Cl$_2^b$	37,040	(7.0x10^4)	"
	42,550	(6.5x10^4)	"
Ni(tu)$_2$py$_2$ Cl$_2^b$	38,460	(8.4x10^3)	"

(a-dimethyl formamide, b-H$_2$O, c-nitromethane)

The values of spectral parameter (Δ_1) for the complexes are given in table 6.

TABLE -6:

Spectral parameters ^{*29}

Complex	Configuration	D_q (cm^{-1})
Ni(tu)$_2$dipy^{++}	planar	22170
Ni(tu)$_2$o-phen^{++}	"	22107
Ni(tu)$_2$py^{++}	"	22107
Ni(tu)$_4$$^{++}$	"	17505

$^*A_1$; $F_2 = 10F_4 = 800$ cm^{-1}

$\triangle_1$ values of the Ni(II) complexes are comparable to strong ligand fields and follow the order: tu $<$ py $<$ o-phen $\sim$ dipy.

The potentiometric titration method was applied to determine the composition of the complexes formed during the substitution reactions of heterocyclic amines with planar $[Ni(tu)_4]Cl_2$ complex.

In the first set, mixtures of $(NiCl_2+L)$ where L = tu, dipy and o-phen were titrated with standard $5\times10^{-2}M$ HNO_3 at a constant ionic strength of 0.166. From the potentiometric titration curves (fig.2(I) to 2(VII)), the formation of species such as $Ni(tu)^{++}$, $Ni(tu)_3^{++}$ and $Ni(tu)_4^{++}$; $Ni(o\text{-}phen)_2Cl_2$; $Ni(dipy)Cl_2$ and $Ni(dipy)_2Cl_2$; and $Ni(py)_4Cl_2$ is indicated (table 2). The existence of such complex species in solutions indicates a sort of stepwise complex formation in which the final species is a stable tetracoordinated product. In the second set, mixtures of $NiCl_2$ + tu + L (where L=py, dipy, o-phen and phOAs) were used for titration against standard HNO_3. From the titration curves (fig.2(VIII) to 2(XII)), we inferred the possibilities of the formation of the complexes, $Ni(py)_2(tu)_3Cl_2$, $Ni(tu)_4dipy\ Cl_2$, $Ni(tu)_4o\text{-}phen\ Cl_2$, $Ni(phOAs)^+$, and $Ni(phOAs)_2$. The existence of such complex species should not be confused with those actually formed in the solution as the former merely represent the products derived from the combining ratios.

Attending to the results of potentiometric titrations for the system: $NiCl_2$ + thiourea + pyridine, from the titrant values, combining ratios of 2(py) and 3(tu) are obtained thus indicating only the consumption of these ligands during complex formation, and the following solvent assisted mechanism may involve during the course of reaction:

$$NiCl_2 + 3tu + aq \longrightarrow Ni(tu)_3aq^{++}$$

$$Ni(tu)_3aq^{++} + 2py \longrightarrow Ni(tu)_2py_2^{++} + tu$$

The reaction of $NiCl_2$, tu and dipy, may proceed by one of the following mechanisms:

$$NiCl_2 + 4tu \longrightarrow Ni(tu)_4^{++}$$

$$Ni(tu)_4^{++} + dipy \longrightarrow Ni(tu)_4dipy^{++} \text{ ———————— } (I)$$

$$Ni(tu)_4dipy^{++} \longrightarrow Ni(tu)_2dipy^{++} + 2tu \text{ ———— } (II)$$

The fact that the species, $[Ni(tu)_2dipy]^{++}$ has actually been isolated indicates that the mechanism (II) is preferable. Similarly, the reaction with o-phenanthroline also seems to proceed by mechanism (II) as the product, $[Ni(tu)_2o\text{-}phen]Cl_2$ has also been isolated. The reaction with phenyl arsonic acid completes with the formation of chelate $Ni(phOAs)_2$ via $Ni(phOAs)^+$.

The third set of titrations consists of the mixtures, $Ni(tu)_4Cl_2$+L where L = py, dipy, o-phen and phOAs, the titrant values obtained from the potentiometric curves (fig.2(XIII) to 2(XVIII)) give some interesting results which are discussed briefly as follows:

With pyridine, a combining ratio of 1:1 is obtained thus indicating the formation of species such as $Ni(tu)_3py^{++}$, obviously the reaction proceeds in this case by the substitution of one thiourea molecule with one pyridine.

With 2,2' dipyridyl, 2 mols. of the ligand are found to be involved in complex formation, thus displacing all the tu molecules in the substitution reaction:

$Ni(tu)_4^{++} + 2\ dipy \longrightarrow Ni(dipy)_2^{++} + 4\ tu$ or we may also expect the following solvent assisted type mechanism:

$$Ni(tu)_4^{++} + 4H_2O \rightleftharpoons Ni(H_2O)_4^{++} + 4tu$$

$$Ni(H_2O)_4^{++} + 2dipy \rightleftharpoons Ni(dipy)_2^{++} + 4H_2O$$

The reaction of $Ni(tu)_4Cl_2$ with o-phenanthroline is relatively complicated in the sense that, from the titration curves (Fig.2(XVII) and 2(XVIII)),we obtain the information regarding the formation of two complexes species viz. , $Ni(o\text{-}phen)tu_3^{++}$ (if the ligand (o-phen) concentration is low) and $Ni(o\text{-}phen)_2^{++}$ (if ligand is in excess).

The kinetic studies on the mechanism of substitution of $Ni(tu)_4Cl_2$ with pyridine, 2,2'dipyridyl and o-phenanthroline, and phenyl arsonic acid were carried out potentiometrically using $Ag-Ag_2S$ as an indicator electrode.

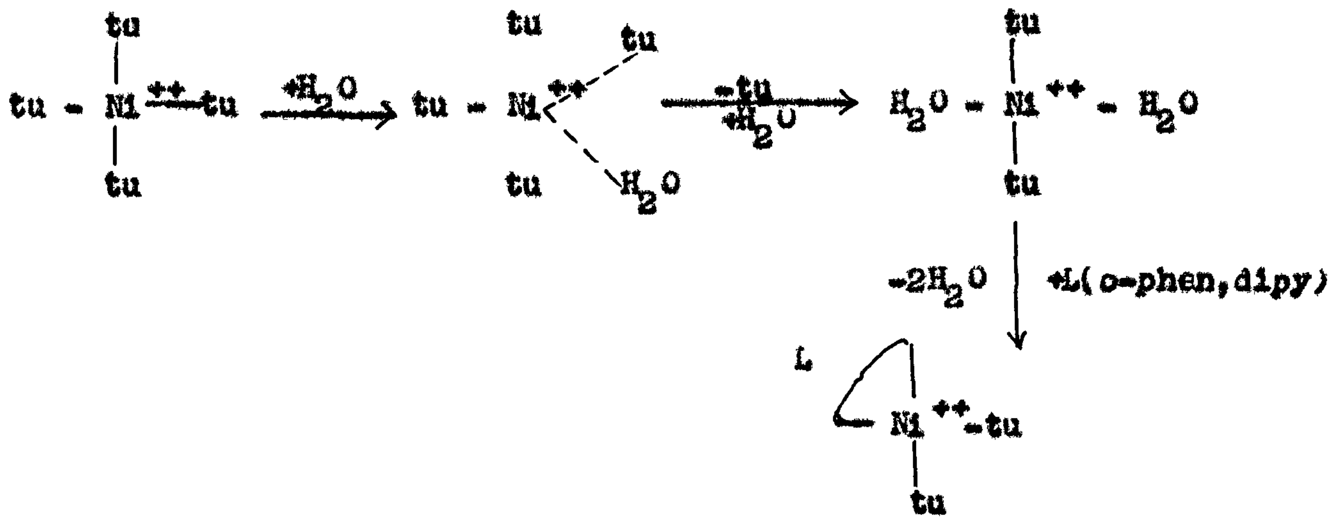
From the potential measurements it follows that the rate of reaction in case of the substitution of pyridine and phenyl arsonic acid with $[Ni(tu)_4]Cl_2$ is too rapid to measure and the equilibrium is attained almost immediately. Such type of behaviour is in conformity with the square planar nickel(II) complexes which are most labile amongst the triad: Pt(II), Pd(II) and Ni(II) (Cf. substitution reaction of pyridine with $Pd(tu)_4^{++}$).

The e.m.f. measurements carried out with the systems: (i) $Ni(tu)_4Cl_2$ + dipy, and (ii) $Ni(tu)_4Cl_2$ + o-phen give a linear relationship between log $\frac{E_t}{E_\infty - E_t}$ (where E_∞ is the maximum potential attained by the system) and time, t. The K_{obs} values computed from the straight line curves (fig.3A to 3C, 4A,4B) are given in table 4.

It was found, however, that the substitutions in these cases (o-phen and dipy) do not follow the two term rate law:

$$K_{obs} = K_1 + K_2 \ [Y]$$

The formation of the dipyridyl and o-phenanthroline substituted complexes could only be explained on considering the following solvent assisted dissociation mechanism:



The infra red spectra of the Ni(II) substituted complexes, $[Ni(tu)_2py_2]^{++}$, $[Ni(tu)_2dipy]^{++}$ and $[Ni(tu)_2o\text{-}phen]^{++}$ were studied in the range 1600-250 cm^{-1}(Fig.5A to 5D). Information regarding the nature of bonding was obtained on comparing the spectra of these complexes with that of the complex, $Ni(tu)_4\ Cl_2$. No pronounced changes were observed in case of pyridine complex thereby not leading to any positive conclusion regarding the bonding in the substituted complex. However, in case of o-phenanthroline and dipyridyl substituted complexes, the spectra are marked by two characteristics namely, (i) appearance of bands typical of coordinated o-phenanthroline and dipyridyl e.g., splitting of bands and shifting to higher frequencies (ii) shifting of frequencies due to coordinated thiourea is less pronounced in comparison to $[Ni(tu)_4]Cl_2$ complex, the latter shows appreciable shifting especially in the regions of NH_2 bending, N-C-N stretching and NH_2 rocking vibrations. The latter characteristic of the spectra is attributed to a stronger bonding through heterocyclic nitrogen in comparison to sulphur in these substituted complexes. The strong bands observed at 280 cm^{-1}, 275 cm^{-1}, 265 cm^{-1} and 270 cm^{-1} in the complexes, $Ni(tu)_4^{++}$, $Ni(tu)_2py_2^{++}$, $Ni(tu)_2dipy^{++}$ and $Ni(tu)_2o\text{-}phen^{++}$, respectively, are assigned to metal - sulphur stretchings in these complexes.

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RESUME

RESUME

CHAPTER - I:

Coordination Compounds of Cuprous Chloride and Iodides with Heterocyclic Amines

Copper(I) chloride and copper(I) iodide form 1:1 complexes with heterocyclic amines. With copper(I) chloride, only complexes with 3-picoline, 2,4 and 2,6 lutidines, quinoline, acridine and piperidine were found to be stable enough to be isolated in the pure state, whereas with copper(I) iodide all the amines e.g., pyridine, picolines (2,3, and 4), lutidines (2,6, and 2,4), quinoline, acridine, isoquinoline, piperidine, o-phenanthroline and 2,2'dipyridyl gave stable products. The complexes with copper(I) chloride are light coloured insoluble in water and subjected to oxidation when allowed to stand for a long time. The copper(I) iodide complexes on the other hand are very stable in solid state as well in solution but like copper(I) chloride complexes they are insoluble in water but soluble in organic solvents such as acetone, chloroform, tetrahydrofuran etc.

All the complexes were found to be diamagnetic as expected from copper(I) species.

The composition of the complexes was also determined by the potentiometric method, using $Cu(I) \rightleftharpoons Cu(II) + e$ couple, from the potentiometric titration curves (chapter I, fig.1) a ratio of 1:1 for Cu^+ and amines was obtained.

The unstable nature of copper(I) chloride - amines complexes is attributed to weak π acceptor properties of amines specially those of pyridine and the substituted pyridines, greater affinity of amines for Cu(II), and the presence of weaker Cu-Cl bond in comparison to Cu-Br and Cu-I bonds. With copper(I) iodide, the conditions for stabilisation are more favourable because of the presence of strong covalent bond between copper(I) and iodide, and strong interaction of heterocyclic nitrogen with the large sized and low positively charged Cu^+ in presence of highly polarized iodide ion. The formation of monocoordinate species in copper(I) is not uncommon and infact it is the characteristic of d^{10} configuration (Ag^+, Au^+, Hg^{++} etc.) to show linear coordination due to small d-s seperation. Another factor which is no less important is the fact that heterocyclic amines have relatively weak π acceptor properties and hence show restricted coordination due to excessive charge accumlation around the copper(I) ion.

The infra red spectra gave some useful information regarding the bonding in copper(I)-heterocyclic amines complexes (vide chapter I, fig.2 to 17). The 1400-1600 cm^{-1} and ca.800 cm^{-1} regions are assigned to ring CC,CN stretching and CH out of plane ring deformation vibrations, respectively. These regions are marked by two distinct changes on coordination (i) reduction in the number of bands and (ii) shifting of the bands to higher wave numbers. The one reason, which seems most plausible for accounting these affects, is the polarization produced on the aromatic ring due to coordination of Cu^+ to heterocyclic nitrogen. The effect is more pronounced in copper(I) iodide complexes than those of corresponding copper(I) chloride complexes.

CHAPTER-II:

Coordination Compounds of Copper(I) Halides with Substituted Thioureas

Thiourea and substituted compounds e.g., diphenyl, o-tolyl, benzyl, naphthyl, allyl,& diisopropyl thioureas form very stable complexes with copper(I) ion. With copper(I) chloride, there is formation of 1:1 and 1:2 complex species, with copper(I) iodide all the substituted ligands give 3-coordinate species. All the complexes are insoluble in water but soluble in acetone, tetrahydrofurane and dimethylformamide, and slightly soluble in alcohols.

Besides chemical analysis, the composition of the complexes was determined by performing potentiometric titrations (both direct and reverse) using $Ag-Ag_2S$ as an indicator electrode (vide Chapter II, fig.3 and 4).

The complexes were diamagnetic at room temperature as indicated by the magnetic susceptibility measurements.

The infra red spectral measurements gave some interesting information regarding the bonding in these complexes. The studies are based upon resonance structures for thiourea which is comprised of keto and enol forms with 20-30% contribution of highly polar structure. It has been assumed that like thiourea, substituted thioureas also give canonical forms with equal contributions. If the coordination takes place through sulphur, it should result in a decrease in the double bond character of C-S and an increase in the double character of C-N bond, whereas if coordination is through nitrogen then just the opposite effect is to be expected together with the reduction in NH frequency. The latter remains unchanged if coordination is through sulphur. On the basis of informations obtained from changes in the region ca.1550 cm^{-1} (NH deformation and CN antisymmetric stretching vibrations) and ca.750 cm^{-1} (C-S stretching with small contribution from symmetric C-N stretching vibrations), the coordination through sulphur is inferred in o-tolyl, benzyl, naphthyl, diisopropyl, and diphenyl thioureas (decrease in C=S stretching frequency and increase in N-H deformation), whereas in case of allyl thiourea coordination through nitrogen is inferred (disappearence of NH deformation band and increase in C-S stretching frequency). The changes are more defined in copper(I) iodide complexes (vide chapter II, fig.5 to 10).

The formation of stable complexes of copper(I) with thiourea and substituted thioureas is expected from the fact that Cu(I) forms $d_{\pi}-d_{\pi}$ bond with sulphur atom of thiourea containing vacant d orbitals which also acts as an acceptor d orbital. Moreover, highly polarised thiourea belonging to class (b), soft bases, has high affinity for class (b) soft acids e.g., Cu^{+} to form stable complexes. This tendency is increased from CuCl to CuI.

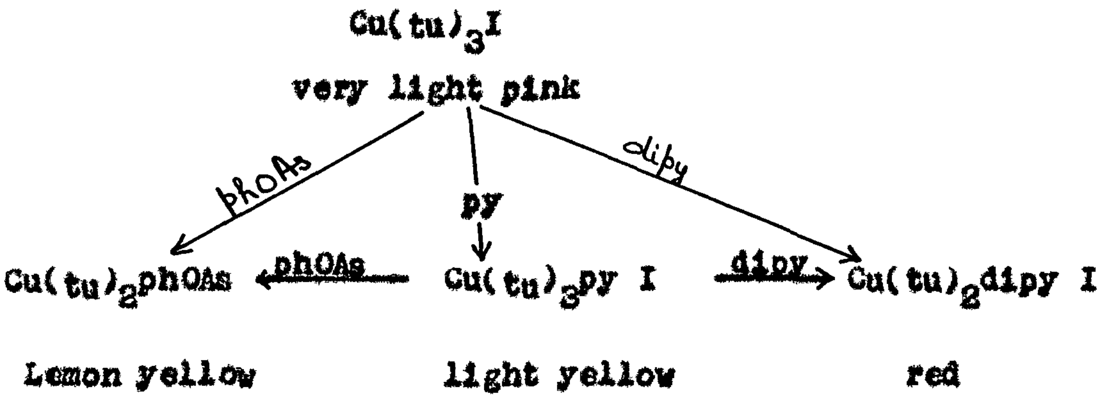
CHAPTER-III:

Studies on Mixed Ligand Complexes of Copper(I)

Starting with tris(thiourea) copper(I) iodide, the following mixed ligand complexes were prepared on interaction with heterocyclic amines:

$[Cu(tu)_3py]I$ (light yellow), $[Cu(tu)_3 2\ pic]I$ (pink), $[Cu(tu)_3 3pic]I$ (light pink), $[Cu(tu)_3\ 4pic]I$ (pink), $[Cu(tu)_3 2,6L]I$ (light pink), $[Cu(tu)_3Q]I$ (dirty yellow), $[Cu(tu)_3I.Q]I$ (pink), $[Cu(tu)_2dipy]I$ (red), $[Cu(tu)_2o\text{-}phen]\ I$ (orange) and $[Cu(tu)(o\text{-}phen)_2]I$ (pink).. With tris(tu) Cu(I) chloride, only the complex, $[Cu(tu)_2dipy]Cl$, was prepared. Except 2,2' dipyridyl and o-phenanthroline all the complexes were soluble in water and organic solvents. The dipy and o-phen complexes were either insoluble or sparingly soluble in water but soluble in organic solvents such as acetone, dimethyl formamide and tetrahydrofurane.

The stereochemical evidence for the formation of 4-coordinate mixed ligand species was provided by the following typical reaction steps:



The formation of tetracoordinate species is further confirmed by performing potentiometric titrations with the mixtures of Cu X + tu + L, and $Cu(tu)_3X$ + L (where L = pyridine or 2,2'dipyridyl, X=Cl^- or I^-), using 0.1M HNO_3 as a titrant (vide chapter III, table 2, fig.3A to 3E). With pyridine, a ratio of 1:1 clearly indicates the formation of tetracoordinate species, $[Cu(tu)_3py]X$, but with dipyridyl the formation of the complex, $[Cu(tu)_3dipy]X$, apparently indicates a coordination number of five for copper(I). The following mechanism, however, could explain the formation of 1:1 ($Cu(tu)_3X$:dipy) complex:

$$Cu(tu)_3^{\ +} + H_2O \longrightarrow \left[Cu(tu)_3\, H_2O\right]^+ \xrightarrow{dipy} \left[Cu(tu)_2dipy\right]^+ + tu$$

The mechanism seems to be plausible as the species, $Cu(tu)_2$ dipy X, have actually been isolated.

The study of the reaction between tris(tu) copper(I) iodide and o-phenanthroline gave some interesting results regarding the formations of the tetra and penta coordinate species. The mechanism of the reaction in such cases may follow the path:

$$Cu(tu)_3I \xrightarrow{\text{o-phen}} \underset{II}{[Cu(tu)_2\text{o-phen}]I} \xrightarrow{\text{o-phen}}$$

$$\underset{III}{[Cu(tu)\text{o-phen}_2]I} \longrightarrow \underset{IV}{[Cu(\text{o-phen})_2]I} + tu.$$

The fact that the species II, III and IV have been isolated from the reaction mixture supports the above mechanism. The potentiometric titrations (vide chapter III, fig.3D and 3E) carried out with mixtures of CuI-tu-o-phen, and $Cu(tu)_3I$ + o-phen., using HNO_3 as titrant gave a ratio of 1:1 and 1:2 indicating thereby the formation of species II, III and possibly IV also.

Using Job's method of continuous variation, the spectrophotometric studies on the reactions of dipy and o-phen with $[Cu(tu)_3]I$ indicate a ratio of 1:2 for $Cutu_3^+$ and o-phen, and 1:1 for $Cutu_3^+$ and dipy (vide chapter III, fig.2a to 2d). The reaction in case of dipy may be explained on considering the following path:

$$Cu(tu)_3^{+} + H_2O \longrightarrow [Cu(tu)_3 H_2O]^{+}$$

$$Cu(tu)_3H_2O^{+} + dipy \longrightarrow [Cu(tu)_3dipy]^{+} + H_2O$$

$$Cu(tu)_3dipy^{+} \longrightarrow [Cu(tu)_2dipy]^{+} + tu$$

The species, $[Cu(tu)_2dipy]^{+}$, has been isolated and characterised, therefore, supporting the above mechanism.

For o-phen complex, the formation of 1:2 complex species supports the results obtained from the potentiometric studies.

The mechanism of the reaction of tricoordinated copper(I)-thiourea complex with heterocyclic amines was studied by e.m.f. measurements using $Ag-Ag_2S$ electrode (chapter III, fig.5 to 9, tables 5 to 10). Advantage was taken of the fact that the concentration of thiourea is directly proportional to the potential, at the pH of the reaction mixture (pH 5-8). Therefore, potential was used as the additive property for finding out the order of reaction.

The reaction of tris(tu) copper(I) chloride with pyridine was found to be a fast one and equilibrium is attained almost immediately (chapter III, fig.7, table 7). The reaction seems to proceed by the following dissociative mechanism involving an increase in the concentration of thiourea at the completion of the reaction:

$$Cu(tu)_3^{+} \longrightarrow Cu(tu)_2^{+} + tu \xrightarrow[fast]{2py} [Cu(tu)_2py_2]^{+}$$

The following mechanism for the substitution reaction of tris(tu) copper(I) chloride with dipyridyl was suggested:

$$[Cu(tu)_3]Cl + dipy \xrightarrow{fast} [Cu(tu)_3dipy]Cl \xrightarrow{slow} [Cu(tu)_2dipy]Cl$$

The above reaction is of second order, first order with respect to each of the reactants. The associative mechanism suggested above is supported by 1:1 ratio obtained from the potentiometric studies and also by the fact that there is gradual decrease in thiourea concentration with time (chapter III, fig.5 and 9, Table 5 and 9).

The reaction of 2,2' dipyridyl with tris(tu) copper(I) iodide proceeds by two reaction rates initially it is a zero order reaction and after about 50 minutes it follows a second order path, first order with respect to each of the reactants (chapter III, Fig.6, Table 6). The potentiometric studies indicate a ratio of 1:1 for the substituent ligand and the complex, $Cu(tu)_3$ I. The following mechanism, involving the formation of aquo complex, $[Cu(tu)_3H_2O]^+$, in the initial stage, is suggested:

$$Cu(tu)_3{}^+ \xrightarrow[slow]{H_2O} [Cu(tu)_3H_2O]^+ \xrightarrow{fast} [Cu(tu)_3dipy]^+ \xrightarrow{slow} [Cu(tu)_2dipy]^+$$

A comparative study of the entering group effect, based upon the rate constant values of the reactions, gives the reactivities of the various ligands in the order: Py$<$dipy$<$ diars$<$o-phen.

The infra red spectra of the mixed ligand complexes (chapter III, fig.10 to 16) were studied keeping in view the changes taking place in the spectra of heterocyclic amine and thiourea on coordination with copper(I). The complexities in the spectra of the mixed ligand complexes did not permit to give conclusive evidence regarding the nature of bonding, however, the region 1600 to 1000 cm^{-1} and 800 to 600 cm^{-1} were found to be of some interest. The spectra in the region 1600 to 1,000 cm^{-1} were marked by two distinct changes: (a) the composite bands assigned to NH_2 bending (ca.1600 cm^{-1}), NH deformations and CN antisymmetric stretchings (ca.1475 cm^{-1}), and N-C-N stretching (ca.1086 cm^{-1}) in thiourea remain almost unaltered on coordination (cf.coordinated thiourea) and (b) the bands arising due to ring CC, CN stretching vibrations (1440, 1485, 1585, 1600, 1635 cm^{-1} in liquid pyridine) are greatly reduced in number on coordination. The appearance of a number of bands in the region 600-800 cm^{-1} may be ascribed to the presence of coordinated amine which brings about splitting of CH out plane deformation vibrations, and also due to the strong polarisation effect of iodide ion on the coordination sphere. The band at 710 cm^{-1} in this region, however, may be assigned to C-S stretching band resulted on coordination through sulphur (730 cm^{-1} in the uncoordinate thiourea).

CHAPTER-IV:

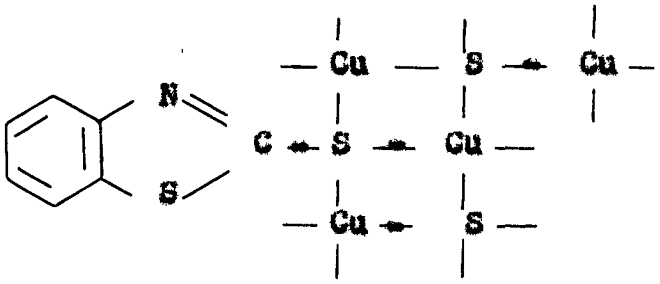
Interaction of Copper(I) Halides with 2,Mercaptobenzthiazole

Copper(I) ion forms complex with 2,mercaptobenzthiazole of 1:1 stoichiometry e.g., Cu(2, mercaptobenzthiazole). The complex is insoluble in water and alcohol but very slightly soluble in acetone. The complex is diamagnetic and the molar conductivity of the complex is 22 cm^2/ohm in $1x10^{-3}$M acetone at 15°C. The thermogravimetric analysis (chapter IV, fig.3 and 4) of the complex indicates its stability upto 150°C.

The reagent, 2, mercaptobenzthiazole may be used as a gravimetric reagent for Cu^+ ion in the concentration range of 2.5-85 mg with an error of less than 0.1% in the pH range 2-3.5 (chapter IV, table 1 and 2).

The infra red spectrum (chapter IV, fig.5A) of the ligand shows the presence of unconjugated thioketo form in the solid state. The spectrum of the complex (chapter IV, fig.5B) does not show any band for N-C=S symmetric and antisymmetric stretching vibrations which are found at 1440 and 1330 cm^{-1}, respectively, in the ligand indicating thereby the removal of a proton on coordination. The displacement of the imino proton is further confirmed by the absence of a band ca.3000 cm^{-1} which is observed at 3100 cm^{-1} in the ligand (NH stretching vibrations).

Out of the three structures: (i) a 4-ring structure resulting by the coordination of Cu(I) through N and S, (ii) simple salt like structure in which hydrogen is replaced by Cu(I), and (iii) a polymeric structure through S bridge in which Cu(I) tends to achieve its maximum coordination number; there is overhalming indication for a polymeric structure as is evident by the insoluble nature of the complex, very low conductivity, presence of Cu-S bond, and absence of Cu-N bond (from the far i.r. spectrum) in the complex. The structure of the polymeric species may be depicted as:



CHAPTER -V:

Coordination Compounds of Rare Earths with Some Substituted Thioureas

Tripositive rare earth ions form 1:1, 1:2, 1:4 and 1:6 complex species with substituted thioureas. Sm^{3+} forms 1:1 species with DIPTU and ATU and 1:2 species with NTU. Gd^{3+} forms 1:4 species with DIPTU, 1:2 species with ATU and TTU, and 1:1 species with DPTU. With Dy^{3+}, 1:2 species is formed with NTU, 1:6 species with TTU, and 1:4 species with DPTU. There is formation of 1:2 species with Er^{3+}-ATU and Er^{3+} - NTU, and 1:1 species with Er-DPTU. The complexes are generally light coloured and highly soluble in water. The formation of 1:1, 1:2, 1:4 and 1:6 species has been explained on considering the nucleophilities of the substituted thioureas which follow the order: DIPTU > ATU > TTU > NTU > DPTU, and the decrease in ionic radii from Sm^{3+} to Er^{3+} (chapter V, table 1). With ligands having lower nucleophilic character, the formation of lower species is anticipated while ligands having higher nucleophilic order the formation of higher species is favoured.

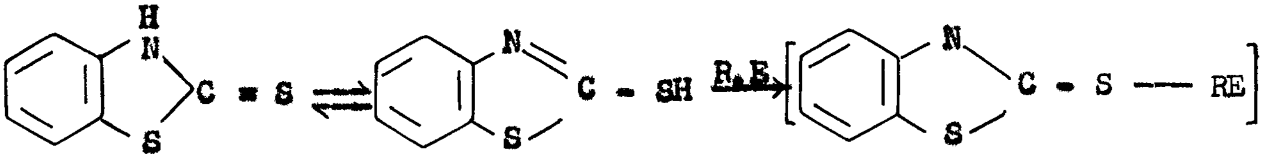
The study of the infra red spectra of the complexes (chapter V, fig.1 to 10) in the regions: ca.1600 cm^{-1} (NH_2 bending modes), ca.1500 cm^{-1} (N-H deformation and C-N anti-symmetric stretching vibrations) and ca.750 cm^{-1} (C-S stretching vibrations), indicates the presence of coordination through sulphur although there is no conclusive evidence in case of o-tolyl thiourea complexes. An interesting feature of of the substituted thioureas complexes is the decrease in NH deformation and C-N antisymmetric stretching frequencies and increase in C-S stretching vibrations with decrease in nucleophilities of the compounds (chapter V, table 3). This shows the strengthening of C-S double bond and decrease in the coordinating ability of sulphur as we move from DIPTU to DPTU.

CHAPTER-VI:

Interaction of Some Rare Earths With 2,Mercaptobenzthiazole

Rare earth (III) ions form 1:1 complex species with 2,mercaptobenzthiazole; Sm^{3+}(pink), Gd^{3+}(light yellow), Er^{3+} (light yellow), Dy^{3+}(pinkish yellow), Tm^{3+} (dirty pink), Pr^{3+}(light green) and Nd^{3+}(light pink). The complexes have the general formula: $R.E.(R')Cl_2$ ($R'H$ = 2,mercaptobenzthiazole), e.g., complex formation takes place by the displacement of one hydrogen by the tripositive cation. The complexes are highly soluble in water but slightly soluble in alcohol.

The conductometric titrations (chapter VI, fig.1), using 2, mercaptobenzthiazole as the titrant, also indicate 1:1 molar ratio for the metal and the ligand. From the infra red spectral studies (chapter VI, fig.2 and 3) two conclusions may be drawn: (i) evidence of strengthening C=N bond and weakening of C=S bond and (ii) little evidence of the elimination of imino proton by the rare earth ions. A possible course for the reaction may thus be depicted as:



CHAPTER-VII:

Studies on Sulphur and Nitrogen Ligated Complexes of Palladium(II)

Palladium(II) chloride forms 1:3 complexes with substituted thioureas, e.g., naphthyl, o-tolyl, diisopropyl and diphenyl thioureas. The analyses of the complexes indicate the presence of one ionisable Cl^- in all the cases thus giving evidence for the formation of the species, $[Pd(L)_3Cl]^+$ (where L = substituted thiourea). The presence of three substituted thiourea molecules in the coordination sphere, however, may be explained on considering the large size of the ligand which is a hindering factor for accomodating more than three molecules of the substituted thioureas, however, to achieve its tetracovalency one Cl^- ion is attached to the central metal ion. The enterance of Cl^- ion in the coordination sphere is entirely nucleophilic and this is enhanced by the d orbital electron contraction as a result of increased positive charge on the complex.

The infra red spectra of the complexes (chapter VII, fig.17 to 21) give some interesting information regarding the coordinating, tendencies of the various substituted thioureas. A gradual increase in N-C-N stretching and decrease in C-S stretching modes is observed as one moves from thiourea to diphenyl thiourea which is in conformity with the nucleophilic order of the ligands e.g., tu > DIPTU > TTU > NTU > DPTU, obviously showing the decreasing tendency to coordinate through sulphur with decreasing nucleophilities of the substituted thioureas. Further, all the evidences from the observed changes in the infra red spectra of the complexes led to the conclusion regarding coordination through sulphur. The strong band at 275-280 cm^{-1} in all the substituted thiourea complexes indicates the presence of a metal-sulphur bond.

The syntheses of the following mixed ligand complexes were achieved: (i) $[Pd(tu)_2py_2]Cl_2$ (brown crystals, soluble in water but insoluble in alcohol and acetone) (ii) $[Pd(tu)_2o\text{-}phen]Cl_2$ (pink crystals, soluble in water slightly soluble in alcohol and acetone) and (iii) $[Pd(tu)_2dipy]Cl_2$ (orange crystals, soluble in water, insoluble in alcohol and acetone). The complex, $[Pd(tu)_2py_2]Cl_2$, should undoubtly be a cis isomer as thiourea has a greater trans effect than pyridine. Substitution of pyridine into $[Pd(tu)_3py]^{++}$ is least likely to occur in position trans to pyridine already present and thus a cis isomer is favoured. The substitution of dipyridyl and o-phenanthroline molecules is explained on the basis of π acceptor character of the ligands leading to the formation of $d_\pi - p_\pi$ bond and their strong nucleophilic character which enables them to enter into coordination sphere by nucleophilic substitution.

The spectrophotometric method was applied to determine the composition and formation constant of the complex formed by the interaction of $[Pd(tu)_4]Cl_2$ and pyridine (chapter VII, fig. 7A and 7B, tables 7A and 7B). From the slopes of the linear plots (log $\frac{A_a - A_o}{A_\infty - A_a}$ versus log X), a ratio of 1:1 ($Pd(tu)_4Cl_2$:py) was obtained and the values of the formation constant, K_f, worked out to be: 2.917 and 2.818 at 20°C and 25°C, respecitvely.

The main characteristics of the infrared spectra of the mixed ligand complexes are:

$[Pd(tu)_2py_2]Cl_2$: Reduction in the number of bands and shifting to higher wave numbers were observed when the spectrum of the complex was compared with those of thiourea and pyridine (chapter VII, fig. 21, 25 and 26). Thus, the presence of thiourea in the mixed ligand complex checked the splitting of the bands, a characteristic of coordinated pyridine, but the bands are shifted to higher frequencies. The band at 730 cm^{-1} observed in the complex corresponds to 735 cm^{-1} band observed in free thiourea and assigned to C-S stretching modes. The strong band at 275-280 cm^{-1} in the complex is attributed to metal-sulphur stretchings.

$[Pd(tu)_2o\text{-}phen]Cl_2$ and $[Pd(tu)_2dipy]Cl_2$: The infra red spectra of these complexes (chapter VII, fig. 21 to 24) show more or less the same behaviour as observed in case of pyridine complex with the difference that there is considerable splitting of the bands in o-phenanthroline complex, which is an indication of the stronger metal to ligand coordination in comparison to pyridine and dipyridyl ligands. The dipyridyl and o-phenanthroline complexes also show strong bands at 275-280 cm^{-1} corresponding to metal-sulphur stretches.

The kinetic studies based upon spectrophotometric measurements can be described by the equation:

$$K_{obs.} = K_1 + K_2 \ [Y] \qquad (1)$$

The equation (1) is equivalent to the general rate law equation (2) for the ligand substitution in square planar metal complexes:

$$Rate = K_1 + K_2 \ [Y] \ [Complex] \qquad (2)$$

where K_1 and K_2 are the first and second order rate constants, respectively, and $[Y]$ is the entering group.

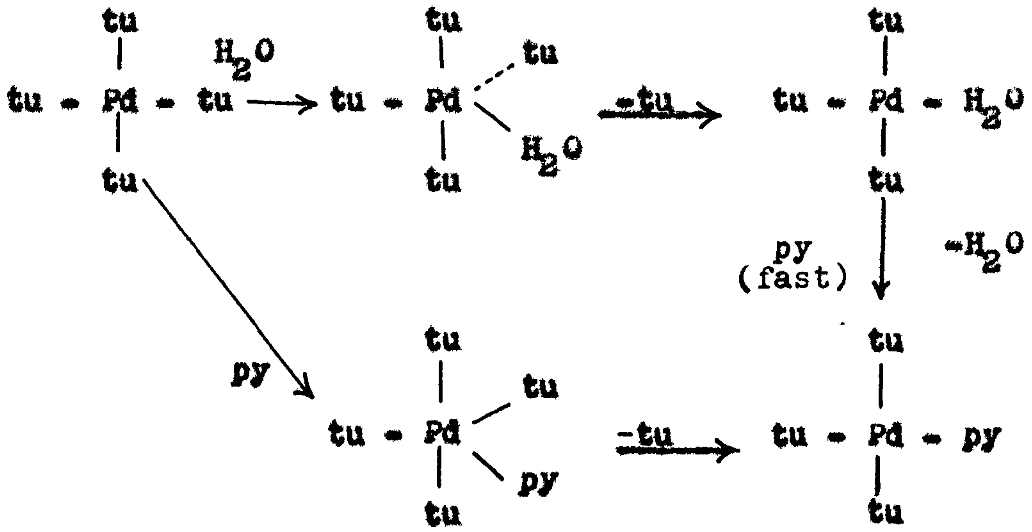
The equation (1) is found to be valid for the substitution reactions of Pd(II) e.g., reaction of $[Pd(tu)_4]Cl_2$ with pyridine and substituted compounds. The reaction involves the displacement of one or more thiourea molecules in the complex by the heterocyclic molecules.

The values of K_1 and K_2 for the substitution reaction of $[Pd(tu)_4]Cl_2$ and pyridine at two different temperatures are as follows:

$Pd(tu)_4^{++} + py$	K_1 min^{-1}	$K_2 mol^{-1}$ min^{-1}
at 20°C	8.0×10^{-3}	3.47×10^{-1}
at 25°C	1.0×10^{-2}	2.60×10^{-1}

(Vide table 2A to 4C and fig.2(a) to 4(c))

The two term rate law applicable in this case requires two step mechanism which has been proposed for ligand substitution square planar complex :



The rate constant K_1 is due to the slow displacement of thiourea by the solvent molecule which then readily replaced by pyridine. A direct nucleophilic replacement of thiourea by pyridine is responsible for K_2 or in other words the second order rate law is simply due to direct bimolecular

(S_N2) reaction between the incoming ligand (py) and the complex, $[Pd(tu)_4]Cl_2$, involving bond making and bond breaking.

The effectiveness of pyridine as an incoming ligand is explained on the basis of its capacity to form metal to ligand bonds ($d_\pi - p_\pi$) and thus it is possible to stabilise the transition state by the formation of π bonds using electrons in 4d orbitals of palladium and vacant or partially vacant ligand orbital (p_π in pyridine). The attacking action of the ligand in such cases, is both electrophilic and nucleophilic.

The kinetics of the substitution was also studied potentiometrically using $Ag - Ag_2S$ as an indicator electrode. The first order rate was determined by plotting log $\frac{E_t}{E_\infty - E_t}$ versus time, t. The plots (chapter VII, fig. and tables 8A to 15D, table 16A) were found to be linear and the $K_{obs.}$ values were determined from 2.3 times of the slopes.

A comparison of the K_{obs} values evaluated from the spectrophotometric (chapter VII, tables 6A, 6B) and potentiometric plots (chapter VII, table 16A) for the various heterocyclic amines reveals the following order :

4 pic > 2,4L > py > 2,6L > 2 pic (spectrophotometric)

2,4L > py > 2 pic > 2,6L > o-phen (potentiometric)

However, on the basis of present studies it is not possible

CHAPTER -VIII:

Studies on Some Substitution Reactions of Square Planar $[Ni(tu)_4]Cl_2$ Complex

The following substitution products were prepared by the interaction of yellowish green square planar complex, $[Ni(tu)_4]Cl_2$, and heterocyclic amines:

(a) $[Ni(tu)_2py_2]Cl_2$ (bluish green), (b) $[Ni(tu)_2dipy]Cl_2$(pink) and (c) $[Ni(tu)_2o\text{-}phen]\ Cl_2$ (pink).

Three types of magnetic susceptibility measurements were performed to investigate the possibility of stereochemical change during substitution, namely by using: (a) complexes in the solid state, (b) solutions of the complexes in the solvents like water, D.M.F., T.H.F. and nitromethane, and (c) solutions of the complex, $[Ni(tu)_4]Cl_2$, in presence of excess of the ligands, e.g., pyridine, 2,2'dipyridyl and o-phenanthroline. The magnetic susceptibility values in all the above cases indicate diamagnetism. This was a conclusive evidence for the absence of any stereochemical changes during substitution.

The electronic absorption spectra of nickel (II) complexes (in solution) were also studied and the possible assignments were made to the various bands present (chapter VIII, fig.1, table 1). For example, the d-d transition

($^1A_{1g} \rightarrow {}^1A_{2g}$) band appeared in the complexes, $[Ni(tu)_2py_2]Cl_2$, $[Ni(tu)_2o\text{-}phen]Cl_2$ and $[Ni(tu)_2dipy]Cl_2$ at 19305 cm^{-1}, 19230 cm^{-1} and 19230 cm^{-1}, respectively. The bands at 25,000 cm^{-1} $[Ni(tu)_4]Cl_2$, 25640 cm^{-1} $[Ni(tu)_2py_2]Cl_2$, 28140 cm^{-1} $[Ni(tu)_2dipy]Cl_2$ and 28570 cm^{-1} $[Ni(tu)_2o\text{-}phen]Cl_2$ are assigned to charge transfer bands arising from M->L transitions. The values of spectral parameter, Dq were calculated for the complexes, $[Ni(tu)_2dipy]^{++}$ 22170 cm^{-1}; $[Ni(tu)_2o\text{-}phen]^{++}$ 22107 cm^{-1}; and $[Ni(tu)_2py_2]^{++}$ 22107 cm^{-1} and $[Ni(tu)_4]^{++}$ 17505 cm^{-1}, and were comparable to strong ligand fields, following the order: tu $>$ py $>$ o-phen $\sim$ dipy.

The potentiometric titration method was also utilized to determine the composition of the mixed ligand complexes of nickel (II). Two sets of reaction mixtures were used for titrations. In the first set, mixtures of ($NiCl_2$ + L), where L = tu, dipy and o-phen, were titrated against standard HNO_3, and in the other, mixtures of $NiCl_2$ + tu + L (L = py, dipy and o-phen) were used. From the titration curves (Chapter VIII, fig.2(I) to 2(XII)), the formation of the complexes, $[Ni(py)_2(tu)_3]Cl_2$, $[Ni(tu)_4dipy]Cl_2$ and $[Ni(tu)_4o\text{-}phen]Cl_2$ was inferred. The formation of these complex species has been explained on the basis of the following solvent assisted mechanisms:

1. $NiCl_2 + 3tu + aq \longrightarrow [Ni(tu)_3aq]^{++}$

$[Ni(tu)_3aq]^{++} + 2py \longrightarrow [Ni(tu)_2py_2]^{++} + tu$

2. $NiCl_2 + 4tu \longrightarrow [Ni(tu)_4]^{++}$

$[Ni(tu)_4]^{++} + L \longrightarrow Ni(tu)_4L^{++}$ where L = dipy or o-phen

$Ni(tu)_4L^{++} \longrightarrow [Ni(tu)_2L]^{++} + 2tu$

The fact that the species, $[Ni(tu)_2py_2]^{++}$, $[Ni(tu)_2dipy]^{++}$ and $[Ni(tu)_2o\text{-}phen]^{++}$ have actually been isolated gives support in favour of the above mechanisms.

The potentiometric titrations were also performed with the mixtures: $[Ni(tu)_4]^{++} + L$ where L = py, dipy and o-phen. With pyridine (fig.2(XIII))and dipyridyl (Fig.2(XIV)), combining ratios of 1:1 and 1:2 were obtained, respectively. This indicates the possibility of the following substitution reactions:

(a) $Ni(tu)_4^{++} + py \longrightarrow [Ni(tu)_3py]^{++} + tu$

(b) $Ni(tu)_4^{++} + 2dipy \longrightarrow [Ni(dipy)_2]^{++} + 4tu$

or the following solvent assisted mechanism:

$$Ni(tu)_4^{++} + 4H_2O \rightleftharpoons Ni(H_2O)_4^{++} + 4tu$$

$$Ni(H_2O)_4^{++} + 2dipy \rightleftharpoons Ni(dipy)_2^{++} + 4H_2O$$

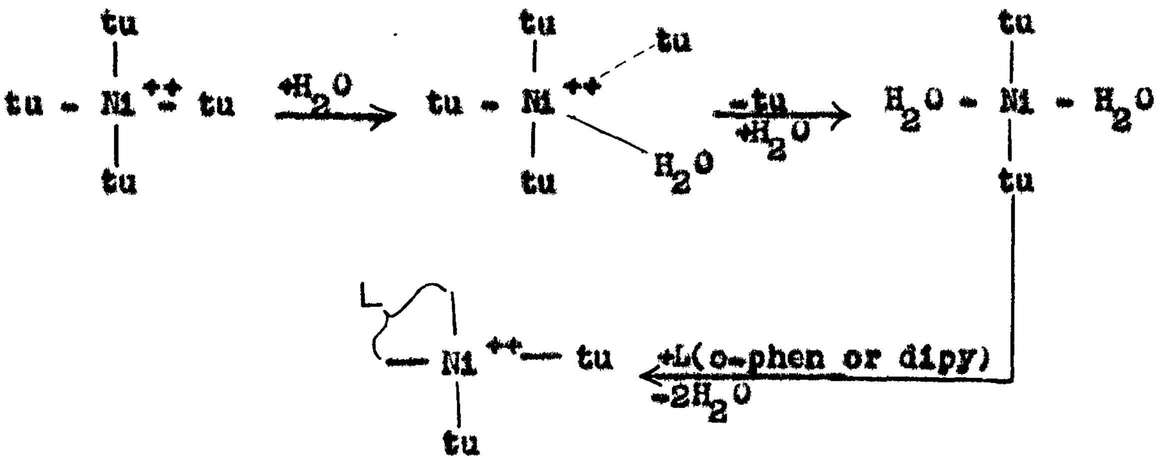
With o-phenanthroline, the titration curves (Chapter VIII, Fig.2(XVII)) indicate the formation of two complex species, $[Ni(tu)_3 o\text{-}phen]^{++}$ if the ligand (o-phen) concentration is low, and $[Ni(o\text{-}phen)_2]^{++}$ if the ligand is in excess.

The kinetic studies on the mechanism of substitution of $[Ni(tu)_4]Cl_2$ with pyridine, 2,2' dipyridyl and o-phenanthroline were carried out potentiometrically using $Ag\text{-}Ag_2S$ as an indicator electrode. The substitution reaction of pyridine with $[Ni(tu)_4]Cl_2$ is too rapid to be measured potentiometrically, and the equilibrium is attained almost immediately. Such a type of behaviour is not surprising since square planar Ni(II) is most labile amongst the triad; Pt(II), Pd(II) and Ni(II).

The e.m.f. measurements with time were carried out for the systems; $Ni(tu)_4Cl_2$ + dipy and $Ni(tu)_4Cl_2$ + o-phen, indicate a linear relationship between $\log \frac{E_t}{E_\infty - E_t}$ (E_t-potential at time, t and E_∞ - equilibrium potential) and time t. The K_{obs} values were computed from the slopes of the linear plots (Chapter VII, fig.3A, 3B, 3C, 4A and 4B), tables 3A, 3B, 3C, 4A and 4B). It was, however, found that the substitution did not follow the two term rate law:

$$K_{obs} = K_1 + K_2 \; [Y]$$

and therefore, it may be assumed to follow a solvent assisted mechanism:



The infra red spectra of the nickel(II) mixed ligand complexes, $[Ni(tu)_2py_2]Cl_2$, $[Ni(tu)_2dipy]Cl_2$ and $[Ni(tu)_2o\text{-}phen]Cl_2$ were studied in the range 1600-250 cm^{-1} (chapter VIII, fig. 5A to 5D). No conclusive evidence is obtained in case of substituted pyridine complex regarding the mode of coordination. However, in case of o-phenanthroline and dipyridyl complexes, the spectra are noted by two marked characteristics, namely: (i) appearance of bands typical of coordinated o-phen and dipy, e.g., splitting of bands and shifting to higher frequencies, and (ii) shifting of the bands due to coordinated thiourea is less pronounced in these complexes in comparison to $[Ni(tu)_4]Cl_2$ complex, the latter shows considerable shifting especially in the regions of NH_2 bending, N-C-N stretchings NH_2 rocking and C-S stretching vibrations. The latter characteristic of the spectra of o-phenanthroline and dipyridyl substituted complexes is attributed to a stronger bonding through heterocyclic nitrogen in comparison to sulphur in these mixed ligand complexes. The band observed at ca. 270-280 cm^{-1} in all the complexes is assigned to metal-sulphur stretching modes.

The substitution reaction of $[Ni(tu)_4]Cl_2$ with phenyl arsonic acid (phOAs) was also studied. The canary yellow complex, $[Ni(phOAs)_2tu]Cl$, is diamagnetic and formation of such type of complex could only be taken place when out of the two arsine ligand one acts as a monodentate group and the other as a bidentate. The potentiometric titrations carried out with the mixtures; $NiCl_2$ + tu + phOAs and $[Ni(tu)_4]Cl_2$ + phOAs indicate the formation of complex species, $[Ni(phOAs)]Cl$, $[Ni(phOAs)_2]$ and $[Ni(phOAs)_2tu_2]$ (Chapter VIII, fig.2(XI), 2(XII), 2(XV) and 2(XVI)). The kinetic study on the mechanism of substitution of $[Ni(tu)_4]Cl_2$ with phOAs, reveals that the reaction was too rapid to be studied potentiometrically and the equilibrium was attained almost immediatly.

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Analytical and Electrometric studies on the behaviour of cuprous bromide in potassium bromide solution

By WAHID U. MALIK, S. M. FAZLUR RAHMAN and ANEESUDDIN MALIK

With 3 Figures

Summary

Chemical studies were carried out to determine the complex ion formation between cuprous bromide and potassium bromide in the aqueous as well as in the solid phase. The formation of complexes in the aqueous phase was also confirmed by potentiometric and conductometric methods. There was no indication of complex formation at room temperature (30 °C). However, at 50 °C rectangular curve showed the formation of complex K_3CuBr_4 and addition compounds like $CuBr \cdot 5\,KBr$; $CuBr \cdot 10\,KBr$ in the liquid phase while complexes K_2CuBr_3, K_3CuBr_4, K_4CrBr_5 are formed in the solid phase. The electrometric studies also show the formation of similar complexes in the liquid phase.

Inhaltsübersicht

Es wurde die Bildung von Komplexen aus CuBr und KBr sowohl in wäßriger Lösung als auch als feste Phasen z. T. mit elektrometrischen Methoden untersucht. Bei 30 °C tritt keine Komplexbildung ein; bei 50 °C entstehen die gelösten Verbindungen K_3CuBr_4, $CuBr \cdot 5\,KBr$ und $CuBr \cdot 10\,KBr$ und als feste Phasen: K_2CuBr_3, K_3CuBr_4 und K_4CuBr_5.

Complex ion formation in the solution of cuprous chloride in hydrochloric acid and potassium chlorid was reported by a number of workers[1–4] and more recently by HARRIS and co-workers[5] and MALIK and collaborators[6]. However, no systematic study of the system CuBr—KBr—H_2O had been carried so far, only WELLS and HURLBURT[7] and

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FLEURENT[8]) reported the preparation of the compounds $(NH_4)_2CuBr_3$ and K_2CuBr_3 respectively. The present communication describes the formation of complex ions in the solid as well as liquid phase resulted due to the solubility of cuprous bromide in potassium bromide and also due to the equilibrium existing between cuprous bromide and potassium bromide in the aqueous phase.

Experimental

Cuprous bromide was prepared by the method recommended by LEAN and WHATMOUGH[9]). The mixture of copper sulphate and sodium bromide was treated with a stream of sulphur dioxide, small white crystals were formed, they were filtered rapidly and washed with sulphurous acid and alcohol and dried with ether and kept in vacuum desiccator over caustic potash. The resulting crystals were coloured pale greenish yellow. Cuprous ions were estimated by titrating the solutions against ammonium thiocyanate using ferric alum as indicator. Potassium bromide was estimated by precipitating potassium as dipotassium monosodiumcolbalti-nitrite. The amount of KBr was calculated from the weight of the precipitate by multiplying with 238.02/450.1. Comparable results[10]) were obtained by dissolving the cobaltinitrite precipitate in ceric sulphate and estimating the exess of Ce^{++++} ions against ferrous ammonium sulphate potentiometrically. All the experiments

Table 1

B. T. No.	Solution		Original Concentration		Wet residue	
	CuBr gm/lit	KBr gm/lit	CuBr gm/lit	KBr gm/lit	CuBr gm/lit	KBr gm/lit
1	75.2	223.6	75.2	223.6	—	—
2	65.4	185.39	71.4	212.41	6.0	27.02
3	58.2	170.31	67.6	201.22	19.4	30.01
4	41.5	164.3	63.9	190.06	20.4	25.7
5	33.3	152.6	60.2	178.8	26.9	26.2
6	31.6	140.9	56.3	167.7	24.7	26.8
7	26.4	134.6	52.6	156.5	26.2	21.9
8	20.3	128.9	48.8	145.3	28.5	16.4
9	15.87	120.3	45.1	131.1	29.3	10.8
10	8.71	73.03	41.3	122.98	22.6	49.9
11	6.88	70.98	37.5	111.6	30.6	40.7
12	4.9	69.1	33.8	100.6	28.9	30.5
13	3.9	63.4	30.72	88.4	26.8	25.0
14	3.6	62.6	26.3	78.2	22.7	15.6
15	3.2	61.2	21.5	67.08	18.3	5.8
16	2.8	54.8	19.68	55.91	16.8	1.1

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Table 2

Conc. of KBr and CuBr gms/lit in solid phase calc. from tie point		Molar ratio in the solid phase CuBr:KBr	Complexes formed	Molar ratio in aqueous phase calc. from tie line. CuBr:KBr	Complexes formed
40.0 KBr 25.0 CuBr	S_1	1:1.8	K_2CuBr_3	1:2.8	K_3CuBr_4
77.0 KBr 33.0 CuBr	S_2	1:2.8	K_3CuBr_4	1:5	$CuBr \cdot 5\,KBr$
146.0 KBr 48.0 CuBr	S_3	1:3.6	K_4CuBr_5	1:10	$CuBr \cdot 10\,KBr$

were carried out in a thermostat which was maintained at 50 ± 0.1 °C. The bromide solution and water were mixed in the following order:

Boiling tube No. 1	0.0 cc water + 40 cc solution
Boiling tube No. 2	2.0 cc water 38 cc solution
Boiling tube No. 19	36.0 cc water 4.0 cc solution
Boiling tube No. 20	38.0 cc water 2.0 cc solution.

Each boiling tube was covered with a thin layer of paraffin and solution was stirred and allowed to settle. The supernatant liquid was then analysed for CuBr and KBr. The results are as follows see Table 1.

The potentiometric and conductometric studies were done using the same stock solution (as was taken during analytical studies), and all the observations were made with mixtures kept immersed in the thermostatic bath at 50 ± 0.1 °C. The cuprous bromide solution and water were mixed in the same order as for the analytical studies.

The complexes obtained in the aqueous and solid phases as determined from the phase diagram given in fig. 1.

Conductometric studies. The conductance of supernatant liquids were measured

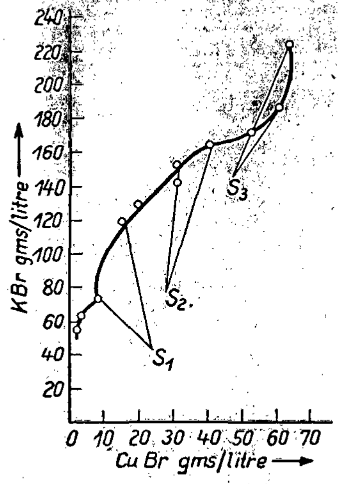

Fig. 1. Phase-diagram

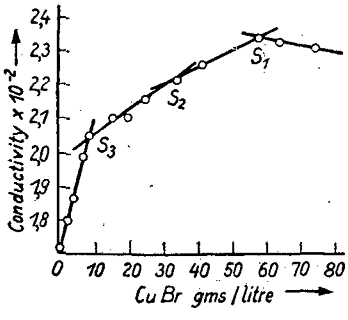

Fig. 2. Conductometric measurements

using a W. T. W. conductivity bridge and dip type conductivity cel for measuring solutions of high conductance a Wheatstone bridge system with a spread of 500 cc wire in conjunction with W. C. Pye resistance box and oscillator and head phone were used. The electrodes of the cell were platinised before use in order to minimise the polarisation effect The conductivity curves are shown in fig. 2.

The complex formation found in the aqueous phase by conductivity measurements is as under

Table 3

Conc. of KBr and CuBr gms/lit at the point intersections		Molar ratio	Complexes formed
73.03 KBr 8.71 CuBr	S_3	1:10	CuBr · 10 KBr
152 15 KBr 33 3 CuBr	S_2	1:5 4	CuBr · 5 KBr
170 31 KBr 58 2 CuBr	S_1	1:2.8	K_3CuBr_4

The conductometric measurements indicate the formation of complex K_3CuBr_4 and addition compounds CuBr · 5 KBr and CuBr · 10 KBr in the aqueous phase thus confirming the results of chemical analysis.

Potentiometric studies

The e. m. f. of the solutions was measured with the help of a clean platinum wire electrode, using the standard calomel electrode as the reference. A Tinsley Vernier potentiometer with a lamp scale galvanometer arrangement was used for determining the potential. In order to check the reversibility of measurements a number of readings were taken for the same sample. The curves are shown in fig 3.

The results obtained by e m f. measurements are as follows see Table 4

The potentiometric measurements indicate the formation of the complex K_3CuBr_4 and addition compound CuBr 5 KBr in the aqueous phase

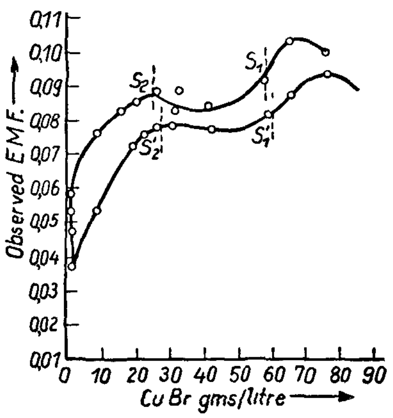

Fig 3 Potentiometric measurements

Discussion

From the results obtained by the chemical analysis of aqueous phase it may be concluded that at relatively high temperature there is higher solubility of cuprous bromide in potassium bromide, and with increasing concentration of potassium bromide the complexes ranging from K_4CuBr_5 to K_2CuBr_3 are formed, however in solutions there is little tendency of complex ion formation and only the complex K_3CuBr_4 can be said to exist. The other two CuBr · 5 KBr and CuBr · 10 KBr are probably addition compounds or may indicate the solubility of cuprous bromide in potassium bromide solution. From the chemical analysis and electrometric studies it may thus be concluded that there is the formation of complexes like K_2CuBr_3; K_3CuBr_4 and K_4CuBr_5 in solid phase and the complex K_3CuBr_4 in the aqueous phase.

Table 4

Conc. of CuBr and KBr gms/lit		Molar ratio	Complex formed
58.2 CuBr 170.31 KBr	S_1	1:2.8	K_3CuBr_4
33.3 CuBr 152.6 KBr	S_2	1:5.4	CuBr · 5 KBr
58.2 CuBr 170.31 KBr	S_1'	1:2.8	K_3CuBr_4
41.5 CuBr 164.3 KBr	S_2'	1:4.8	CuBr · 5 KBr

Further studies are in progress on the phase studies of cuprous chloride, cuprous bromide with alkali and alkaline earth metallic halides.

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Aligarh (India), Muslim University, Department of Chemistry.

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Solubility Behaviour of Copper(I) Iodide in Potassium Iodide Acetone Media. I.

By M. MAHFOOZ KHAN, S. A. A. ZAIDI and A. U. MALIK

With 4 Figures

Abstract. The solubility behaviour of CuI was studied in KI-acetone media in the concentration range of approximately 0.05 to 0.2 M. Within this range of iodide concentration, CuI_2^- was the only complex species found to occur in the liquid as well as in the solid phase. Conductometric studies also indicated the existence of the same species. At 20 °C, the concentration equilibrium constant $K_1K_2K_{sol}$ for the reaction CuI (sol) + $I^- = CuI_2^-$ is 1.65 ± 0.2.

Inhaltsübersicht. Es wurde die Löslichkeit von CuJ in KJ/Aceton im Konzentrationsbereich 0,05—0,2 M untersucht. Als einzige Komplexspezies sowohl in Lösung als auch im Bodenkörper wurde dabei CuJ_2^- nachgewiesen. Auch konduktometrische Untersuchungen zeigen deren Existenz an. Bei 20 °C hat die Konzentrationsgleichgewichtskonstante $K_1K_2K_{sol}$ der Reaktion $CuJ_{(sol)} + J^- \rightarrow CuJ_2^-$ den Wert 1,65 ± 0,2.

The solubility behaviour of Cu(I) halides presents an interesting area of research and has attracted a number of workers to investigate the quantitative aspects concerning the identities and stabilities of the soluble Cu(I) species existing in various halide solutions.

Amongst the earliest contributors in this field, BODLANDER and STORBACK[1]) made a systematic study on the behaviour of CuBr in bromide solution. Complex ion formation in the solutions of cuprous chloride and bromide in respective chloride and bromide solutions has been reported[2-5]). PETERS and CALDWELL[6]) more recently studied the solubility behaviour of CuBr in sodium bromide media. They have employed the technique of controlled — potential coulometry to study the complex ion formation and evaluation of equilibrium constants of the complex species.

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[1]) G. BODLANDER and O. STORBACK, Z. anorg. Chem. **31**, 72 (1902).

[2]) L. N. SZABÓ and Z. SZABÓ, Z. physik. Chem. **166**, 228, (1933).

[3]) C. M. HARRIS, J. Proc. Roy. Soc. New South Wales **82**, 218 (1948); **85**, 130 (1952)

[4]) W. U. MALIK, S. M. F. RAHMAN and S. A. ALI, Z. anorg. allg. Chem. **299**, 322 (1959); **301**, 220 (1959).

[5]) W. U. MALIK, S. M. F. RAHMAN and A. U. MALIK, Z. anorg. allg. Chem. **314**, 276 (1962).

[6]) D. G. PETERS and R. L. CALDWELL, Inorg. Chem. [Washington] **6**, 1478 (1967).

From the existing literature it appears that no systematic study was carried out to investigate the solubility behaviour of CuI in iodide solutions. This is perhaps due to the low solubility of the compound in aqueous iodide solutions[7]. The present work deals with the solubility behaviour of CuI in KI using acetone as a solvating medium. The studies include the determination of Cu^+ and I^- at various iodide concentrations and subsequently the information regarding the existence of complex species. These studies are further supplemented by conductometric measurements.

Experimental

Copper(I) iodide was prepared by mixing solutions of copper sulphate and potassium iodide and then subsequently passing sulphur dioxide to remove free iodine liberated during the rection. A. R. grade potassium iodide and acetone were used during experiments. Stock solutions containing known initial concentrations of CuI were prepared by dissolving accurately weighed amounts of CuI in acetone containing potassium iodide. The solution was slightly warmed over water bath and then filtered and used for subsequent measurements. Copper(I) iodide was estimated by precipitating it from the acetone solution by adding excess of distilled water. The insoluble CuI was filtered through a weighed sintered G4f crucible. The filtrate was collected and iodide ions present were estimated by precipitating as silver iodide. At least two separate determinations were carried out for each estimation.

Conductometric measurements were carried out with Philip Conductivity bridge model PR 9500 using dip type conductivity cell (cell const. 1.482).

Results and Discussion

The present studies were concerned with the behaviour of copper(I) iodide in potassium iodide. The solubility of CuI in aq. potassium iodide is not appreciable but preliminary experiments carried out with nonaqueous solvents showed appreciable dissolution of copper(I) iodide in potassium iodide in presence of organic phase. The present studies are limited to the behaviour of copper(I) iodide in potassium iodide using acetone as a solvating medium.

Table 1
Solubility at 20°C.

No.	Found CuI gm/20 ml	KI gm/20 ml	Calculated CuI gm/20 ml	KI gm/20 ml	Difference (wet residue) CuI gm/20 ml	KI gm/20 ml
(1)	0.113	0.104	0.138	0.127	0.025	0.022
(2)	0.146	0.130	0.185	0.169	0.039	0.038
(3)	0.257	0.229	0.277	0.254	0.020	0.024
(4)	0.316	0.272	0.323	0.296	0.007	0.024
(5)	0.349	0.295	0.370	0.339	0.020	0.043

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[7] A. U. Malik (unpublished results).

The solubility measurements were carried out with five different iodide concentrations and each observed value is the average of 2—3 separate determinations of the same sample. Table 1 gives the observed and calculated values of copper(I) iodide and potassium iodide at 20°C. The difference between the theoretical and observed values gives the value of wet residue.

Fig. 1 is a straight line curve obtained by plotting observed concentrations of copper(I) iodide and potassium iodide. There is evidence for the formation of only one complex CuI_2^- in solid as well as in liquid phase.

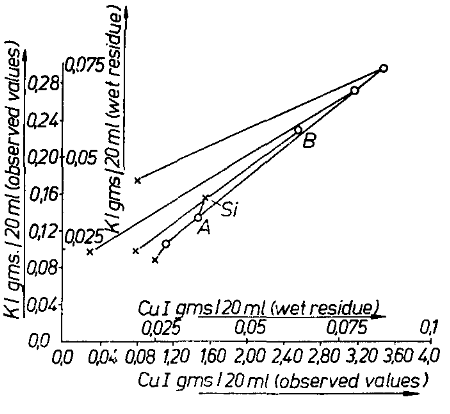

Fig. 1. Phase diagram

Table 2

Evaluation of the complex species according to Fig. 1

Conc. of KI and CuI gms/lit. in solid phase calc. from the tie point (Fig. 1)	Molar ratio the solid phase CuI:KI	Complex	Conc. of KI and CuI gms/lit. in acetone phase (Fig. 1)		Molar ratio in acetone phase calc. from the tie line CuI:KI	Complex formed.
19.25 KI S_1 19.50 CuI	1:1.1	$KCuI_2$	6.54 KI 7.30 CuI	A	1:1.0	$KCuI_2$
			11.47 KI 12.86 CuI	B	1:1.0	

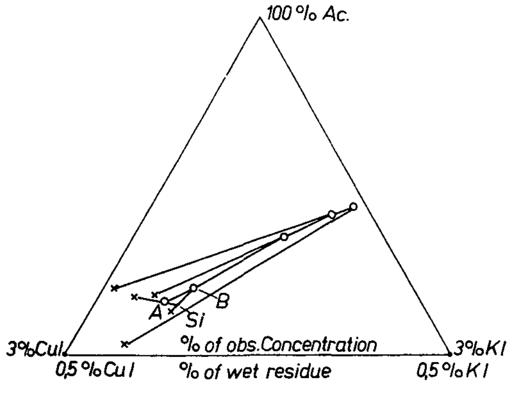

Fig. 2. Phase diagram

Triangular phase diagram was also plotted (Fig. 2) considering all the three components e. g., cuprous iodie, potassium iodide and acetone. From the intersection of the tie lines and considering the concentrations at the tie points, there is evidence of only one species e. g. $KCuI_2$ in the solid and liquid phases.

From the result by the chemical analyses of the organic physe it may be concluded that there is sufficient solubility of copper(I) iodide in potassium iodide (Table 1) to warrant the possibility of complex formation. There is evidence for the formation of only one complex species CuI_2^- even with increasing iodide concentrations and the same species seems to exist in the solid phase. These results are, however, not in conformity with the aqueous phase studies carried out with the copper(I) bromide in aqueous potassium bromide where species like $CuBr^-_2$, $CuBr_3^{2-}$ and $CuBr_4^{3-}$ are reported[5][6]. The absence of higher species other than CuI_2^- may be attributed to the low dielectric of the medium resulting in the non-availability of sufficient number of iodide ions.

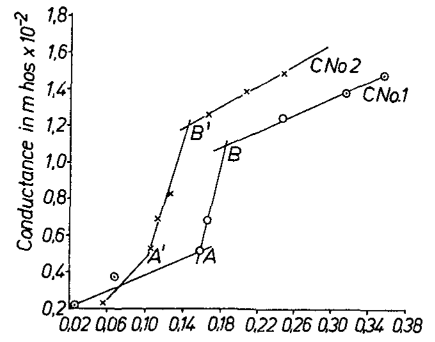

Fig. 3. Conductometric measurements
Curve No. 1: Conc. of CuI gm/20 ml
Curve No. 2: Conc. of KI gm/20 ml

The conductivity of copper(I) iodide at various iodide concentrations shows a steep increase in conductance with increasing iodide concentrations. (Fig. 3). However, sharp inflexions were observed at some points corresponding to the ratio of 1:1 for CuI and KI.

Table 3
Evaluation of the complex species according to Fig. 2

% of KI and CuI in solid phase calc. from tie point.	Molar ratio in the solid phase CuI:KI	Complex formed.	% of KI and CuI in acetone phase.	Molar ratio in acetone phase calc. from tie line CuI:KI	Complex formed.
0.080 KI S_1 0.115 CuI	1:0.8	$KCuI_2$	0.519 KI 0.561 CuI A	1:1.1	
			0.644 KI 0.724 CuI B	1:1.0	$KCuI_2$

The solubility behaviour of CuI in potassium iodide was studied by a plot of logarithm of the solubility versus the logarithm of free iodide concentrations.

The latter values were also plotted against logarithms of the calculated CuI_2^-. A linear relationship exists between the logarithm of iodide concentrations and logarithms of $[CuI_2^-]$ and S. The slopes of the straight lines obtained on plotting $\log [I^-]$ versus $\log [CuI_2^-]$ and $\log S$ were found to be unity in both the cases.

In table 5 the theoretical values of solubility, $[CuI_2^-]$ and observed solubility S are given at various final equilibrium iodide concentrations. The free iodide concentration was calculated by the relation.

Table 4
Molar ratios from conductivity data

Conc. of KI and CuI gm/20 ml. at the point intersections (Fig. 3)		Molar ratio
0.107 KI 0.163 CuI	A (Curve I)	1:1.3
0.140 KI 0.187 CuI	B (Curve I)	1:1.1
0.108 KI 0.160 CuI	A (Curve 2)	1:0.77
0.146 KI 0.230 CuI	B (Curve 2)	1:0.73

$$[I^-] = [I^-]_0 - [Cu^+] - 2[CuI_2^-].$$

where $[I^-]$ is the final equilibrium iodide concentration, $[I^-]_0$ the original iodide concentration derived from the amounts of potassium iodide and copper(I) iodide from the stock solution. $[Cu^+]$ is the amount of iodide precipitated as copper(I) iodide.

Table 5
Solubility and $[CuI_2^-]$ data

$[I^-]$ M	Observed solubility, S M × 10^{-2}	Calc. solubility S M × 10^{-2}	Calc. $[CuI_2^-]$ M × 10^{-2}
0.0567	4.217	6.928	3.715
0.5760	4.273	5.204	3.698
0.117	8.128	12.130	6.607
0.1465	9.580	10.400	7.390
0.2021	12.84	13.86	9.970

The solubility in our system may be expressed as $S = [Cu^+] + [CuI\,(ac.)] + [CuI_2^-] + \cdots$. The value of S may be represented by the equation:

$$S = \frac{K_{sol}}{[I^-]} + K_1K_{sol} + K_1K_2K_{sol}[I^-] + \cdots$$

The equilibrium const. for the reaction

$$CuI(s) + I^- \leftrightharpoons CuI_2^-$$

is $K_1K_2K_{sol}$ and may be evaluated from the equation for the straight line (Fig. 4. curve no. 2) and found to be 1.65 ± 0.2 at 20°C.

The individual values for K_1K_2 and K_{sol} are not determined from the present solubility data. The solubility measurements could not be extended below 0.05 M due to the lack of reproducibility in the estimations of Cu(I) and I^- in this concentration range. Therefore, it was not possible to ascertain the areas of Cu(I) and CuI (ac.) predominance and subsequently the correct evaluation of these constants.

The present investigation on the solubility of copper (I) iodide in potassium iodide and acetone give conclusive evidence for the existence of CuI_2^- in solid as well as in the liquid phase. The presence of Cu^+ and CuI (ac.) in solution can not be ruled out, however, on the basis of limited experimental data no conclusive evidence is obtained. The existence of species like CuI_3^{2-} and CuI_4^{3-} is ruled out on the basis of present investigations.

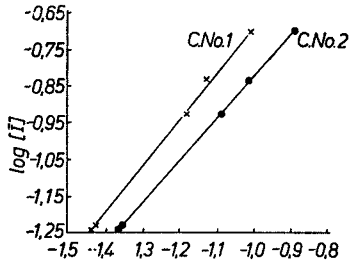

Fig. 4. Curve No. 1: Logarithm of the observed solubility of CuI as a funktion of log [I^-]
Curve No. 2: Logarithm of the calculated CuI_2^- as a function of log [I^-]

The authors express their sincere thanks to Dr. S. M. F. Rahman, Head, Department of Chemistry for providing facilities. One of the authors (M. M. Khan) is also grateful to University Grants Commission, New Delhi for the award of a senior fellowship.

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Solubility Behaviour of Copper(I) Bromide in Aqueous Hydrobromic Acid, Potassium Bromide and Magnesium Bromide. II.

By M. MAHFOOZ KHAN and A. U. MALIK

With 3 Figures

Abstract. The solubility of copper(I) bromide in aqueous HBr, KBr and $MgBr_2$ solutions has been determined at varying free bromide equilibrium concentrations. On the basis of solubility data the presence of species like $CuBr_2^-$ and $CuBr_3^{2-}$ is indicated in the aqueous phase *in HBr and KBr systems, whereas in the case of* $MgBr_2$ *the presence of only one species,* $CuBr_3^{2-}$, is concluded. The calculated values of the equilibrium concentration constant $K_1 \cdot K_2 \cdot K_{sol}$ are 3.16×10^{-1}, 9.01×10^{-1} and 4.78×10^{-1} for the HBr (50 °C), KBr (20 °C) and $MgBr_2$ (20 °C) system, respectively.

Inhaltsübersicht. Es wurde die Löslichkeit von CuBr in wäßrigen HBr-, KBr- und $MgBr_2$-Lösungen bei unterschiedlicher Gleichgewichtskonzentration des freien Bromids ermittelt. Aus den Löslichkeitsdaten wird auf die Spezies $CuBr_2^-$ und $CuBr_3^{2-}$ in der flüssigen Phase des HBr- und des KBr-Systems geschlossen, und auf nur eine Spezies, $CuBr_3^{2-}$, im $MgBr_2$-System. Die ermittelten Werte der Gleichgewichtskonstante $K_1 \cdot K_2 \cdot K_{fest}$ für das HBr- (50 °C), KBr- (20 °C) und $MgBr_2$-System (20 °C) sind: $3{,}16 \cdot 10^{-1}$; $9{,}01 \cdot 10^{-1}$ bzw. $4{,}78 \cdot 10^{-1}$.

In recent years the solubilities of copper(I) halides in alkali halide solutions have been investigated[1–3]. In our laboratory a systematic study on the behavior of copper(I) halides in various halides solutions was carried out during the last so many years.[4–5] The earlier studies were mainly based upon the composition of the complexes formed in the aqueous and solid phases. Recently the solubility behavior of copper(I) iodide in potassium iodide using acetone as a nonaqueous media has been studied.[6] This study deals with the composition of the complexes and the calculation of solubility constants.

The present study essentially deals with the evaluation of solubility constants of the systems $CuBr-KBr-H_2O$, $CuBr-HBr-H_2O$ and $CuBr-MgBr_2-H_2O$. Subsequently, an attempt has been made to determine the complex species formed in aqueous media.

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[1] G. BODLANDER and O. STORBACK, Z. anorg. Chem. **31**, 72 (1902).

[2] L. N. SZABO and Z. SZABO, Z. physik. Chem. **166**, 228 (1933).

[3] C. M. HARRIS, J. Proc. Roy. Soc. New South Wales 82, 218 (1948); 85, 130 (1952).

[4] W. U. MALIK, S. M. F. RAHMAN and S. A. ALI, Z. anorg. allg. Chem. **299**, 322 (1959); **301**, 220 (1959).

[5] W. U. MALIK, S. M. F. RAHMAN and A. U. MALIK, Z. anorg. allg. chem. **314**, 276 (1962).

[6] Part I: M. M. KHAN, S. A. A. ZAIDI and A. U. MALIK, Z. anorg. allg. Chem. **375**, 291 (1970).

Experimental

Copper(I) bromide was prepared[7] by treating a mixture of copper sulphate and sodium bromide solutions with a stream of sulphur dioxide.

Copper(I) ions were estimated gravimetrically by titrating the solutions against standard thiocyanate using iron(III) allum as an indicator.[4] Potassium bromide (E. Merck) was recrystallised and used during the experiment. Potassium was gravimetrically estimated as dipotassium cobaltinitrite, HBr (E. Merck) was distilled and employed during the experiment, it was estimated by titerating against standard caustic soda solution. $MgBr_2$ was recrystallised, dried at 110 °C and estimated as magnesium ammonium phosphate hexa hydrate.

In all the experiments an excess of CuBr was dissolved in aqueous bromide solution. The supernatant liquid containing CuBr—XBr (in equilibrium with complex species $CuBr_2^-$, $CuBr_3^{2-}$ etc.) and water were mixed in various proportions. The concentration of solid phase in equilibrium with the adhering mother liquor (wet residue) was obtained by substracting the concentrations of CuBr and XBr (determined from the analysis) from the concentration of CuBr and XBr (had it not been precipitated by adding water).

Results and discussion

The solubility behavior of CuBr in aqueous bromide solutions was quantitatively studied by calculating free bromide concentration $[Br^-]$ which is given by the relation

$$[Br^-] = [Br^-]_0 - [Cu^+] - 2[CuBr_2^-]$$

where $[Br^-]_0$ is the original bromide concentration derived from the amounts of XBr ($X = K^+$, H^+ and Mg^{++}) and CuBr from the stock solution. $[Cu^+]$ is the amount of bromide precipitated as CuBr on addition of water. $[CuBr_2^-]$, ($[CuBr_3^-]$ in case of Mg^{++}) $[CuBr_3^{2-}]$ etc. are the complex species formed in the aqueous phase.

Table 1
$CuBr—HBr—H_2O$ at 50 °C

M $[Br^-]$	Observed solubility, S F × 10^{-1}	Cal. solubility, S_1 F × 10^{-1}	Cal. $[CuBr_2^-]$ M × 10^{-1}
1.000	5.62	5.74	3.68
0.967	4.90	5.35	3.45
0.924	4.85	5.06	3.26
0.871	4.36	4.76	3.07
0.838	3.91	4.50	2.91
0.802	3.38	4.22	2.72
0.757	2.87	3.91	2.52
0.703	2.74	3.64	2.35
0.663	2.18	3.36	2.17
0.613	2.01	3.08	1.98
0.564	1.55	2.80	1.80
0.500	1.58	2.53	1.63
0.450	1.27	2.23	1.44
0.398	1.12	1.94	1.24
0.337	1.01	1.68	1.08
0.283	0.73	1.39	0.90
0.220	0.75	1.11	0.71
0.167	0.52	0.83	0.53
0.118	0.29	0.51	0.32
0.056	0.14	0.27	0.18

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[7] B. Lean and W. H. Whatmough, J. chem. Soc. [London] **73**, 148 (1898).

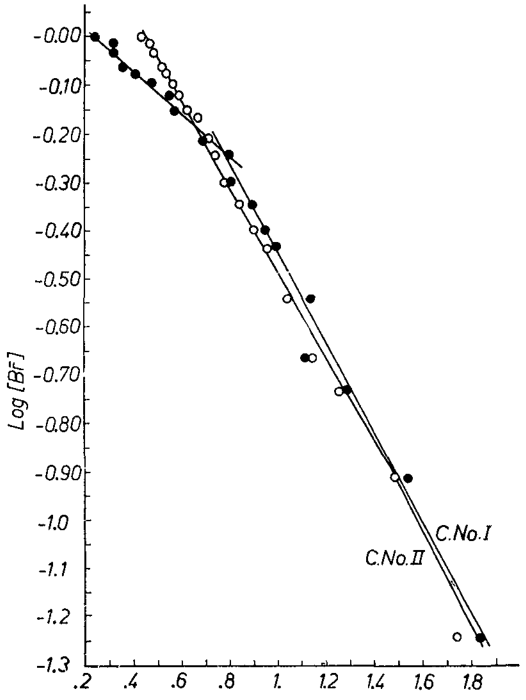

Fig. 1. $CuBr-HBr-H_2O$ System at 50 °C
Curve I Logarithm of observed solubility of CuBr as a function of log [Br^-]
Curve II Logarithm of calculated $CuBr_2^-$ as a function of log [Br^-]

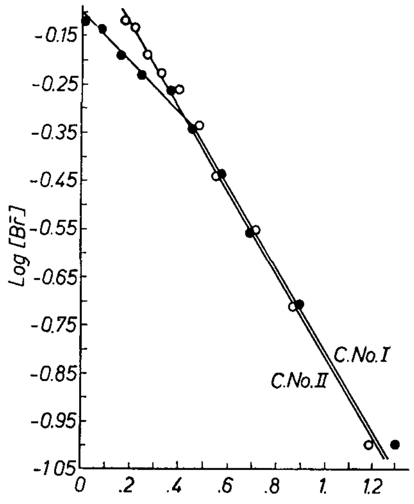

Fig. 2. $CuBr-KBr-H_2O$ System at 20 °C
Curve I Logarithm of observed solubility of CuBr as a function of log [Br^-]
Curve II Logarithm of calculated $CuBr_2^-$ as a function of log [Br^-]

For the systems $CuBr-HBr-H_2O$ at 50 °C and $CuBr-KBr-H_2O$ at 20 °C the values of calculated solubility S_1, $CuBr_2^-$ and observed solubility S are given at various final equilibrium bromide concentrations [Br^-] (Table 1 & 2).

A plot of logarithm of the solubility versus the logarithm of free bromide concentrations reveal a linear relationship in both the systems. Each of the plot constitutes of two straight lines with slopes of one and two indicating the presence of two complex species $CuBr_2^-$ and $CuBr_3^{2-}$ (Fig. 1 & 2). In case of HBr, species $CuBr_3^{2-}$ exists in the concentration range of 0.56 M—1.0 M of free bromide concentration, in the lower concentration range (below 0.564 M) species $CuBr_2^-$ appears to exist. In KBr system species $CuBr_3^{2-}$ and $CuBr_2^-$ exist in the concentration ranges of 0.46 M—0.76 M and 0.1 M—0.45 M respectively. A linear relationship with a unity slope also appears when the logarithm of [$CuBr_2^-$] is plotted against the log [Br^-].

In table 3 the values of S_1, $[CuBr_3^{2-}]$ and S are given at various free bromide concentrations $[Br^-]$ for $CuBr-MgBr_2-H_2O$ system. A plot of logarithms of the solubility versus free bromide concentration gives a straight line with a unity slope indicating thereby the existence of species $CuBr_3^{2-}$. The logarithmic plot between $[CuBr_3^{2-}]$ and $[Br^-]$ comes almost to a straight line and the slope was found to be unity. The absence of higher species e. g., $CuBr_5^{4-}$ may be due to the small ionic radius of cuprous ion which cannot accommodate so many bromide ions, moreover, at high concentrations of bromide the possibility of hydrolysis of magnesium bromide cannot be ruled out.

Table 2
$CuBr-KBr-H_2O$ at 20°C

M $[Br^-]$	Observed solubility, S F × 10^{-1}	Cal solubility, S_1 F × 10^{-1}	Cal $[CuBr_2^-]$ M × 10^{-1}
0 758	9 59	9 59	6 63
0 735	8 17	8 70	6 00
0 641	6 85	7 67	5 30
0 587	5 62	6 70	4 63
0 544	4 14	5 74	3 97
0 457	3 47	4 78	3 31
0 362	2 67	3 91	2 71
0 276	1 98	2 87	1 98
0 189	1 29	1 91	1 32
0 098	0 50	0 95	0 65

Table 3
$CuBr-MgBr_2-H_2O$ at 20°C

M $[Br^-]$	Observed solubility, S F × 10^{-1}	Cal solubility, S_1 F × 10^{-1}	Cal $[CuBr_3^{2-}]$ M × 10^{-1}
1 019	5 18	5 18	5 06
0 941	3 67	4 65	4 56
0 768	3 17	4 06	4 02
0 746	2 45	3 62	3 55
0 649	1 59	3 09	3 03
0 541	1 18	2 58	2 54
0 434	1 13	2 06	2 02
0 323	1 06	1 53	1 50
0 213	0 66	1 03	1 01
0 105	0 46	0 50	0 49

The equilibrium constant for the reactions

$$CuBr(S) + Br^- = CuBr_2^-$$

and $$CuBr(S) + 2Br^- = CuBr_3^{2-} \qquad (1)$$

is $K_1K_2K_{SO}$ and may be defined by the equations 2 and 3.

$$S = [Cu^+] + [CuBr(aq)] + [CuBr_2^-] + \cdots \qquad (2)$$

$$S = \frac{K_{SO}}{[Br^-]} + K_1K_{SO} + K_1K_2K_{SO}[Br^-] + \cdots \qquad (3)$$

The values of the equilibrium concentration constant $K_1K_2K_{s0}$ are evaluated from the straight lines (Fig. 1(II), 2(II) and 3(II)) and found to be 3.16×10^{-1}, 9.01×10^{-1} and 4.78×10^{-1} for HBr (50 °C), KBr (20 °C) and $MgBr_2$ (20 °C) systems respectively.

The solubility behaviour of copper(I) bromide in HBr, KBr and $MgBr_2$ has been investigated in the present studies. These studies showed the formation of 1:1 species in all the system, the presence of higher species like $CuBr_3^{2-}$ is also indicated for the system $CuBr-HBr-H_2O$ and $CuBr-KBr-H_2O$, but in the case of $CuBr-MgBr_2-H_2O$ the presence of higher species is eliminated on the basis of present work.

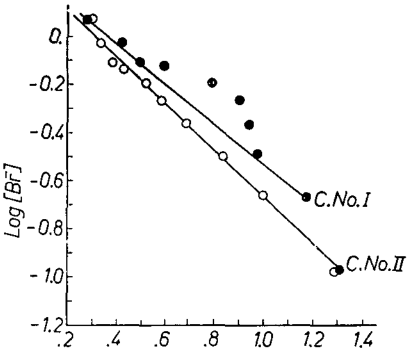

Fig. 3. $CuBr-MgBr_2-H_2O$ System at 20 °C
Curve I Logarithm of observed solubility of CuBr as a function of log $[Br^-]$
Curve II Logarithm of calculated $CuBr_3^-$ as a function of log $[Br^-]$

The authors express their sincere thanks to Dr. S. M. F. Rahman Head, Department of Chemistry, for providing facilities. One of the authors (M. M. Khan) is also grateful to the University Grants Commission, New Delhi, for the award of a senior fellowship.

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Selenocyanat-Komplexe der Seltenen Erden

Von A. M. Golub, M. V. Kopa, V. W. Skopenko und G. W. Zinzadse

Mit 2 Abbildungen

Inhaltsübersicht. Es wird uber die Darstellung von Selenoxyanaten der SE unter Stabilisierung mit organischen Liganden (Phenanthiolin, Dipyridyl, Urotropin, Diantipyrilmethan) berichtet. Die insgesamt 70 Verbindungen werden infrarotspektroskopisch und röntgenographisch charakterisiert. Aus den Messungen wird auf N-gebundene Komplexe geschlossen mit Ausnahme bei den Verbindungen des Typs SE(Diantipyrilmethan)$_4$(NCSe$^-$)$_3$, in denen die SeCN-Gruppe mit dem SE-Metall durch Ionenbindung gebunden ist.

Abstract. 70 rare earths selenocyanate complexes with Phen, Dipy, Urt and Diap as the ligands have been synthetized for the first time.

From IR-spectral and X-ray data it has been established that in the compounds Ln(Phen)$_3$ · (NCSe)$_3$, Ln(Dipy)$_3$(NCSe)$_3$, Ln(Dipy)$_2$(NCSe)$_3$ · 2CH$_3$OH, Ln(Urt)$_2$(NCSe)$_3$ · 3C$_2$H$_5$OH, and Ln(Diatp)$_3$(NCSe)$_3$, where Ln–La, Ce, Pr and Nd, the selenocyanate groups are monodentate and coordinated to the rare earths metal through the nitrogen atom, whereas in Ln(Diatp)$_4$ · (NCSe)$_3$ ionic NCSe$^-$ is present.

Das Selenocyanation besitzt ähnliche Eigenschaften wie das Thiocyanation und bildet entsprechende Koordinationsverbindungen. Im Gegensatz zu diesen sind aber die Selenocyanate der Übergangsmetalle bisher nur wenig untersucht worden¹). Dies gilt insbesondere für die Selenocyanate der Seltenen Erden (SE), die von uns seit 1960 untersucht werden²). In den letzten Jahren erschienen ferner Mitteilungen anderer Autoren über die Darstellung der Verbindungen $[(n\text{-}C_4H_9)_4N]_3$ $[SE(NCSe)_6]$ der Metalle Yttrium³) sowie Pr, Nd, Sm, Gd, Ho, Er und Yb⁴).

Da Verbindungen, die Selenocyanatliganden im Anion enthalten, wenig stabil sind, untersuchten wir die Bildung der Koordinationsverbindungen eines gemischten Typs, indem am Zentralatom außer SeCN-Gruppen noch einige neutrale Molekeln gebunden waren.

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Coordination Compounds of Copper(I) chloride with Pyridine and related Ligands

By Anees Uddin Malik

With 2 figures

Summary

Complexes of Cu(I) with pyridine, picolines, lutidines, quinolines, piperidine and acridine have been studied by potentiometric method. Only the complexes 3 picoline, 2.4 and 2.6 lutidines, quinoline, piperidine and acridine could be isolated in pure form. The elementary analyses and the infra red spectra of the 1:1 complexes suggest that they behave like pyridine complexes and the increase in γ(CH ring) contributes most to N—M bond strength.

Inhaltsübersicht

Die Komplexbildung zwischen Cu(I) und Pyridin, Picolinen, Lutidinen, Chinolinen, Piperidin sowie Acridin wurde potentiometrisch verfolgt. Für einige 1:1-Komplexe, die in fester Form isoliert wurden, wird aus IR-Spektren ein pyridinkomplexartiges Verhalten gefolgert und die beobachtete Frequenzerhöhung der γ(CH-Ring)-Schwingung mit der Ausbildung einer starken N—Cu-Bindung in Zusammenhang gebracht.

The coordination compounds of heterocyclic amines with transitional metals are well known. Amongst the metals which have been studied extensively include Zn1)2), Co3)4), Ni5)6) Cr(III)7), Cu(II)1) Mn(II)8), Ag(I)9),

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Ir[10]) etc., However, it is surprising that very little work has been done on Cu(I) that complexes with heterocyclic amines. Recently, Douglas and Coworkers[11]) studied Cu(I) complex with allyl pyridine. The investigations on Cu(I) complexes are limited, probably, because of the rapid oxidation of Cu(I) to Cu(II) and because of the insolubility of Cu(I) compounds.

The present communication deals with the studies of the complexes formed by the interaction of copper (I) chloride with pyridine and related ligands.

Experimental

Pyridine (Baker Analysed Reagent), 2-, 3-, and 4 picolines, 2.4 and 2.6 lutidines (all E. Merck products), quinoline and isoquinoline (Light Products) and Acridine (B.D.H. product) were used during the experiments. Solutions of the reagents were prepared in doubly distilled water, in case where some of the reagents were insoluble in water, water-acetone mixture were used as solvents.

Copper(I) chloride was prepared by method recommended by Keller and Wycoff.[12]) Solutions of Copper(I) chloride were prepared in concentrated potassium chloride. The Cu^+ ions were estimated gravimetrically by precipitating them as Copper(I) thiocyanate.[13])

Table 1

Complexes prepared

Compound	Formula*)	Colour	m. p.	M at 33.5 °C
Cu(I)-Pyridine	Cu(py)Cl	light yellow changes to green	—	—
Cu(I)-2 picoline	Cu(2pic)Cl	light yellow changes to green	—	—
Cu(I)-3 picoline	Cu(3pic)Cl	deep yellow	119 °C	Diamagnetic
Cu(I)-4 picoline	Cu(4pic)Cl	yellow changes to green	—	—
Cu(I)-2.4 lutidine	Cu(2.4L)Cl	Light yellow	211 °C	Diamagnetic
Cu(I)-2.6 Lutidine	Cu(2.6L)Cl	white (sensitive to light)	205 °C	Diamagnetic
Cu(I)-Quinoline	Cu(Quin)Cl	yellow	242 °C	Diamagnetic
Cu(I)-Isoquinoline	Cu(Isoquin)Cl	white changes to green	—	—
Cu(I)-Acridine	Cu(Ac)Cl	red	210 °C	Diamagnetic
Cu(I)-Piperidine	Cu(Pip)Cl	red	above 360 °C	Diamagnetic

*) Composition determined by potentiometric methods.

py — pyridine, pic — picoline, L — lutidine, Quin — quinoline, Ac — Acridine, Pip — piperidine.

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Apparatus: Potentiometric measurements were carried out by using Pye precision potentiometer (type 7568) using saturated calomel and Pt as reference and indicator electrodes (employing $Cu^+ \rightleftharpoons Cu^{2+} + e$ couple) respectively.

Infra red spectra were taken a double beam PERKIN ELMER recording spectrometer type 221 equipped with NaCl grating (700—4000 cm^{-1}).

Magnetic susceptibility measurements were made with Gouy magnetic balance with temperature adjustments.

Preparation of the Complexes: The complexes were prepared by adding excess of amines to a solution of cuprous chloride. The products settle readily and the whole substance was transfered on a sintered funnel. The product was washed with small aliquots of distilled water and finally washed with absolute alcohol. The product so obtained was dried in vacuuo in a nitrogen atmosphere.

Only complexes of 3 picoline, 2.4 and 2.6 lutidine, quinoline and acridine were isolated in sufficiently purified form and therefore capable of further investigations where as the other products are extremely sensitive to moisture and transform into greenish product on drying and decompose by organic solvents.

The complexes prepared together with their colours, melting points or decomposition temperatures and magnetic moments are listed in Table 1.

Infra red Absorption Spectra: Absorption frequencies (700 cm^{-1}—1700 cm^{-1} region) of the complexes arising from the coordinated amines are as follows:

Cu(3-pic.)Cl: 715 (v. s.)[a], 805 (v. s.), 9.35 (m)[b], 990 (v. w.)[c], 1020 (m), 1055 (S)[d], 1115 (S), 1125 (w)[e], 1195 (v. s.), 1335 (w), 1370 (S), 1475 (v. s.), 1575 (S), 1595 (S).

Cu(2,4 L)Cl: 730 (w), 755 (w), 820 (v. s.), 910 (m), 925 (w), 995 (w), 1030 (S), 1160 (w), 1230 (w), 1265 (v. s.), 1295 (S), 1365 (m), 1390 (w), 1435 (S), 1455 (w), 1485 (w), 1550 (S), 1600 (S), 1615 (S).

Cu(2,6 L)Cl: 730 (w), 790 (v. s.), 810 (V. s.), 830 (v. w.), 865 (v. w.), 910 (w), 925 (v. w.), 990 (m), 1030 (m), 1110 (w), 1156 (m), 1370 (s), 1460 (v. s.), 1575 (m), 1610 (m).

Cu(Quin.)Cl: 730 (m), 740 (m), 805 (v. s.), 815 (s), 865 (m), 955 (w), 980 (w), 1020 (w), 1050 (w), 1136—40 (w and b)[e], 1205 (w), 1310 (m), 1370 (v. s.), 1455 (v. s.), 1500 (s), 1580 (m), 1590 (m), 1615 (m).

Cu(Pip.)Cl: 710 (w), 825 (b and m), 860—865 (b and m), 925 (m), 985 (m), 1365 (s), 1450 (s).

Cu(Acridine)Cl: 735 (v. s.), 780 (m), 795 (w), 815 (v. w.), 830 (m), 845 (w), 860 (m), 920 (s), 955 (m), 985 (w), 1000 (b and m), 1140 (m), 1290 (v. w.), 1305 (v. w.), 1370 (s), 1460 (v. s.), 1510 (s), 1545 (v. w.), 1565 (v. w.), 1615 (s).

[a] v. s. — very sharp; [b] m — medium; [c] v. w. — very weak; [d] S-sharp; [e] w — weak;) b-broad.

Table 2
Analyses

	Cu %		Cl %	
	Found	Calcd.	Found	Calcd.
Cu(3 pic)Cl	32.75	33.08	17.71	18.42
Cu(2.4 L)Cl	28.61	30.83	16.95	17.22
Cu(2.6 L)Cl	27.54	30.83	18.10	17.22
Cu(Quin)Cl	27.53	27.85	15.45	15.57
Cu(pip)Cl	31.30	34.71	21.19	19.39
Cu(Ac)Cl	21.88	22.03	12.59	12.76

Results and Discussion

The composition of the complexes formed by the interaction of copper(I) chloride with pyridine and other heterocyclic amines was determined by potentiometric tritrations making use of Cu(I) $\rightleftharpoons$ Cu(II) + e couple. In each case a ratio for 1:1 complex was obtained by the inflexion point of the curves (Fig. I). As some on the complexes could not be isolated in pure form, the potentiometric method gave an idea about the composition of the complexes which actually formed by the interaction of cuprous chloride with hetero cyclic amines.

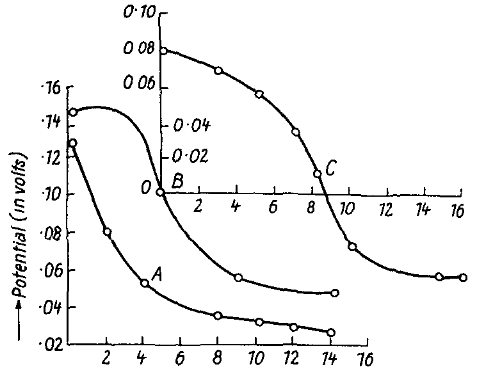

Fig. 1. Titration curves: 10.0, 6.6, 0.10 M CuCl against (A) 0.260 M β picoline (B) 0.160 M Isoquinoline and (C) 0.112 M, 2.4 Lutidine

The complexes formed with 3-picoline (deep yellow), 2.4-Lutidine (light yellow), 2.6 lutidine (white), Quinoline (yellow), Piperidine (red) and Acridine (red) are quite stable in drined state and remained unchanged even after keeping for months. The complexes are fairly soluble in acetone and alcohol insoluble in water but slowly change to gree on standing.

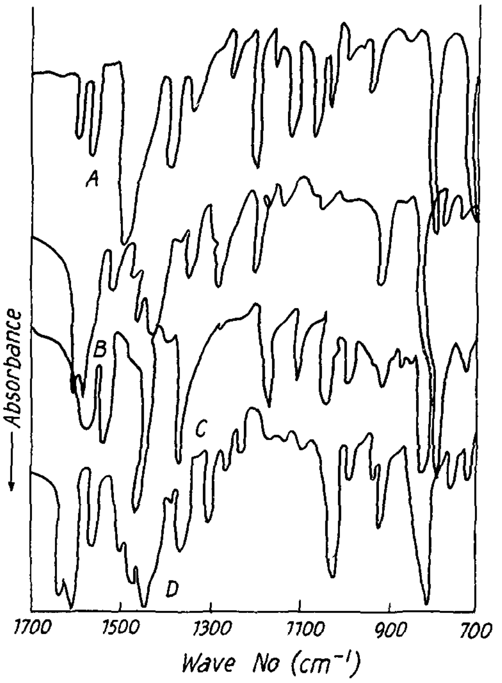

Fig. 2. Infra red spectra of: (A) Cu(3pic)Cl, (B) Cu(2.4L)Cl, (C) Cu(2.6L)Cl, and (D) Cu(pip)Cl

All these complexes were found to be diamagnetic as it should be expected from Cu(i) complexes.

The infra red band observed in the spectra of 3-picoline, 2,4 lutidine and 2,6 lutidine complexes with CuCl are assigned[14][15] in Table 3, (Fig. 2). The band assignment for the complexes were made by correlating

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[14–15] see p. 111.

the spectrum of liquid amines and the spectra of mulls of the solid complexes with the assumption that upon coordination these amines should behave similarly to those of pyridine. There exist great similarities between the spectra of the complexes and the spectrum of free pyridine[10]. Similar observations were reported by Yingst and Douglas for allylpyridine complexes.

Table 3

	${}^{a}\nu$ (ring CC, CN)	${}^{b}\gamma$ (ring CH)
3 picoline[17]	1578 (s), 1479 (v. s.), 1452 (s), and 1414 (v. s.)	788 (v. s.), and 708 (v. s.)
Cu(3pic)Cl	1595 (s), 1575 (s), and 1475 (v. s.)	805 (v. s.), and 795 (v. s.)
2.4 Lutidine[18]	1600 (v. s.), 1560 (v. s.), 1482 (v. s.), and 1444 (v. s.)	817 (v. s.), 754 (m), and 727 (s)
Cu(2.4L)Cl	1615 (s), 1600 (s), 1550 (s), 1485 (w), 1455 (a), and 1435 (s)	820 (v. s.), 755 (w), and 730 (w)
2.6 Lutidine[19]	1464 (v. s.), 1471 (v. s.), and 1456 (v. s.)	775 (v. s.), 729 (m), and 716 (m)
Cu(2.6L)Cl	1610 (m), 1575 (m), and 1460 (v. s.)	830 (v. w.), 810 (v. s.)

[a] — stretching vibrations, [b] — out of plane deformations.

The 1650 to 1400 cm^{-1} region includes the CC and CN streching vibrations for free ligands and their complexes were where as ca. 760 the out of plane CH deformation. For the complexes of CuCl with the ligands there is shift to higher frequencies in case of $\nu(C{=}C)$, $\nu(C{=}N)$ and γ(ring CH) vibrations. Such a change has been observed for pyridine complexes[16] where coordination is quantitatively distinguished from the free ligand by a shift of the strong 1578 to ca. 1600 cm^{-1}. The CH out of plane deformation vibrations of picoline (788), 2.4 lutidine (817) and 2.6 luticline (775) are also shifted to higher frequencies on complexation. The increase is greatest for 3-picoline (17), less so for 2.4 lutidine (3) and least for 2.6 lutidine (5. The increase is frequency in γ(CH) is attributed to increase in N—M bond strength[20].

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Cu(Pip.)Cl complex: The infra red spectra of Cu(Pip.)Cl can be explained by emperically correlating the spectrum of liquid piperidine[21]) and the spectra of the solid mull complex.

The two bands at 1443(s) and 1468(m) due H—C—H bending modes are replaced by a sharp single band at 1450. Also, the five H—C—C wagging vibns. at 1260 (m), 1279 (w), 1319 (w), 1332 (s), and 1338 (m) are replaced by a sharp single band at 1365 (s) at higher frequency. The four H—C—C twisting modes appear in piperidine at 1010 (v. w.), 1151 (s), 1170 (m), and 1194 (w) are disappeared on complexation. There are 5 ring vibns. in piperidine viz., 862 (s), 941 (w), 1038 (w), 1055 (m), and 1119 (m) they are replaced by two bands of medium intensity viz. 985 and 925. The three H—C—C rocking modes at 749 (m), 770 (w) and 800 (s) are replaced by three bands at 865, 825, and 710 respectively, there is large increase in frequency as well as in intensity which attributes to strong N—M bond strength in case of piperidine complexes. Similar behaviour is also observed in case of BCl_3 — piperidine complexes.[21])

In case of quinoline and acridine complexes, the spectra could not be fully resolved because precise data are lacking and require further investigations.

It can be concluded from the infra red investigations that the complexes formed by CuCl with 3-picoline, 2. 4 lutidine and 2. 6 lutidine show almost the same behaviour as it is observed in case of pyridine complexes, the increase in frequency in ν(CC,CN) and γ(CH) ring. On complexation, the latter contributes most to increasing stability of the complexes.

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Co-ordination compounds of cuprous iodide with heterocyclic amines

(*First received* 26 *March* 1966; *in revised form* 19 *February* 1967)

A LARGE number of metal complexes with pyridine and related ligands have been studied. Amongst the metal complexes which have been studied are those of Ni(II),(1,2) Cr(II),(3) Cr(III),(4) Cu(II),(5) Ag,(6) Rh,(7) Ir(8) and CuCl.(9) The present communication deals with an investigation on some complexes of cuprous iodide with pyridine (py), 2 picoline (2 pic), 3-picoline (3 pic), 4-picoline (4 pic), 2,4 lutidine (2,4 L), 2,6 lutidine (2,6 L), Quinoline (Q), Isoquinoline (I.Q.), Piperidine (Pip) and Acridine (Ac).

RESULTS AND DISCUSSION

Cuprous iodide forms 1:1 complexes with py, pic (2, 3, 4), L(2, 4 and 2, 6), Q, I.Q., Pip and Ac. These complexes are very stable and remained unchanged even after keeping for more than a year. They are insoluble in water, soluble in organic solvents. All the complexes were found to be diamagnetic as expected from Cu(I) compounds.

The i.r. spectra of the complexes were measured in the region 6 to 15 μ.(10) The spectra of the complexes were compared with those of corresponding amines with the assumption that on co-ordination there occur no major changes in the spectra of amines.(11,12)

The i.r. absorption bands observed at about 1600 cm^{-1} are assigned to ring CC, CN stretching vibrations, there are two distinct changes on complexation namely the reduction in the number of bands and increase in frequencies. There does not seem to be any simple interpretation of these changes except that they are very likely due to the strong polarization of the aromatic ring caused by the co-ordination of Cu^+ to pyridine. The absorption bands near 1000 cm^{-1} are due to ring vibrations or hydrogen deformation modes. In almost all cases there is a shift to higher frequencies as well as an increase in intensity together with reduction in the number of bands. These changes in out of plane deformation vibrations may be due to the very strong co-ordination of the ring nitrogen with the small Cu^+ ion, the very large polarized I^- very close to the co-ordination sphere will also affect the normal bending modes. This charge distribution may bring stability to the system.

Preparation of the complexes

The complexes were prepared by adding excess amine to a solution of cuprous iodide in water containing excess of KI. The product settled readily, was filtered, washed several times with distilled water, and dried *in vacuo* over CaO. The product was then dissolved in acetone and after a few days, crystals formed which were separated from the supernatant liquid and dried *in vacuo*. In some cases several crystallizations were required.

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Composition and properties of the complexes

Magnetic susceptibility measurements carried out at 36°C showed that all complexes are diamagnetic.

Cu(py) I. amethyst crystals, decomp. temp: 190°C. Anal. Calc. for C_5H_5N Cu I, C, 22·3; H, 1·8, N, 5·2; I, 47·1 and Cu, 23·6. Found, C, 22·1; H, 2·2; N, 5·0; I, 46·8 and Cu, 23·4.

Cu(2pic) I. Light brown crystals, decomp. temp. 155°C. Anal. Calc. for C_6H_7N Cu I, C, 25·4; H, 2·5; N, 4·9; I, 44·8 and Cu, 22·4. Found, C, 24·8; H, 2·5; N, 4·5; I, 44·3 and Cu, 22·4.

Cu(3 pic) I. Light brown crystals, decomp. temp. 150°C. Anal. Calc. for C_6H_7N Cu I, C, 25·4; H, 2·5; N, 4·9; I, 44·8 and Cu, 22·4. Found, C, 24·7; H, 2·2; N, 4·6; I, 44·2 and Cu, 21·7.

Cu(4 pic) I. Dark brown crystals, decomp. temp. 240°C. Anal. Calc. for C_6H_7N Cu I, C, 25·4; H, 2·5; N, 4·9; I, 44·8 and Cu, 22·4. Found, C, 24·7; H, 2·3; N, 4·6; I, 44·1 and Cu, 22·1.

Cu(2,4 L) I. Light buff crystals, decomp. temp. 145°C. Anal. Calc. for C_7H_9N Cu I, C, 28·2; H, 3·0; N, 4·8; I, 42·7 and Cu, 21·0. Found, C, 27·6; H, 2·8; N, 4·6; I, 41·8 and Cu, 20·7.

Cu(2,6 L) I. Brownish black crystals, decomp. temp. 145–150°C. Anal. Calc. for C_7H_9N Cu I, C, 28·2; H, 3·0; N, 4·8; I, 42·7 and Cu, 21·0. Found, C, 27·7; H, 2·8; N, 4·3; I, 41·6 and Cu, 20·7.

Cu(Q) I. Light yellow product, decomp. temp. 155°C. Anal. Calc. for C_9H_7N Cu I, C, 33·8; H, 2·2; N, 4·4; I, 39·7 and Cu, 19·9. Found, C, 32·7; H, 2·2; N, 4·1; I, 39·5 and Cu, 19·6.

Cu(I.Q.) I. Dark yellow product, decomp. temp. 204°C. Anal. Calc. for C_9H_7N Cu I, C, 33·8; H, 2·2; N, 4·4; I, 39·7 and Cu, 19·9. Found, C, 32·2, H, 2·3; N, 3·9; I, 39·3 and Cu, 19·7.

Cu(Pip) I. Dirty white product, decomp. temp. 175°C. Anal. Calc. for $C_5H_{10}N$ Cu I, C, 21·9; H, 3·6; N, 5·1; I, 45·9 and Cu, 23·1. Found, C, 20·8; H, 3·6; N, 4·7, I, 4·8 and Cu, 22·8.

Cu(Ac) I. Brick red crystals, decomp. temp. 335°C. Anal. Calc. for $C_{13}H_9N$ Cu I, C, 40·5; H, 2·3; N, 3·8; I, 34·3 and Cu, 17·2. Found, C, 38·1; H, 2·2; N, 3·4; I, 34·2 and Cu, 16·9.

C,H,N analyses were carried out by Australian Micro-analytical Service, Division of Organic Chemistry, University of Melbourne, Australia. For the estimation of copper and iodine, the solution of the complexes were prepared in dilute HNO_3 and estimations of copper and iodine were carried out separately. Copper was estimated iodometrically by first precipitating as copper sulphide and dissolving the latter in dilute HNO_3. Iodine was estimated as silver iodide.

EXPERIMENTAL

Pyridine (Baker Analysed reagent), 2-, 3- and 4- picolines, 2, 4 and 2, 6 lutidines (all E. Merck products), quinoline, isoquinoline (Light chemicals), Acridine and Piperidine (B.D.H. products) were used. The solutions of the reagents were prepared in doubly distilled water, and where the reagents were insoluble in water, water-acetone and water–ethanol mixture were used as solvents.

Cuprous iodide was prepared by adding potassium iodide to a copper sulphate solution and subsequently passing SO_2 to remove free iodine. Solution of cuprous iodide were prepared in aqueous KI.

Infrared spectra were taken with a Perkin–Elmer 21 recording spectrometer equipped with NaCl prism.

Magnetic susceptibility measurements were made with Gouy magnetic balance with temperature adjustments.

Acknowledgements—The author is thankful to Dr. S. M. F. Rahman for helpful suggestions and Prof. A. R. Kidwai for providing facilities during the course of this work.

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Studies on Mixed Ligand Complexes of Cu (I). I

Mixed Ligand Complexes of Tris(tu)Cu(I) Iodide with Heterocyclic Amines

By ANEES UDDIN MALIK

Summary

Tris-(tu)-Cu(I) iodide reacts with pyridine, 3-picoline and 2,2'-dipyridyl to form tetracoordinated complexes of the type [Cu(py)tu$_3$]I, [Cu(3-pic)tu$_3$]I and [Cu(dipy)tu$_2$]I respectively. Infra red spectra give evidence for the coordination through nitrogen and sulphur in these complexes.

Inhaltsübersicht

Tris-thioharnstoff-kupfer(I)-jodid gibt mit Pyridin, 3-Picolin- und 2,2'-Dipyridyl die tetraedrischen Komplexe [Cu(py)tu$_3$]J, [Cu(3-pic)tu$_3$]J und [Cu(dipy)tu$_2$]J (tu = Thioharnstoff), in denen nach Aussage der IR-Spektren die Koordination über Stickstoff und Schwefel erfolgt.

In recent years, much interest has been shown on the chemistry of mixed ligand complexes. Amongst the latter, tetra and hexacoordinated complexes of Cu(II) have been extensively studied by a number of workers$^{1-3}$). However, from the existing information it appears that no work has yet been carried out on the mixed ligand complexes of Cu(I). In continuation of our work on the amine and thiourea complexes of Cu(I)$^{4-6}$), the present communication deals with the studies on the mixed ligand complexes of copper(I) iodide with thiourea (tu), pyridine (py), 3 picoline (3 pic) and 2,2' dipyridyl (dipy).

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Experimental

Pyridine (Baker analysed reagent), 3-picoline, 2,2′-dipyridyl, thiourea and phenyl arsonic acid (E. Merck products) were used. Copper(I) iodide was prepared as described earlier[5]). IR spectra were taken with a Perkin-Elmer 237 recording spectrometer in the region 6 to 15 μ employing the standard KBr technique using spectral grade KBr.

Magnetic susceptibility measurements were made with Gouy magnetic balance at 30 °C.

Preparation of the complexes

Tris(tu)Cu(I) iodide: About 2 gms of copper(I) iodide were dissolved in 100 ml. of acetone (containing about 5 gms of solid KI) and to it about 6 gms of thiourea were added. The resulting solution was boiled for about 5 mts. over a water bath, filtered and the filtrate was evaporated to dryness. The light pink product so obtained was washed several times with small aliquots of water and alcohol and finally dissolved in acetone, concentrated and crystallised. Very light pink product, soluble in water und organic solvents:

Calc. for $C_3H_{12}N_6S_3CuI$: S 22.9, N 20.1, Cu 15.2, I 30.3. Found: S 24.0, N 20.5, Cu 15.1, I 30.5.

Tris(tu)mono(py)Cu(I) iodide: About 5 gms of tris(tu)Cu(I) iodide were treated with 10 ml. of pyridine added in small aliquots with constant mixing, to the resulting mixture about 100 ml. of acetone were added and the whole solution was refluxed over a waterbath for about half an hour, the refluxed solution was then evaporated slowly to dryness. The pink product so obtained was crystallised from acetone. Light pink cyrstals, m. p. 125 °C. soluble in water and organic solvents.

Calc. for $C_8H_{17}N_7S_3Cu$ I: S 19.3, N 19.7. Cu 12.8 and I 25.5; S 19.6, N 20.15, Cu 12.6 and I 25.3.

The preparation of tris(tu)mono(3 pic)Cu(I) iodide was carried out in exactly the same manner as described in case of pyridine complex.

Tris(tu)mono(3 pic)Cu(I) iodide: Light pink crystals. m. p. 122 °C, soluble in water and organic solvents.

Calc. for $C_9H_7N_{10}S_3Cu$ I: N 19.2. S 18.8, Cu 12.4, I 24.6. Found: N 19.1, S 17.9. Cu 12.0. I 24.1.

Bis(tu)mono(Dipy)Cu(I) iodide: About 2 gms of 2,2′ dipyridyl were added to 200 ml. of acetone containing 4.2 gms of tris(tu)Cu(I) iodide. The resulting red solution was refluxed for about half an hour and then evaporated slowly over a water bath. The pinkish red product so obtained was washed several times with small aliquots of absolute alcohol and then dissolved in acetone and crystallised.

Red Crystals, m. p. 135 °C, insoluble in H_2O, soluble in acetone Calc. for $C_{12}H_{16}N_6S_2CuI$: N 16.8, S 12.8, Cu 12.7, I 25.5. Found: N 16.5, S 12.7, Cu 12.6, I 25.6.

Bis(tu)mono(phOAs)Cu(I). About 0.5 g of phenyl arsonic acid (phOAs) was added to 100 ml. of 2.5% alcoholic solution of tris(tu)mono(py)Cu(I) iodide. The whole mass was heated over a water bath for about 15 mts. filtered and the filtrate was evaporated to dryness. The yellow product so obtained was washed several times with small quantities of 80% ethanol and then dissolved in acetone and crystallised.

Lemon yellow Crystals. soluble in Acetone, alcohol and hydrolysed in presence of water.

Calc. for $C_8H_{14}N_4S_2AsO_3Cu$: N 13.4. S 15.4 and Cu 15.25. Found N 13.2, S 15.5 and Cu 14.8.

Preparation of Bis(tu)mono(dipy)Cu(I) iodide obtained by the action of 2,2′ dipyridyl on tris(tu)mono(py)Cu(I) iodide: 100 ml. of 2.5% alcoholic soln. of 2,2′ dipyridyl were added to a solution of tris(tu)mono(py)Cu(I) iodide (5 gm in 100 ml. of acetone). The resulting red coloured solution was concentrated by evaporating to half of its volume and then kept for crystallisation. After few hours red crystals of the product appeared which were seperated, dissolved in acetone and crystallised. Red Crystals, insoluble in H_2O, soluble in acetone. m. p. 136 °C.

Calculated for $C_{12}H_6N_6S_2CuI$: N 16.8, S 12.8, Cu 12.7, I 25.5. Found: N 16.5, S 12.5, Cu 12.6, I 25.4.

Copper was estimated iodometrically and I was estimated as silver iodide. The sulphur and nitrogen analyses were carried out by Australian Micro-analytical service, Division, of organic chemistry, University of Melbourne, Australia.

Results and Discussion

Cuprous iodide forms mixed ligand complexes of the type $[Cu(tu)_3py]I$, $[Cu(tu)_3\ 3\ pic]I$, $[Cu(tu)_2dipy]\ I$ and $Cu[(tu)_2(PhOAs)]$. The complexes are very stable, and remain unchanged even after keeping for a long time. The complexes are found to be diamagnetic as expected from Cu(I) compounds. Attempts to prepare complexes with 2 and 4 picolines, 24 and 2.6 lutidines, quinoline and isoquinoline and o-phen anthroline in pure state could not be successfull.

Copper(I) iodide forms 1 : 1 complexes with heterocyclic amines, also, with thiourea a 1 : 3 complex is formed[4–6]. In the formation of mixed nitrogen and sulphur ligated complexes a maximum coordination number of four is achieved. The replement of thiourea and pyridine molecules by dipyridyl and phenyl arsonic acid confirms the tetra coordinated structure for the complexes.

$$\begin{tikzcd}
 & Cu(tu)_3I \arrow[dl, "PhOAs"'] \arrow[d, "py"] \arrow[dr, "dipy"] & \\
{[Cu(tu)_2Ph(OAs)]} & {[Cu(tu)_3py]I} \arrow[l, "PhOAs"'] \arrow[r, "dipy"] & {[Cu(tu)_2(dipy)]I}
\end{tikzcd}$$

The infra red spectra gives interesting information regarding the bonding in these complexes. All the complexes (except. phenyl arsonic acid adduct) give 4 strong bands in the region 1600–1000 cm⁻¹ namely Ca. 1600, Ca. 1475, Ca. 1370 and Ca. 1085 which are assigned to composite bands of NH_2 bending, N–H deformation and C–N stretching vibrations in thiourea[6]. The band at 1600 and 1400 cm⁻¹ may also be assigned to ring CC, CN stretching vibrations of coordinated amino respectively[7]. The simplicity of the spectra in this region may only be due to the presence of coordinated sulphur when composite bands of NH_2 bending N–H deformation and C–N stretching remain almost uneffected. Further in coordinated amines the bands due to ring CC, CN stretching vibrations are greatly reduced in number as reported earlier[5][8]. The spectrum in the region 600–800 cm⁻¹ is marked by a number of bands, only a strong band at Ca. 710 cm⁻¹ is easily distinguishable from other

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bands. The latter essentially corresponds to C—S stretching band of thiourea at 730 cm^{-1} which lowers on coordination[9]). The complexity of spectra in this region may be due to the splitting of CH out of plane deformation vibrations on coordination with amines and the strong polarisation effect in the coordination sphere by the large I atom.

No quantitative data is available about the relative bond capacities of the ligands as a π acceptor but from the available evidence it seems that the π bonding capacity may follow the order[10]), py $<$ thiourea $<$ dipy $<$ tertiary arsine. The formation of 1:1 complex with pyridine may be explained on the basis of stabilisation of Cu^+ with ligand with π bond acceptor properties but weak σ dionor properties. In case of pyridine complex there is formation of a d_π—p_π bond and the charge accumulation is minimised by transfer of charge from the metal ion to the p_π delocalised orbital. Due to weak π bonding capacity of the pyridine it may not possible for Cu^+ ion to coordinate with more than one pyridine molecule as the coordination with two or more pyridine molecules should result in the excessive charge accumulation round the Cu^+ ion. With thiourea a $d_\pi - d_\pi$ bond is formed due to the availability of vacant d orbital in sulphur which act as acceptor d orbital. Hence in the formation of 3 coordinated thiourea complexes there is strong possibility to minimise the excess charge on Cu^+ by transfer it to d_π levels of the ligands. In the formation of mixed ligand complexes of the type $[Cu(tu)_3py]I$, $[Cu(tu)_2dipy]I$ and $[Cu(tu)_2(PhOAs)]$. The Cu^+ ion attains its maximum coordination number of four due to the contribution of the ligands e.g. tu, dipy and PhOAs which have strong π bonding capacities.

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SHORT COMMUNICATION

Studies on the mixed ligand complexes of copper(I)
Part II. Potentiometric studies on the reaction of heterocyclic amines on tristhiourea copper(I) chloride and iodides

The complexes of copper(I) with heterocyclic amines are well known[1–3]; usually there is formation of 1 : 1 or 1 : 2 species. This is due to the weak π-bonding capacities of heterocyclic amines and because of this property it may not be possible for copper(I) ion to coordinate with more heterocyclic molecules as this would result in excessive charge accumulation around the copper(I) ion[4]. Considering the possibility of the interaction of heterocyclic amines with thiourea (Tu) complexes, in these complexes a $d\pi$–$d\pi$ bond is formed owing to the availability of vacant d-orbitals in sulphur which may also act as acceptor d-orbitals by taking excessive charge from the metal. The reaction of heterocyclic amines with tris Tu copper (I) iodide has recently been reported[5]. Mixed complexes such as [CuTu$_3$Py]I, [CuTu$_3$3-Pic]I and [CuTu$_2$Dipy]I are formed. In the formation of these complexes there is a tendency for copper(I) ion to attain its maximum coordination number of four. The present study is an extension of the work on the mixed ligand complexes of copper(I) iodide with sulphur and nitrogen-containing ligands. The composition and stability of the complex species are reported on the basis of potentiometric studies, and in a few cases spectrophotometric methods have also been employed. These studies are mainly concerned with the formation of mixed ligand complexes formed by the interaction of pyridine and dipyridyl with tris Tu copper(I) iodide and chlorides.

Experimental

Pyridine and 2,2-dipyridyl (analytical grade reagents) were used. Copper(I) chloride and copper(I) iodide were prepared as described earlier[1,2]

Potentiometric measurements were carried out with a Kaycee potentiometer type MG3 with a lamp and scale arrangement. Platinum and calomel were employed as indicator and reference electrodes, respectively.

Preparation of the complex tristhiourea copper(I) iodide. This complex was prepared by the method described earlier[5]. The purity of the sample was authenticated by C, H, N and S analyses.

Preparation of the complex tristhiourea copper(I) chloride. A concentrated solution of copper(I) chloride (2 g) was prepared in concentrated KCl solution. The cuprous solution was mixed with an aqueous solution containing about 4 g of thiourea. The resulting solution was warmed slightly with constant stirring and was then filtered. The filtrate was evaporated to dryness over a water bath. The product so obtained was washed several times with small aliquots of distilled water and was then dissolved in absolute alcohol. The insoluble portion was filtered out. The resulting solution was concentrated and then allowed to stand for about one hour when colourless crystals appeared. The crystals were separated and dried in a vacuum desiccator Found Cu 19 3 (19 4), Cl 10 9 (10 85), N 25 4 (25 7), S 29 1 (29 3)% Calculated values for $C_3H_{12}N_6S_3CuCl$ in brackets

Standard 1 × 10^{-1} *M* nitric acid solution was used as a titrant in potentiometric titrations A constant ionic strength was maintained in the solution by the addition of potassium chloride

Spectrophotometric studies were carried out with a Bausch and Lomb spectronic-20 colorimeter using a 1 cm diameter cuvette The wavelengths selected were chosen by the Vosburgh and Cooper method[8], and the composition was determined by Job's method of continuous variation[9]

Results and discussion

Potentiometric titrations were carried out with a view to investigating the composition and stability of the complexes formed on interacting heterocyclic amines and copper(I) thiourea complex The composition and the calculated values of the stability constants of the complexes are given in Table 1

TABLE 1

Curve No	*Ionic strength*	$\bar{n}$	*Complex formed*	*Stability constant K/l mol* ^{1}
V	0 44	2	$Cu(Py)_2Cl$	—
VI	0 44	3	$Cu(Tu)_3Cl$	—
VII	0 62	1	Cu(Dipy)Cl	3 02 × 10^{2}
VIII	0 25	3(Tu)	$Cu(Tu)_3Cl$+	—
		2(Py)	$Cu(Py)_2Cl$	—
IX	2 0	—	—	—
X	0 44	1	$Cu(Tu)_3Py$ Cl	—
XI	0 62	1	$Cu(Tu)_3Dipy$ Cl	—
XIII	0 44	1	Cu(Py)I	—
XIV	0 44	3	$Cu(Tu)_3I$	—
XV	0 62	1	Cu(Dipy)I	1 82 × 10 ^{2}
XVI	0 25	3(Tu)	$Cu(Tu)_3I$	—
		1(Py)	Cu(Py)I	—
XVIII	0 44	1	$[Cu(Tu)_3Py]I$	1 92 × 10^{-2}
XIX	0 62	1	$[Cu(Tu)_3Dipy]I$	

On the basis of potentiometric titrations, there is evidence for the formation of 1 1 species such as $[CuTu_3Py]Cl$, $[CuTu_3Dipy]Cl$, $[CuTu_3Py]I$ and $[CuTu_3Dipy]I$ $\bar{n}$ is the average number of ligands attached to one central group

The mechanism of the reaction of pyridine with the thiourea complex is a simple one, a pyridine molecule is coordinated to the central atom with the result that copper attains its maximum coordination number of four The copper atom in the central group $[Cu(Tu)_3]^+$ is capable of accepting at least one pyridine molecule as the resulting excessive charge accumulation on Cu^+ will be minimised by transferring it to the vacant $d\pi$ level of the ligand In order of nucleophilicity the pK_a values for thiourea and pyridine are 0 4 and 5 3, respectively[7] The higher pK_a value for pyridine is an indication of the greater tendency of the ligand to attach with the central metal

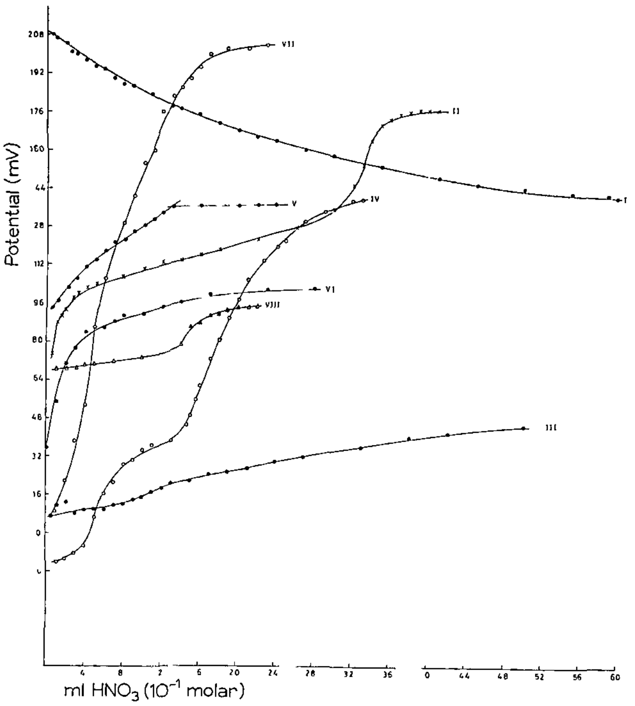

Fig 1 Potentiometric titration curves using 1 × 10^{-1} M HNO$_3$ as titrant (I) 10 ml CuCl (9 75 × 10^{-2} M), (II) 35 ml pyridine (1 × 10^{-1} M), (III) 35 ml thiourea (1 × 10^{-1} M), (IV) 22 ml dipyridyl (1 × 10^{-1} M), (V) I + II, (VI) I + III, (VII) I + IV, (VIII) I + II + III

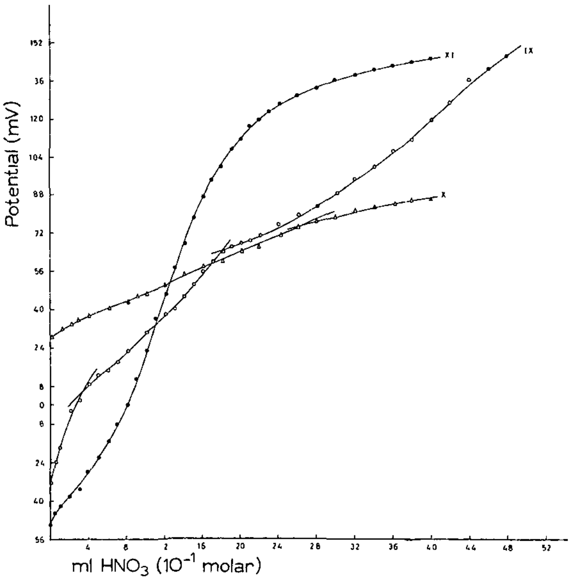

Fig 2 Potentiometric titration curves using 1 × 10^{-1} M HNO$_3$ as titrant (IX) 10 ml Cu(Tu)$_3$Cl (1 × 10^{-1} M), (X) IX + 35 ml pyridine (1 × 10^{-1} M), (XI) IX + 22 ml dipyridyl (1 × 10^{-1} M)

ion On the other hand, in the case of the 1 1 copper pyridine complex there is not much possibility of another pyridine molecule entering into the complex as it has weaker π-bonding ability and thereby an accumulation of excessive charge results on the copper(I) ion

The reaction between $\mathrm{Cu(Tu)_3X}$ (X=Cl, I) and dipyridyl is rather complex Apparently the composition (on the basis of potentiometric studies) leads to the complexes (1 1) having a coordination number of five which is unusual for the d^{10} configuration The mechanism

$$\mathrm{CuTu_3^+ + H_2O \xrightarrow{H_2O} [CuTu_3(H_2O)]^+ \xrightarrow{Dipy} [CuTu_2(Dipy)]^+ + Tu}$$

would explain the formation of 1 1 ($\mathrm{CuTu_3X}$ Dipy) complex as obtained from potentiometric titration curves The mechanism suggested is substantiated by the isolation of the red crystalline mixed ligand complex $\mathrm{[CuTu_2Dipy]I}$, which is fully characterised[4]

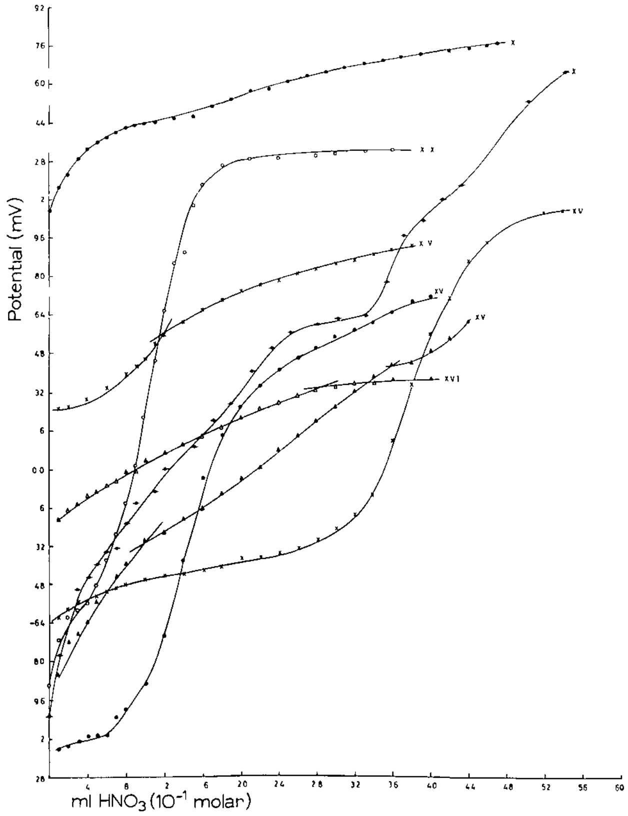

Fig 3 Potentiometric titration curves using 1 × 10^{-1} M $\mathrm{HNO_3}$ as titrant (XII) 10 ml CuI (8 76 × 10^{-2} M) (XIII) XII+35 ml pyridine (1 × 10^{-1} M), (XIV) XII+35 ml thiourea (1 × 10^{-1} M), (XV) XII+22 ml dipyridyl (1 × 10^{-1} M), (XVI) XIII+35 ml thiourea (1 × 10^{-1} M), (XVII) 10 ml $\mathrm{Cu(Tu)_3I}$ (1 × 10^{-1} M), (XVIII) XVII+35 ml pyridine (1 × 10^{-1} M), (XIX) XVII+22 ml dipyridyl (1 × 10^{-1} M)

An interesting aspcct of the reaction between $\mathrm{CuTu_3X}$ and dipyridyl is the result obtained on the basis of spectrophotometric studies. These studies showed that there is a combination of two dipyridyl molecules with one central group which may be explained by the mechanism:

$$\begin{aligned} [\mathrm{CuTu_3}]^+ + \mathrm{H_2O} \rightarrow [\mathrm{CuTu_3(H_2O)}]^+ &\xrightarrow[+\mathrm{Dipy}]{-\mathrm{Tu},\,-\mathrm{H_2O}} [\mathrm{CuTu_2(Dipy)}]^+ + \mathrm{Tu} \\ [\mathrm{Cu(Dipy)_2}]^+ &\xleftarrow[+\mathrm{Dipy}]{-\mathrm{Tu_2}} \end{aligned}$$

The above mechanism is not unlikely as the preliminary experiments showed that the absorbance of the complexes decreased rapidly with time and the concentration of dipyridyl is the rate-determining step in these reactions. The replacement of the remaining two thiourea molecules by a dipyridyl molecule with time is considered probable since the dipyridyl molecule is a better nucleophile and also a potential π-bonding ligand.

Further work on the mechanism of the above reaction is in progress.

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STUDIES ON MIXED LIGAND COMPLEXES

PART III MECHANISM OF THE REACTION OF HETEROCYCLIC AMINES WITH TRIS THIOUREA COPPER(I) CHLORIDE AND IODIDES

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The coordination compounds of copper(I) with nitrogen and sulphur-containing ligands are well known, the coordination number in these complexes usually varies[1,2] from 1 to 3 A few tetra-coordinated complexes have also been reported such as cyano, substituted phosphine and arsine complexes The latter are formed by coordination through bridging and occur more frequently with iodide[3] It has been reported that copper(I) may also form stable mixed ligated complexes with four coordination through substitution and addition reactions Interesting examples[4] of such types of compounds are the products formed by the substitution or addition of heterocyclic amines to copper(I) thiourea complexes, *e g* $[Cu(Tu)_3Py]I$, $[Cu(Tu)_3 3\text{-}Pic]I$, and $[Cu(Tu)_2Dipy]I$ Mixed ligand chloro and iodo copper(I) complexes have also been investigated potentiometrically[5] The stereochemistry of such coordination complexes is explained on the basis of the formation of a $d\pi$–$d\pi$ bond, due to the availability of a vacant *d*-orbital in the ligand which may also act as an acceptor $d\pi$-orbital by taking the excessive charge from the metal The present study is an extension of the earlier work carried out on the mixed ligand complexes of copper(I) This study includes investigations by a potentiometric method on the composition of the complex species formed in solution and their reaction mechanism

EXPERIMENTAL

The silver–silver sulphide electrode used in the potentiometry was prepared by depositing silver metal on a platinum wire The platinum wires were immersed in a solution of potassium argentocyanide and subjected to electrolysis using a 2 V accumulator The silver coated wire was then dipped in dilute H_2S water for about 12–18 h until a uniform dark grey coating of Ag_2S was obtained The reversibility of the electrode was tested by measuring the potentials of thiourea solutions of varying concentrations From the concentration–potential calibration curve the concentration of the known thiourea solution was checked

Tristhiourea copper(I) chloride and iodide complexes, were prepared as described earlier[4,5] Thiourea, pyridine, 2,2-dipyridyl and phenylarsonic acid were all E Merck products and purified before use

Potentiometric measurements were made with a Toshniwal potentiometer type CL06 using Ag–Ag_2S and calomel as indicator and reference electrodes, respectively. The measurements were carried out at 20°C by immersing the solutions in a thermostatic water bath with a temperature control of ±0.5°C.

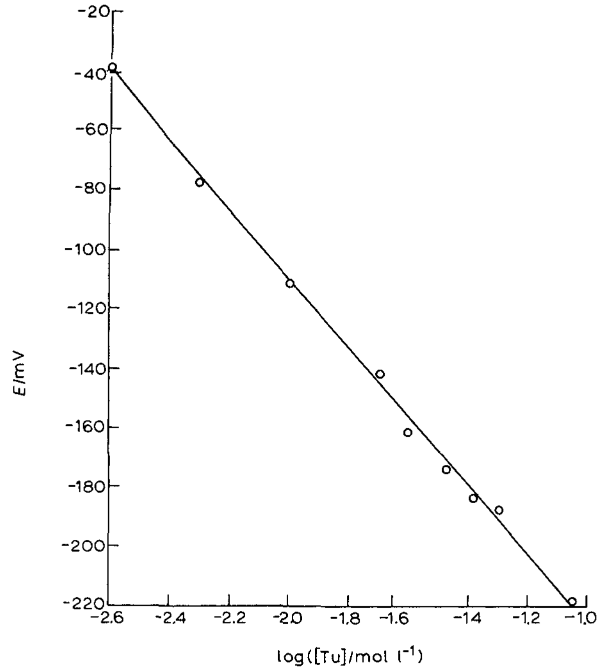

Fig. 1. Calibration curve: log [Tu] *vs.* potential at pH ≈ 7.80.

Equilibrium potentials are rapidly obtained. The plot of log [Tu] *vs.* potential gives straight lines (see Fig. 1) in a wide pH range covering moderately acidic (pH ≈ 3) to feebly basic solutions (pH ~ 8.0), showing that the electrode may be successfully employed for the estimation of thiourea in this pH range but not with the solutions of higher pH (> 8). In the system used the pH of the solution varied in the range 6–8 and therefore, the electrode could be used for determining the concentration of thiourea in the various substitution and addition reactions discussed here.

The reaction rate studies were carried out by measuring the potential of the various solutions with time. Some typical solution compositions were: (i) 10 ml of 0.09 *M* cuprous chloride + 40 ml of 0.1 *M* thiourea, (ii) 10 ml of 0.095 *M* cuprous chloride + 40 ml of 0.1 *M* thiourea + 22 ml of 0.1 *M* 2,2-dipyridyl, (iii) 4 ml of 0.095 *M* cuprous chloride + 12 ml of 0.1 *M* thiourea + 12 ml of 0.1 *M* phenyl arsonic acid, (iv) 10 ml of 0.1 *M* $[Cu(Tu)_3]Cl$ + 22 ml of 0.1 *M* 2,2-dipyridyl, (v) 10 ml of 0.1 *M* $[Cu(Tu)_3]Cl$ + 35 ml 0.1 *M* pyridine, (vi) 10 ml of 0.1 *M* $[Cu(Tu)_3]I$ + 22 ml of 0.1 *M* 2,2-dipyridyl. A constant ionic strength of 0.2 was maintained in these solutions by the addition of potassium chloride.

Preparation of the 2,2-dipyridyl substituted complexes

The complexes were prepared by the method described earlier for bis(Tu)-mono(Dipy)Cu(I) iodide[4].

1 *Bis(Tu)mono(Dipy)Cu(I) iodide* This was prepared as red crystals soluble in acetone Calcd for $C_{12}H_{16}N_6S_2CuI$ N, 16 8, S, 12 8, C, 28 8, H, 3 2, Cu, 12 7, I, 25 5 Found N, 16 5, S, 12 7, C, 29 00, H, 3 21, Cu, 12 6, I, 25 6%

2 *Bis(Tu)mono(Dipy)Cu(I) chloride* This was formed as orange crystals, soluble in acetone Calcd for $C_{12}H_{16}N_6S_2CuCl$ N, 20 63, S, 15 72, C, 35 38, H, 3 93, Cu, 15 60, Cl, 8 70 Found N, 20 38, S, 15 80, C, 35 62, H, 3 85, Cu, 15 71, Cl, 8 82%

Carbon, hydrogen and nitrogen analyses were carried out by the Indian Institute of Technology, Kanpur

DISCUSSION

The mechanism of the reactions of tri-coordinated copper(I) thiourea complexes with neterocyclic amines has been studied potentiometrically using silver–silver sulphide as indicator electrode Table 1 summarises the results of these studies for various reactions

The reaction of pyridine with tristhiourea copper(I) chloride was found to be fast, the equilibrium being attained almost immediately The reaction seems to proceed by the following dissociative mechanism

$$[Cu(Tu)_3]^+ \rightleftharpoons [Cu(Tu)_2]^+ + Tu \xrightarrow[fast]{2Py} [CuTu_2Py_2]^+$$

involving an increase in concentration of thiourea at the completion of the reaction The formation of the complex $[Cu(Tu)_2Py_2]Cl$ by the substitution of pyridine and subsequent elimination of thiourea is expected owing to the higher nucleophilic order of pyridine and the tendency of copper(I) to achieve its maximum stable coordination number (Fig 2, curve 1)

The mechanism of the substitution of tristhiourea copper(I) chloride with dipyridyl has been studied by carrying out kinetic studies with mixtures of cuprous chloride, thiourea and dipyridyl in one case (curve II) and using the thiourea complex and dipyridyl in the other The potentiometric studies and analytical data reveal the formation of the complex, $[Cu(Tu)_2Dipy]Cl$ In both cases, the reaction is second order in the complex and reactant The mechanism of substitution in this case appears to be an associative mechanism involving trigonal–bipyramidal or square pyramid intermediate structures

$$[Cu(Tu)_3]Cl + Dipy \xrightarrow{fast} [Cu(Tu)_3Dipy]Cl \xrightarrow{slow} [Cu(Tu)_2Dipy]Cl + Tu$$

This associative mechanism is further supported on considering the gradual decrease in thiourea concentration with time (curve III)

Potentiometric studies and analytical data show that the interaction of 2,2-dipyridyl with tristhiourea copper(I) iodide results in the formation of a mixed ligand complex $[Cu(Tu)_2Dipy]I$ Unlike the chloride complex, the iodide complex shows an interesting behaviour In the initial stages it shows a zero-order reaction and after about 50 min the reaction proceeds with a second-order dependent We suggest the formation of aquo complexes $[Cu(Tu)_3H_2O]^+$ in the initial stages with the formation of an intermediate penta-coordinated species which subsequently dissociates into $[Cu(Tu)_2Dipy]^+$ (curve IV)

$$[Cu(Tu)_3]^+ \xrightarrow[slow]{+H_2O} [CuTu_3(H_2O)]^+ \xrightarrow{fast} [CuTu_3Dipy]^+ \xrightarrow{slow} [CuTu_2Dipy]^+$$

An interesting substitution study in the tri-coordinated copper(I) complex is the study of the reaction of phenylarsonic acid with tristhiourea copper(I) chloride. Potentiometric studies carried out with the mixture of copper(I) chloride, thiourea and phenylarsonic acid indicate the presence of only two thiourea molecules after the completion of the reaction. The formation of the mixed ligand complex, $Cu(Tu)_2$-PhOAs can be represented by the following reaction mechanism which follows a second-order rate law (curve V).

$$Cu + Tu \xrightarrow{fast} [CuTu_3]^+ \overset{slow}{\rightleftharpoons} [CuTu_2] + Tu \xrightarrow[fast]{PhOAs} [CuTu_2PhOAs]$$

The associative type mechanism is supported by the observed increase in thiourea concentration with time indicating the slow dissociation of the complex into thiourea and lower coordination species and ultimate substitution by the strong π-bonding tertiary arsine. The isolation of this complex has already been reported in the study of the reaction of tristhiourea copper(I) iodide and tristhiourea monopyridine copper(I) iodide with phenylarsonic acid[4].

The coordination chemistry of copper(I) is unique in the sense that the complexes formed are usually of lower coordination number ($n < 4$). These complexes are generally formed with ligands having greater π-bonding capacities; however, there is always a tendency for complexes with lower coordination numbers to achieve the stable coordination maximum either by bridging through ligand atoms or by the

TABLE 1

Original concn of species present	*Curve No*	*Time required for completion of reaction (e g constant potential)/min*	*Concn of species after completion of reaction*
(1) $[CuTu_3]Cl$ (2 2 × 10^{-2} *M*) and Py (7 7 × 10^{-2} *M*) in 45 ml	I	fast	Tu (1 85 × 10^{-2} *M*) in 45 ml
(2) Tu (5 5 × 10^{-2} *M*), Dipy (2 86 × 10^{-2} *M*) and CuCl (1 1 × 10^{-2} *M*) in 77 ml	II	145	Tu (2 25 × 10^{-2} *M*) in 77 ml
(3) $[CuTu_3]Cl$ (2 8 × 10^{-2} *M*) and Dipy (6 28 × 10^{-2} *M*) in 35 ml	III	200	Tu (2 3 × 10^{-2} *M*) in 35 ml
(4) $[CuTu_3]I$ (2 8 × 10^{-2} *M*) and Dipy (6 28 × 10^{-2} *M*) in 35 ml	IV	135	Tu (2 75 × 10^{-2} *M*) in 35 ml
(5) Tu (4 28 × 10^{-2} *M*), PhOAs (4 28 × 10^{-2} *M*) and CuCl (1 3 × 10^{-3} *M*) in 28 ml	V	60	Tu (1 9 × 10^{-2} *M*) in 28 ml

addition of another more reactive group. The present studies on substitution and addition in the tristhiourea copper(I) chloro and iodo complexes come into the second category. The reactions of tri-coordinated copper(I) thiourea complexes were studied with ligands of varying π-bonding capacities. It is well known that the π-bonding capacities follow the order $Py < Tu < Dipy <$ tertiary arsine[6]. There is the likelihood that the addition of a ligand to the tri-coordinated copper(I) complex gives a tetra-coordinated complex, moreover, there is also a possibility of the replacement of a weak π-bonding ligand *e.g.* thiourea, by ligands with stronger π-bonding capacities, *e.g.*, dipyridyl, tertiary arsine, etc. The present studies show that pyridine is added in the coordination sphere of copper(I) to form a tetrahedral $Cu(Tu)_3Py^+$. The reaction proceeds more rapidly and equilibrium is achieved within a short time. However, with the potential nucleophile, dipyridyl, the reaction is a substitution reaction and proceeds with an associative mechanism involving the formation of a penta-coordinated trigonal–bipyramidal intermediate. The resulting intermediate converts into the tetrahedral species $[CuTu_2Dipy]^+$. The second-order rate law dependent on these reactions and the gradual decrease in thiourea concentration indicates an associative mechanism. Another interesting aspect of these reactions which has not yet been fully studied is the complete replacement of thiourea by dipyridyl molecules giving the final product $[CuDipy_2]^+$ identified from spectrophotometric studies[5]. This is not surprising since there is always a possibility of the replacement of a weaker π-bonding ligand by a stronger one. The mechanism of the above reaction may follow the course

$$[CuTu_2Dipy]^+ \rightarrow [CuTuDipy_2]^+ \rightarrow [CuDipy_2]^+$$

Concn of species consumed during reaction	*Complex formed*	*Order of reaction*	*Rate constant/ mol s⁻¹*	*Mode of reaction*
Tu (4.75×10^{-2} *M*)	$[CuTu_2Py_2]^+$	—	—	$Cu(Tu)_3^+ \rightleftharpoons [Cu(Tu)_2]^+$ $+Tu \xrightarrow[fast]{2Py} [CuTu_2Py_2]^+$
Tu (3.25×10^{-2} *M*)	$[Cu(Tu)_2Dipy]Cl$	2nd	6.6×10^{-3}	$CuCl + Tu \xrightarrow{fast} [CuTu_3]Cl + \xrightarrow{Dipy}$ $[Cu(Tu)_3Dipy]Cl \xrightarrow{slow} [Cu(Tu)_2\text{-}$ $Dipy]Cl + Tu$
Tu (6.1×10^{-2} *M*)	$[Cu(Tu)_2Dipy]Cl$	2nd	2.6×10^{-3}	$[Cu(Tu)_3]Cl + Dipy \xrightarrow{fast} (Cu(Tu)_3$ $Dipy]Cl \xrightarrow{slow} (Cu(Tu)_2Dipy]Cl + Tu$
Tu (5.6×10^{-2} *M*)	$[CuTu_2Dipy]I$	2nd	2.5×10^{-3}	$[Cu(Tu)_3]^+ \xrightarrow[slow]{+H_2O} [CuTu_3(H_2O)]$ $\xrightarrow{fast} [CuTu_3Dipy]^+ \xrightarrow{slow}$ $[CuTu_2Dipy]^+$
Tu (2.38×10^{-2} *M*)	$[CuTu_2PhOAs]$	2nd	3.3×10^{-3}	$Cu + 3Tu \xrightarrow{fast} CuTu_3^+ \xrightarrow{slow}$ $[CuTu_2PhOAs] \xleftarrow[fast]{PhOAs} CuTu_2^+ + Tu$

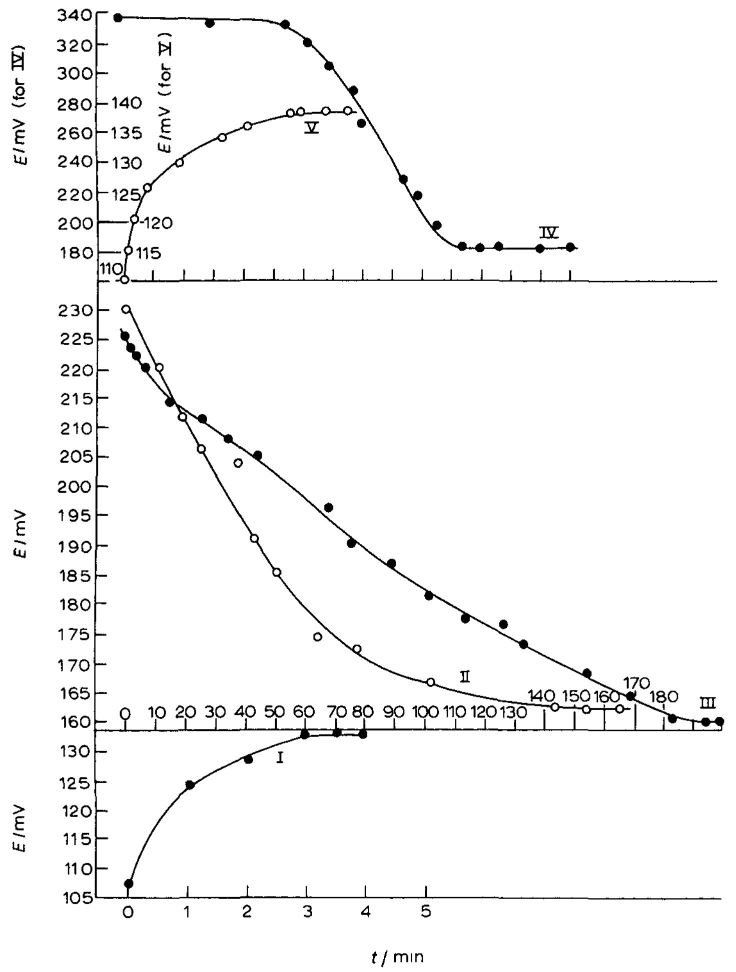

Fig. 2. Variation of potential with time. (I) $(CuTu_3)Cl$ (2.2×10^{-2} M) and Py (7.7×10^{-2} M) in 45 ml; (II) Tu (5.5×10^{-2} M), Dipy (2.86×10^{-2} M) and CuCl (1.1×10^{-2} M) in 77 ml; (III) $(CuTu_3)Cl$ (2.8×10^{-2} M) and Dipy (6.28×10^{-2} M) in 35 ml; (IV) $(CuTu_3)I$ (2.8×10^{-2} M) and Dipy (6.28×10^{-2} M) in 35 ml; (V) Tu (4.28×10^{-2} M) PhOAs (4.28×10^{-2} M) and CuCl (1.3×10^{-3} M) in 28 ml.

In case of *o*-phenanthroline a penta-coordinated intermediate $[CuTu(o\text{-}Phen)_2]^+$ has been isolated and characterised which again supports the above mechanism[7].

The substitution reaction of phenylarsonic acid with tri-coordinated copper(I) thiourea complex seems to proceed with a dissociative mechanism involving the dissociation of the tri-coordinated complex into a lower coordinating species and subsequent addition of tertiary arsine. The gradual increase in concentration of thiourea with time and the second order dependent indicates as dissociative mechanism involving the formation of the complex [Cu(Tu)PhOAs].

A comparative study of the effect of the entering group in copper(I) complexes, based upon the rate constant values of the reactions, gives the relative reactivities of the various ligands as· thiourea < dipyridyl < diarsine A comparison of the reactivities of dipyridyl in the substitution reactions of the chloro and iodo complexes gives a higher value for the former which may be attributed to the greater stability of the iodide complex compared to that of the chloride complex These results are in agreement with the nucleophilic order of the substituent ligands[7]

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SUMMARY

The mechanism of the reactions of heterocyclic amines with tristhiourea copper(I) chloride and iodides has been studied potentiometrically using silver–silver sulphide as an indicator electrode The interaction of pyridine and dipyridyl with tristhiourea copper(I) chloride and iodides results in the formation of complexes such as $[Cu(Tu)_2Py_2]^+$, and $[Cu(Tu)_2Dipy]^+$ The formation of $[Cu(Tu)_2Py_2]Cl$ and $[Cu(Tu)_2Dipy]I$ takes place through a dissociative mechanism but that of $[Cu(Tu)_2Dipy]Cl$ proceeds by an associative mechanism

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Coordination Compounds of Cu(I) with Substituted Thioureas

Anees Uddin Malik

Cuprous chloride forms complexes with diphenyl thiourea, diisopropyl thiourea, naphthyl thiourea (1:2), allyl thiourea, benzyl thiourea hydro chloride and o-tolyl thiourea (1:1). Infra red spectra of Cu (I) complexes have been studied in the region 5.0 to 15.0 μ. From the studies it is concluded that Cu (I) coordinates through sulphur in all cases except that of allyl thiourea. In the latter it appears that there is coordination through nitrogen.

In recent years, infra red spectra of a number of metal thiourea complexes have been investigated.[1-4] These studies are mainly based on Kumler and Fohler's[5] resonance structure for thiourea with 20-30% contribution of highly polar structures. Assuming that like thiourea the substituted compounds also give cannonical structure with equal contributions, coordination through sulphur should result in a decrease in double bond character of C=S and an increase in double bond character of C-N bond; whereas if coordination is through nitrogen then just the opposite effect is to be expected together with the reduction in N-H frequency. The latter remains unchanged if the coordination is through sulphur.

The present communication deals with infra red absorption studies on the complexes of cuprous chloride with s-diphenyl thiourea (D. P. T. U.), naphthyl thiourea (N. T. U.), benzyl thiourea hydrochloride (B. T. U.), allyl thiourea (A. T. U.), di isopropyl thiourea (D. I. P. T. U.) and o-tolyl thiourea (T. T. U.)

EXPERIMENTAL

A. T. U. and D. I. P. T. U. (E. Merck products); N. T. U., D. P. T. U., and T. T. U. (B. D. H. products) and B. T. U. (Light products) were used during the experiments. The products were purified by crystallisation from acetone. The solutions of the reagents were prepared in acetone.

Cuprous chloride was prepared by the method recommended by Keller and Wycoff[6]. Solutions of cuprous chloride were prepared in concentrated KCl.

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Physico-Chemical Studies on the Composition of Chromium(III) hydrazine Complex

By S. M. Fazlur Rehman and Anees Uddin Malik

With 5 Figures

Summary

The composition of the bluish green insoluble hydrazine chromium(III)- chloride complex was determined by applying potentiometric and amperometric methods. The composition may be represented as $3\,CrCl_3 \cdot N_2H_4$. Data obtained by the analysis of the dried product give to some extent the similar information about the composition of the complex.

Inhaltsübersicht

Auf Grund potentiometrischer, amperometrischer und analytischer Untersuchungen wird die Zusammensetzung des schwerlöslichen blaugrünen Hydrazin-Chrom(III)-chlorid-Komplexes zu $3\,CrCl_3 \cdot N_2H_4$ ermittelt.

Although a large number of metal-hydrazine complexes[1–7] have been investigated, studies on the chromium complexes have been of a very limited nature.

The only reference worth mentioning is that of Traube and Passarge[8] who for the first time, analysed the Cr(II) hydrazine complex in order to establish its composition. More recently a systematic approach on the chromium complexes of hydrazine was made in these

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laboratories, Cr(II) hydrazine complex on the bases of purely analytical and physico-chemical studies⁹).

The present communication deals with our studies on the nature and composition of the complex (bluish green in colour) obtained by the interaction of chromic chloride and hydrazine.

Experimental

Reagents used were of the A. R. grade. Chromic chloride solution was standardised by converting it into dichromate and estimating it iodometrically. The strength of the hydrazine solution was estimated as follows¹⁰). A known volume of hydrazine hydrate was treated with excess of potassium ferricyanide followed by the addition of sodium hydroxide to make the solution alkaline. The unreacted ferricyanide was estimated iodometrically against sodium thiosulphate solution.

Amperometric titrations: Fisher Elecdropode with multiflex galvanometer (Type MGF 2) was used for amperometric studies. The electrodes used were the d. m. e. and the calomel. Purified nitrogen (obtained by passing through alkaline pyragallol and chromous chloride) was used to maintain an inert atmosphere in the polarographic cell. KCl and gelatin were used as the supporting electrolyte and maximum suppressor respectively. In order to determine the potential to be applied for the amperometric titrations: 1.0 cc of $CrCl_3$ ($1 \cdot 10^{-1}$ M), 5.0 cc of KCl (2 M, 2.0 cc of gelatin ($1 \cdot 10^{-1}$%) (total volume made upto 20 cc by air free distilled water) were taken in the polarographic cell and a current of purified nitrogen was passed for about ten minutes. The apparatus was then standardised and the current measured (2× and 1:10 sensitivity of the elecdropode and the galvanometer respectively) at increasing applied voltage. From the voltage — current curve (Fig. 1) the potential to be applied for was found to be —1.2 volt. The results of the amperometric titrations (both direct and reverse) are tabulated in Tables 1 and 2 and figures 2 and 3.

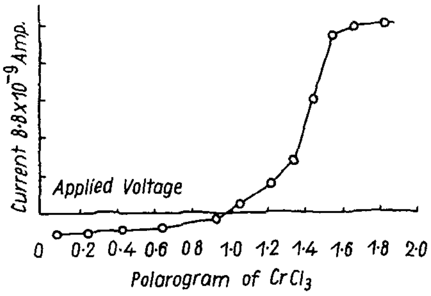

Fig. 1. Determination of the potential to be applied for the amperometric titrations

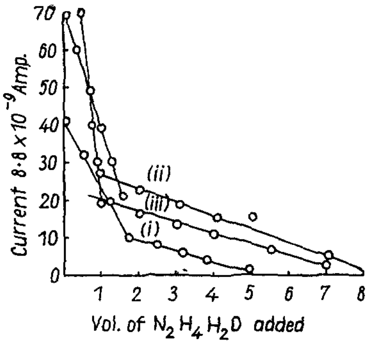

Fig. 2. Direct amperometric titration

Potentiometric Titrations: Assuming that the presence of minute amount of hydrazine in the chromic chloride solution is enough to create a $Cr^{+++} + e \rightleftharpoons Cr^{++}$ couple,

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Table 1
Direct Titrations

Vol. of $CrCl_3$ in the cell	Vol. of $N_2H_4 \cdot H_2O$ (from the curves)	Molar ratio $CrCl_3:N_2H_4$ (from the inflexion point)
20.0 cc ($5 \cdot 10^{-3}$ M)	1.7 cc ($2.0 \cdot 10^{-2}$ M)	2.9:1
20.0 cc ($1 \cdot 10^{-2}$ M)	1.0 cc ($6.66 \cdot 10^{-2}$ M)	3.0:1
20.0 cc ($1 \cdot 10^{-2}$ M)	1.4 cc ($5 \cdot 10^{-2}$ M)	2.8:1

Table 2
Reverse Titrations

Vol. of $N_2H_4 \cdot H_2O$ in the cell	Vol. of $CrCl_3$ from the curve	Molar ratio $CrCl_3:N_2H_4$ (from the inflexion point)
30.0 cc ($5 \cdot 10^{-3}$ M)	1.45 cc ($3.3 \cdot 10^{-1}$ M)	3.2:1
20.0 cc ($5 \cdot 10^{-3}$ M)	1.45 cc ($2.0 \cdot 10^{-1}$ M)	3.0:1
20.0 cc ($5 \cdot 10^{-3}$ M)	1.50 cc ($2.0 \cdot 10^{-1}$ M)	3.0:1

Table 3
Direct Titrations

Vol. of $CrCl_3$ in the cell	Vol. of $N_2H_4 \cdot H_2O$ (from the curve)	Molar ratio $CrCl_3:N_2H_4$
10.0 cc ($2 \cdot 10^{-1}$ M)	2.1 cc ($3.3 \cdot 10^{-1}$ M)	1:2.9
10.0 cc ($1 \cdot 10^{-1}$ M)	1.9 cc ($3.3 \cdot 10^{-1}$ M)	1:3.0
10.0 cc ($5 \cdot 10^{-1}$ M)	1.8 cc ($1 \cdot 10^{-1}$ M)	1:2.8

Table 4
Reverse Titrations

Vol. of $N_2H_4 \cdot H_2O$ in the cell	Vol. of $CrCl_3$ from the curve	Molar ratio $CrCl_3:N_2H_4$
10.0 cc ($1 \cdot 10^{-1}$ M)	11 cc ($2.5 \cdot 10^{-1}$ M)	3.15:1
10.0 cc ($2 \cdot 10^{-1}$ M)	8.5 cc ($6.66 \cdot 10^{-1}$ M)	2.99:1
10.0 cc ($5 \cdot 10^{-2}$ M)	9.0 cc ($1.66 \cdot 10^{-1}$ M)	2.88:1

a bright platinum electrode dipped in the chromic chloride solution could serve well as indicator electrode. This was found to be true and both direct (chromic chloride in the cell) and reserve titrations (hydrazine in the cell) could be performed, giving sharp inflexion points (Figs. 4 and 5).

Analysis of the complex: The sample of the complex was obtained by mixing chromic chloride and hydrazine in the molar ratio 3:1, and washing the product formed several times with small aliquots of distilled water and alcohol and finally drying with ether. The resulting substance was bluish green in colour and was kept over conc. H_2SO_4 in a vacuum dessicator. The details of the analysis of the complex were the same as described earlier[9]). Chromium was estimated gravimetrically as Cr_2O_3; hydrazine was determined by the indirect iodate method while the amount of chlorine in the complex was found after weighing as AgCl. The amount of water in the complex was estimated after drying a known weight of the sample at 110 °C.

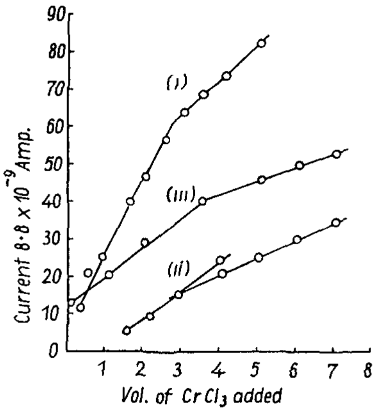

Fig. 3. Reverse amperometric titration

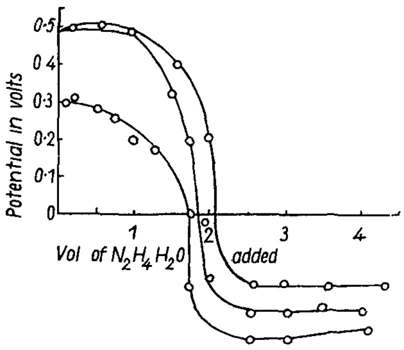

Fig. 4. Direct potentiometric titration

Found: Cr 34.26%; N_2H_4 5.76%; Cl 3.7%; H_2O less than 0.1%; Cr 34.26%; N_2H_4 5.76%; Cl 59.98% (bydifference) gives an emperical formula corresponding to $3\,CrCl_3 \cdot N_2H_4$; Cal: Cr 30.73%; N_2H_4 6.30%; Cl 62,97%.

Magnetic susceptibility measurements: The magnetic susceptibility measurements were carried out with the help of GOUY's magnetic balance having temperature control arrangement. The value of X was found to be 36.49 · 10^{-6} at 32 °C.

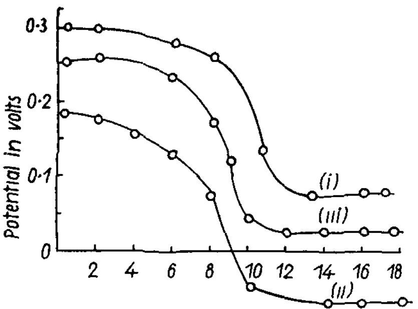

Fig. 5. Reverse potentiometric titration

Discussion

The most striking feature about the *chromic chloride hydrazine reaction* would be that the hydrazine should reduce chromic chloride to the Cr(II) state and this chromium should now react with hydrazine to give Cr(II)-hydrazine complex of the type studied by us earlier. Results on amperometric and potentiometric studies (as well as those of chemical analysis) do not support this view point. On the other hand a combining ratio of $CrCl_3$:N_2H_4 3:1 is obtained, pointing towards the formation of 3 $CrCl_3 \cdot N_2H_4$ complex.

A critical survey of the results of chemical analysis would reveal that the percentage of chlorine in the complex is much lower than the theoretical value (Cl 62.97%). This fact besides proving that the chloride ion is unusually strongly bound, goes to show there exists very little possibility of a chromous complex being obtained by the interaction of chromic chloride with hydrazine (all the chlorine in the Cr(II) hydrazine complex could be precipitated by silver nitrate). Again the difference in the colour of the two complexes combined with the data on magnetic susceptibility go to show that the likelihood of a chromous complex being formed is very remote (chromous complex being violet) in colour as against bluish green for the chromic; $\chi_M = 2.29 \cdot 10^{-6}$ for Cr(II) [9]) as against $36.49 \cdot 10^{-6}$ for Cr(III) complex.

The only observation which can not be explained with out introducing the reducing action of hydrazine for the particular reaction is the establishment of a $Cr^{+++} + e \rightleftharpoons Cr^{++}$ couple at the platinum electrode. It is quite likely that hydrazine is able to reduce a little of the chromic to chromous in the initial stages thereby developing a redox potential in the solution, after which the chromic chloride hydrazine reaction takes place more quickly and the complex is formed between Cr(III) and hydrazine. The marked discrepancy in the experimental values of the direct potentiometric titrations and slight variation from the theoretical values in the case of amperometric titrations go in favour of such a view point.

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Physico-Chemical Studies on Chromous Chloride and Hydrazine Complex

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With 2 Figures

Summary

The composition of the hydrazine chromous chloride complex was determined using potentiometric and amperometric methods. The complex is bluish violet in colour and its composition may be represented as $[Cr(N_2H_4)_3]Cl_2 \cdot 3\,H_2O$. Data obtained by the analysis of the dried product also give the same information about the composition of the complex. Further, the value of magnetic moment came out to be 3.4, which indicates the presence of two unpaired electrons.

Inhaltsübersicht

Analyse sowie potentiometrische und amperometrische Titration eines blauvioletten Hydrazin-Chrom(II)-chlorides ergaben die Zusammensetzung $[Cr(N_2H_4)_3]Cl_2 \cdot 3\,H_2O$. Das magnetische Moment von 3.4 Bohrschen Magnetonen entspricht zwei ungepaarten Elektronen.

Physico-chemical methods have been employed by a number of workers to study the nature and composition of metal hydrazine complexes. Schwarzenbach and Zobrist[1]) study the zinc-hydrazine complex using Bjerrum method while polarographic studies on this very compound were undertaken by Laitenen and Bailer[2]). Recently hydrazine complexes of Ce(iv) and Tl(iii)[3]) have been studied by potentiometric and other electrometric methods.

Amongst the large number of metal hydrazine complexes quoted in the literature, those of Cr(ii) have not been fully investigated. Traube and Passarge[4]) reported the existence of a dihydrazinate of chromous chloride, on the basis of his results on chemical analysis. A similar approach was made

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[1]) G. Schwarzenbach and A. Zobrist, Helv. chim. Acta **35**, 1291 (1952).

[2]) R. L. Robertus, H. A. Laitinen and J. C. Bailer jr., J. Amer. chem. Soc. **75**, 3051 (1953).

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[4]) W. Traube and W. Passarge, Ber. dtsch. chem. Ges. **46**, 1505 (1913).

by HEIN and BÄHR[5]) who reported the existence of $CrI_2 \cdot 3\, N_2H_4$ for the product obtained by the interaction of chromous iodide and hydrazine. These studies, however, remain incomplete unless supported by physical methods because chromous solution invariably contains Cr(iii) which also reacts with hydrazine. Under the circumstances, correct information about the composition of the complex cannot be arrived at by merely employing the method of chemical analysis. The difficulty can be overcome by using purely physical methods.

The present communication deals with our potentiometric and amperometric studies on the chromous chloride and hydrazine reaction. Results of chemical analysis are also included for the sake of comparison.

Experimental

Hydrazine hydrate (B. D. H.) was used during the experiments. An approximately (N) solution of hydrazine hydrate was prepared by adding 50 cc. of hydrazine in one litre of air free distilled water. Hydrazine was estimated by the ferricyanide method of DERNBACH and MEHLING[6]).

A neutral solution of chromous chloride was prepared by the method recommended by BATHIS and BAILER[7]) with slight modifications. The solution was prepared by the Zinc—HCl reduction of chromic-chloride. The chromous chloride thus obtained was treated with sodium acetate and resulting chromous acetate after a number of washings was dissolved in dilute HCl to give acidic chromous chloride. The solid chromous chloride was precipitated by passing HCl and N_2 for two hours in ice cold solution of the salt. The crystals thus obtained were dissolved in water to give a neutral solution of chromous chloride. The solution was standardized by oxidising it with excess of $KMnO_4$ and titrating the excess of the latter against ferrous ammonium sulphate potentiometrically. The total chromium in the sample was estimated by converting it into dichromate and titrating it iodometrically against thiosulphate.

For Amperometric titrations, a LANGE's polarometer with multiflex galvanometer type MGF 2 in the external circuit was used.

The potentiometric titrations were carried out with a TINSLEY-VERNIER potentiometer (Type 3387 B) connected to a sensitive mirror galvanometer with lamp and scale arrangement. The indicator electrode was bright platinum electrode and calomel electrode served as the reference electrode.

Amperometric Titrations

Standard solutions of chromous chloride and hydrazine hydrate were prepared as described earlier. A 0.1% solution of gelatin was used as maximum suppressor while 1.0 M KCl was used as the supporting electrolyte.

1 cc. of $CrCl_2$ solution (0.401 N) was added to the polarographic cell containing 10 cc. of 1 M KCl and 2.0 cc. of gelatin (0.1%) and 7.5 cc. of air free distilled water in the mixture, the purified nitrogen was passed for about 10 minutes. The apparatus was standardised

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[5]) F. HEIN and G. BÄHR, Z. anorg. allg. Chem. **252**, 55 (1942).

[6]) C. J. DERNBACH and J. P. MEHLING, Ind. Engng. Chem. analyt. Edit. **14**, 58 (1942).

[7]) J. H. BATTHIS and J. C. BAILER jr., Inorganic Synthesis, vol. I. Macgraw Hill (1939) page 123.

and the increasing voltage was applied. Noting the galvanometer deflection at each potential the mean of the maximum and minimum oscillations were taken as the correct reading. A graph was plotted between galvanometer deflections and the applied voltage. It extended in two parts, namely, cathodic and anodic where the reduction of Cr^{+++} to Cr^{++} and oxidation Cr^{++} to Cr^{+++} takes place. The potential to be applied in titration was found from the plateau of the polarogram.

Titrations were carried out between $CrCl_2$ and $N_2H_4 \cdot H_2O$. A known volume of $CrCl_2$ was taken in the cell (under inert atmosphere of nitrogen and covered with kerosine oil) containing the base electrolyte and maximum suppressor. The droptime (about 3 secs.) was adjusted and a constant potential of −0.2 volt was applied. Aliquots of hydrazine hydrate were added from the burette and the readings of the galvanometer were taken after thorough mixing of the reagents by the current of nitrogen.

The results are summarised in the following table, and the typical curves are shown in Fig. 1.

Table 1

No.	Solution	Vol. of $N_2H_4 \cdot H_2O$ from the curve	Strength of $CrCl_2$ in the mixture	Strength of $N_2H_4 \cdot H_2O$	Approximate Molar ratio $CrCl_2 : N_2H_4$
1.	1.0 cc. $CrCl_2$ (0.401 N) + 10 cc. KCl (1 M) + 2 cc. gelatin (0.01%)	5.9 cc.	0.02 N	0.178 N	1:2.6
1.	1.0 cc. $CrCl_2$ (0.401 N) + 0.5 cc. $CrCl_3$ (0.5 M) + 10 cc. KCl (1 M) + 2 cc. gelatin (0.01%) + 6.5 cc. H_2O	5.3 cc.	0.02 N	0.195 N	1:2.6
3.	1.0 cc. $CrCl_2$ (0.353 N) + 0.1 cc. $CrCl_3$ (0.5 M) 10 cc. KCl (1 M) + 2 cc. gelatin (0.01%) + 6.9 cc. H_2O	7.5 cc.	0.1765 N	0.150 N	1:3.1
4.	1.0 cc. $CrCl_2$ (0.353 N) + 10 cc. KCl (1 M) + 2 cc. gelatin (0.01%) + 7.0 cc. H_2O	8.0 cc.	0.1765 N	0.150 N	1:3.3

Potentiometric Titrations

The potentiometric titrations were carried out by using indicator electrode consisted of the bright platinum electrode dipped in chromous chloride solution thereby forming $Cr^{++} \rightleftharpoons Cr^{+++} + e$. couple, calomel electrode serving as the reference electrode. 2 cc. of $CrCl_2$ (0.6 N) was taken in a small wide mouthed bottle with a cork fitted with electrodes and arrangement for passing CO_2 and inserting the nozzle of the burette. Hydrazine hydrate of concentration 0.75 N was then added to the solution and readings were taken after each addition and stirring the mixture well.

The results are summarised in the following table, and the curves are shown in Fig. 2.

Table 2

No.	Vol. of 0.684 N $CrCl_2$	Vol. of 0.75 N $N_2H_4 \cdot H_2O$	Vol. of 1.2 M $CrCl_3$	Strenght of $CrCl_3$ in the $CrCl_2$ sample	Vol. of $N_2H_4 \cdot H_2O$ equivalent to total $CrCl_3$	Vol. of $N_2H_4 \cdot H_2O$ reacted with $CrCl_2$	Vol. of $N_2H_4 \cdot H_2O$ of the same strength as that of $CrCl_2$	Molar ratio $CrCl_2:N_2H_4$
1.	2.0 ccs.	9.0 ccs.	2.0 cc.	0.1 N	3.46	5.54	6.08	1:2.9
2.	2.0 ccs.	12.1 ccs.	4.0 cc.	0.1 N	6.76	5.34	5.86	1:2.8
3.	2.0 ccs.	15.5 ccs.	6.0 cc.	0.1 N	9.96	5.54	6.08	1:2.9

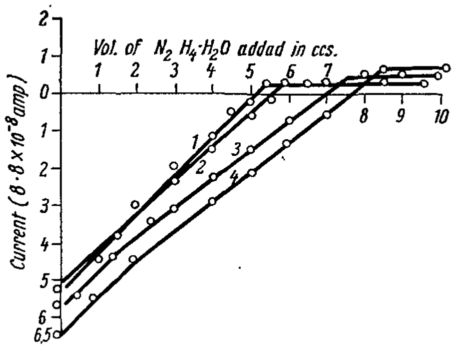

Fig. 1. Amperometric titrations

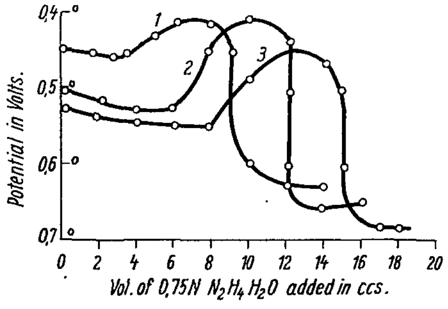

Fig. 2. Potentiometric titrations

Analysis of the sample

The dried sample of the complex was analysed for chromium, chloride, hydrazine and water. The following is the brief account of the procedure adopted for analysis.

About 0.5 g. of the complex was dissolved in dil HNO_3 and the volume of the solution was made upto 100 cc. To a known volume (40 cc.) of the solution, ammonia was added to precipitate chronium as hydroxide and estimated it gravimetrically as chromium oxide by igniting the dried hydroxide. The chloride was precipitated from the filterate by adding silver nitrate and weighing it as silver chloride.

For the estimation of hydrazine about 0.5 g of the dried sample was dissolved in dil HCl and the volume was made upto 100 cc. The amount of hydrazine in the sample was determined by employing indirect iodate method[8].

The amount of water in the complex was found out by keeping a known weight (about 0.5 g.) of the dried sample at 110 °C for over two hours.

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[8] E. J. CUY and W. C. BRAY, J. Amer. chem. Soc. 46, 1786 (1924).

The percentages were found: Cr 19.5%; Cl 23.1%; N_2H_4 34.1% and H_2O 22.8% (calc. for $CrCl_2 \cdot (N_2H_4)_3 \cdot 3\,H_2O$: 19.01%; 26.00%; 35.22%; 19.72%).

Magnetic Susceptibility Measurements

The Magnetic Susceptibility measurements were carried out with the help of GOUY's magnetic balance having temperature control arrangement. The results are given as follows.

Complex	Mass Susceptibility $\cdot 10^{-6}$	Temperature	$\varkappa_M$	$\mu_{eff.} = 2.83\ \varkappa_M \cdot T$
Cr(ii)-hydrazine	2.29	32.8 °C	$5.10 \cdot 10^{-2}$	3.4

Number of unpaired electrons	Expected Number of unpaired electron
2	2

Discussion

The amperometric titrations carried out between chromous chloride and hydrazine at -0.20 volt give the combining ratio of $CrCl_2$ to hydrazine as 1:3 thereby showing the existence of the complex $CrCl_2 \cdot 3\,NH_4$. The method is trustworthy since at this potential Cr^{+++}, which also reacts with hydrazine, would not give variations in the current values by the addition of titrants and whatever the changes would be due to the reaction between chromous chloride and hydrazine.

The results are further confirmed by potentiometric studies. This method was utilized by taking advantage of the use of Cr(ii) $\rightleftharpoons$ Cr(iii) + e couple at the bright platinum electrode.

The analysis of the dried sample also give more or less same information regarding the composition of the complex. The empirical formula calculated from the percentages of the elements: Cr 19.5%, Cl 23.1%; N_2H_4 34.1%; and H_2O 22.8% was worked out as $CrCl_2 \cdot 3\,N_2H_4 \cdot 3\,H_2O$.

Our investigations do not confirm the results of TRAUBE and PASSARGE[4]) who found the existence of the complex $CrCl_2 \cdot 2\,N_2H_4$. On the other hand the composition of the complex is similar to that of chromous iodide hydrazine complex reported by HEIN and BÄHR[5]). Another discrepancy observes is in the colour of the complex. While TRAUBE and PASSARGE reported the colour of the complex as red but we isolated it as a bluish violet product. It is quite likely that some free acetate ions might be present in their solution in whose presence a red coloured compound is formed.

According to BAILER[9]), most of the hydrazine complexes which have been isolated do not contain enough hydrazine molecules to fill the coordination sphere, however, such a state of affair is not likely to exist in our case since the coordinating sphere gets itself completely filled in with three bidentate hydrazine molecules. The complex should have an octahedral structure with two unpaired electrons; the structure of the complex may be depicted as $Cr(N_2H_4)_3Cl_2 \cdot 3\ H_2O$. The magnetic susceptibility measurements confirm the above view, as the value of μ_{eff} came out to be 3.4, which indicates the presence of two unpaired electrons.

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[9]) J. C. BAILER jr., "Chemistry of the Coordination Compounds", Reinhold Publishing Corporation, 1956, page 69.

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Studies on the complexes of chromium(II) chloride with some amino acids

Introduction

The complexes of transition metals with amino acids are of interest[1–3] because of the biological importance of this family of compounds, and the presence of potential coordinating amino and carboxylic groups Albert[4] has carried out a detailed study on the stability constants of various amino acid complexes, based upon pH and potentiometric measurements He showed that the reactivities of various amino acids towards a metal ion were dependent on the stability of the resulting complexes and ionization constants However, no attempt has been made so far to study the amino acid complexes with unstable oxidation states The present communication reports on the composition and stabilities of chromium(II) chloride complexes of some amino acids

Experimental

The amino acids, glycine, L-proline, DL-serine, β-alanine, DL-α-alanine, L-asparagine, L-leucine and DL-valine (B D H biologically pure products) were used and 0.01 *M* solutions were prepared in doubly-distilled, air-free water.

Chromous chloride was prepared by the method of Bathis and Bailer[5]. Chromic chloride was first reduced to chromous chloride with zinc–hydrochloric acid, and then precipitated as chromous acetate by adding ammonium acetate. The red precipitate of chromous acetate was dissolved in a minimum quantity of hydrochloric acid. The chromous chloride formed was precipitated with absolute alcohol, separated, and washed several times with small aliquots of ice-cold, air-free, doubly-distilled water. It was then dissolved in doubly-distilled water and the solution kept in an air-tight storage vessel in an atmosphere of nitrogen (pH of solution, 3.5). The solution was standardized potentiometrically by titrating with standard copper sulphate.

Carbonate-free KOH was used for preparing the aqueous solution of KOH which was stored in a Pyrex bottle fitted with a tube containing KOH for protection against atmospheric carbon dioxide. The solution was standardized by titrating with standard oxalic acid, and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out using a Tinsley potentiometer with lamp and scale arrangements using platinum and calomel as indicator and reference electrodes, respectively. The pH-metric titrations were made with a direct reading EIL pH-meter, model 23A (England), using glass and calomel electrodes. All titrations were carried out in a specially designed cell with provision for transferring the chromous chloride solution from the storage vessel and for passing oxygen-free nitrogen in order to stir the solutions. The concentration of the chromous chloride solution was checked before the study of each system.

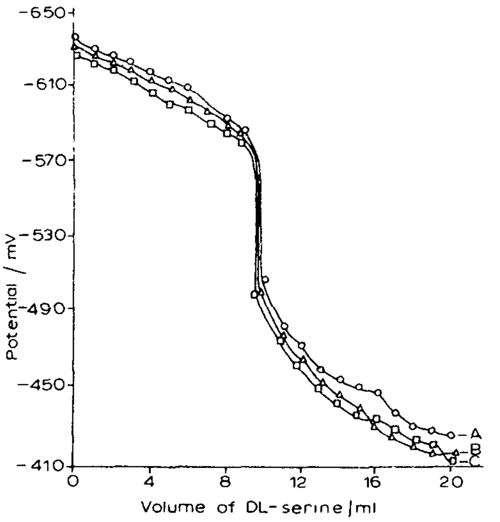
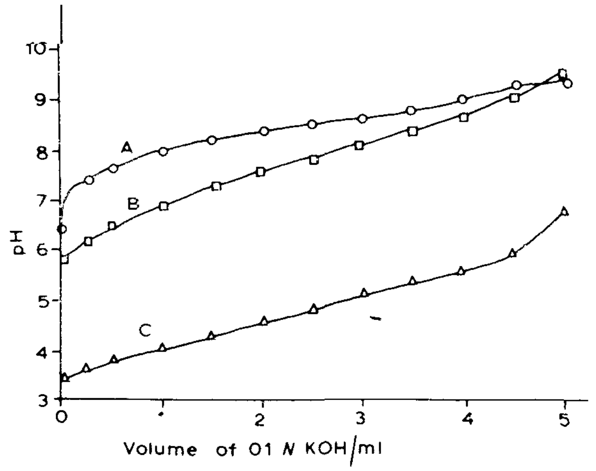


Fig. 1. Potentiometric titrations (A) 10 ml 0.666×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.666×10^{-1} *M* DL-serine (from burette), (B) 10 ml 0.50×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.50×10^{-1} *M* DL-serine (from burette), (C) 10 ml 0.44×10^{-1} *M* $CrCl_2$ (in cell) *vs.* 0.44×10^{-1} *M* DL-serine (from burette).

Result and discussion

The composition of the complexes with amino acids was determined potentiometrically by taking various concentrations of chromous chloride (in the cell) and equimolar solutions of amino acids (from the burette) In all cases a ratio of 1 1 (chromium(II) amino acid) was obtained from the potential concentration curves (Fig 1 for DL-serine) Information concerning complex formation was obtained from pH-metric titration curves For each amino acid three sets of pH-metric titrations were carried out in the order (*a*) amino acid (0 01 *M*), (*b*) chromous chloride (0 005 *M*), and (*c*) a mixture of chromous chloride and amino acid having a total concentration of 0 005 *M* and 0 01 *M* respectively using 0 1 *N* KOH as titrant The pH curves of all the amino acids show a definite shift indicating the formation of complexes of chromous chloride with amino acids (Fig 2 for DL-serine)

The complex formation constant, K_s was evaluated following the method of Albert[4] The values of log K_s at $n = 1$ (where n is the average number of molecules of amino acid bound by one atom of the metal) for various amino acids were calculated from the values of $-\log$ [Sc] obtained by the plot of $\bar{n}$ against $-\log$ [Sc] (Fig 3) ([Sc] is the concentration of free amino acid) By application of relation (xii) of ref 4



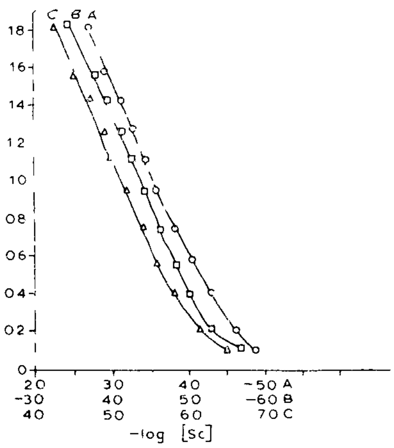


Fig 2 pH metric titrations (A) 50 ml 0 01 *M* DL serine (in cell) (B) 25 ml 0 02 *M* DL serine + 25 ml 0 01 *M* CrCl$_2$ (in cell) (C) 50 ml 0 005 *M* CrCl$_2$ (in cell)

Fig 3 Formation curves (A) DL serine chromium(II) complex (B) DL valine chromium(II) complex (C) DL proline chromium(II) complex

TABLE 1

	Graphically	*Calculated*
1 L Asparagine	6 92	6 97
2 DL α Alanine	6 72	6 76
3 β Alanine	9 86	9 89
4 Glycine	9 02	9 05
5 DL Leucine	8 40	8 40
6 L Proline	10 32	10 35
7 DL Serine	7 20	7 21
8 DL Valine	8 70	8 68

the values of log K_s for various amino acids were evaluated. The values obtained graphically and by calculation are given in Table 1.

The values of overall stability constants obtained from the formation curve (Fig. 3) are in good agreement with those calculated.

There does not seem to be any definite correlation between the nature of the amino acid and the K_s value; however, with a few exceptions the value of K decreases with increase in chain length of carbon atoms and also seems to decrease as the distance between amino and carboxylic groups increases. These observations could not be quantitatively substantiated as no information could be obtained as to the nature of the bounding because the complexes could not be isolated. The present studies are the first to report on the chemical reaction of unstable chromium(II) ions with amino acids, and the stabilities of the resulting complexes.

Acknowledgement

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Complexes of chromium(II) chloride with some sulphur-containing amino acids

The interaction of transition metal ions with amino acids covers a vast area of research because of its biological importance, and the coordinating ability of amino and carboxylic groups[1-3]. However, very few papers deal with the interaction of amino acids with transition metals having abnormal oxidation states. Recently a systematic study on this aspect of the problem was undertaken by the authors and the complexes of Cr^{2+}, UO_2^{2+}, VO^{2+} and Ti^{3+} with non-sulphur containing amino acids were studied[4,5]. The present communication deals with the composition of various sulphur-containing amino acid complexes, based upon pH-metric and potentiometric measurements.

Experimental

The amino acids, DL-methionine, taurine and cysteine (B.D.H. Biologically pure products) were used and 0.01 *M* solutions were prepared in doubly distilled air-free water. Chromous chloride was prepared by the method of Bathis and Bailer[6]. The aqueous solution of chromous chloride was prepared as described previously, and stored in an air-tight storage vessel under an atmosphere of oxygen-free nitrogen (pH 3.5). The solution was standardized potentiometrically by titration with standard copper sulphate. Carbonate-free KOH was used to prepare an aqueous solution of KOH and the solution was kept in a Pyrex bottle fitted with a guard tube containing KOH for protection against atmospheric carbon dioxide. The solution was standardized by titrating with standard oxalic acid and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out with a Tinsley potentiometer having a lamp and scale arrangement and employing platinum and calomel electrodes. The pH-metric titrations were performed with a direct reading EIL pH-meter model 23A (England). All the titrations were carried out in a specially designed cell described previously. The concentration of chromous chloride was checked before studying each system. All investigations were carried out at 25°C.

Results and discussion

Chromous chloride forms 1:1 complexes with DL-methionine, taurine and cysteine as determined from potentiometric curves (Fig. 1). The titrations were carried out using various concentrations of chromous chloride in the cell and equimolar solution of amino acids. The information regarding complex formation was obtained by noting the shifts in the pH-titration curves.

For each amino acid three sets of pH-metric titrations using 0.1 *N* KOH as a titrant were carried out in the order: (a) amino acid 0.01 *M*, (b) chromous chloride 0.005 *M* and (c) a mixture of chromous chloride and amino acid having a total concentration of 0.005 *M* and 0.01 *M*, respectively, (Fig. 2).

The values of the logarithm of the formation constant, log K_s at $\bar{n}=1$ (where $\bar{n}$ is the average number of molecules of amino acid bound by one atom of the metal) for the amino acids were calculated from the values of $-\log [Sc]$ obtained by the plot of $\bar{n}$ *vs.* $-\log [Sc]$, where $[Sc]$ is the concentration of free amino acid (Fig. 3). By applying the relation $\log K_s = -2 \log [Sc]$, values of the formation constants for all three amino acids were evaluated[7]. The values obtained graphically and by calculation

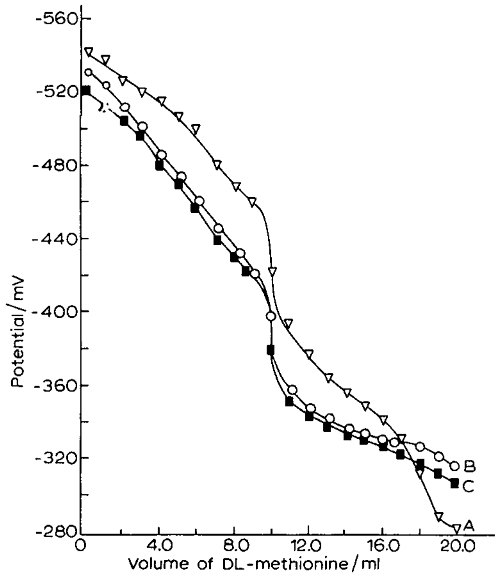
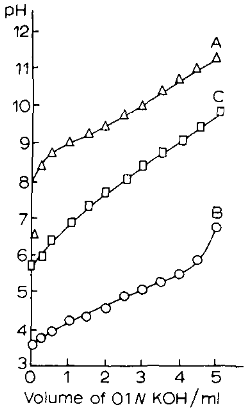


Fig. 1. Potentiometric titrations: (A) 10 ml 0.666×10^{-1} *M* $CrCl_2$ (in cell) *vs.* 0.666×10^{-1} *M* DL-methionine (from burette), (B) 10 ml 0.50×10^{-1} *M* $CrCl_2$ (in cell) *vs.* 0.50×10^{-1} *M* DL-methionine (from burette), (C) 10 ml 0.44×10^{-1} *M* $CrCl_2$ (in cell) *vs.* 0.44×10^{-1} *M* DL-methionine (from burette).



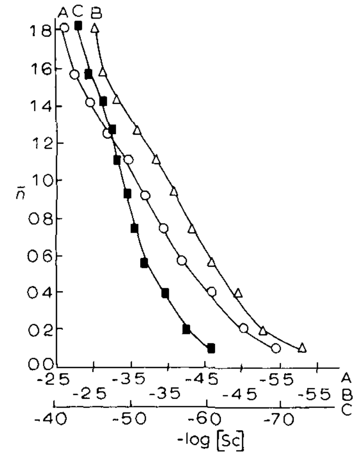


Fig 2 pH-metric titrations (A) 50 ml 0.01 M DL-methionine (in cell), (B) 50 ml 0.005 M $CrCl_2$ (in cell), (C) 25 ml 0.02 M DL-methionine + 25 ml of 0.01 M $CrCl_2$ (in cell)

Fig 3 Formation curves: (A) DL-methionine–chromium(II) complex, (B) taurine–chromium(II) complex, (C) cysteine–chromium(II) complex

are given in Table 1.

The values of overall stability constants obtained from the formation curves are in good agreement with those calculated. The values of log K_s given in Table 1

TABLE 1

		$log\ (K_s/mol^2\ l^{-2})$	
		Graphically	*Calcd*
1	Cysteine–chromium(II) chloride complex	9.80	9.77
2	DL-Methionine–chromium(II) chloride complex	7.32	7.30
3	Taurine–chromium(II) chloride complex	7.02	7.06

give an indication of the possible correlation between the nature of the amino acids and overall stability constants. The value of log K_s decreases as the distance between amino and carboxylic group increases (between NH_2 and $-SO_2OH$ in the case of taurine). The present studies do not clarify the part played by sulphur atoms.

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SHORT COMMUNICATIONS

Studies on the composition and stability of uranyl, vanadyl and titanous complexes with some aminoacids

A number of papers on the metal complexes of amino acids[1–4] have appeared in the literature in recent years. These studies are mainly concerned with the determination of the stability constant of a complex by various electrometric methods, *viz.* potentiometry, pH-metry, polarography, etc. References to studies on the complexes of Cu, Zn, Fe, Ni, Co, Mn, Cd and other transition metals are available but no attempt has yet been made to investigate possible complex formation between VO^{2+}, UO_2^{2+} and Ti^{3+} ions with amino acids.

The present communication deals with the behaviour of these ions towards some amino acids. Formation of 1 : 1 complexes has been indicated by conductometric titrations, and the stability constants of the complexes have been computed from the results of pH-metric titrations.

Experimental

Amino acids such as glycine, β-alanine, DL-α-alanine, L-asparagine, DL-serine, L-leucine, DL-valine and L-proline (B.D.H. biologically pure) were used for the experiments, and their solutions (0.01 *M*) were prepared in doubly-distilled water.

Uranyl sulphate (B.D.H. AnalaR), and vanadyl sulphate (B.D.H.) were employed and solutions of these salts were analysed gravimetrically as the metal oxides[5,6]. An aqueous solution of titanium(III) chloride was prepared by dissolving crystals[7] of $TiCl_3 \cdot 6\,H_2O$ in air-free doubly-distilled water, and the solution standardized[8]. Fresh solutions were always prepared before use and kept covered with a layer of kerosene oil or toluene throughout the investigations to avoid oxidation.

Carbonate-free KOH solution was used for pH-metric titrations. It was stored in a Pyrex bottle fitted with a KOH tube for protection against atmospheric CO_2. The solution was standardized by titrating with standard oxalic acid solution, and the strength was checked periodically before carrying out pH-metric titrations.

The conductometric titrations were performed using a Philips conductivity bridge model PR 9500/90 and a dip type conductivity cell (cell constant 1.48). The pH-metric titrations were carried out with a direct reading EIL pH-meter model 23A using glass and calomel electrodes. All the titrations were carried out in a specially designed cell, with provision for adding metal salt solutions from a burette, to a stirred oxygen-free system.

Results and discussion

The composition of the vanadyl, uranyl and titanous complexes with various amino acids was determined conductometrically. The conductometric titrations were reversible. In all cases a ratio of 1 : 1 (metal : amino acid) was established. Typical curves are given in Fig. 1. The pH-metric titrations were performed in triplicate for each amino acid. The titrations were carried out in the order: (a) amino acid (0.01 *M*),

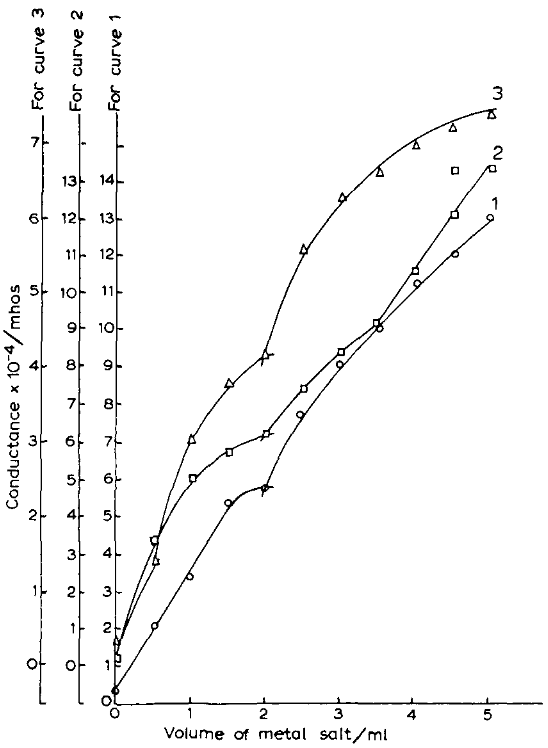

Fig 1 Reverse conductometric titrations (1) $M/15$ $TiCl_3$ added to 40 ml of $M/300$ DL-serine, (2) $M/12$ UO_2SO_4 added to 40 ml of $M/240$ DL-α-alanine, (3) $M/15$ $VOSO_4$ added to 40 ml of $M/300$ DL-valine

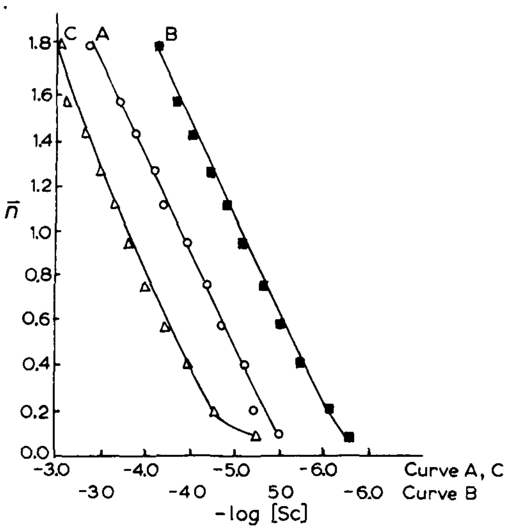

Fig 2 Formation curves (A) DL-valine–$VOSO_4$ complex, (B) DL-α-alanine–UO_2SO_4 complex, (C) DL-serine–$TiCl_3$ complex

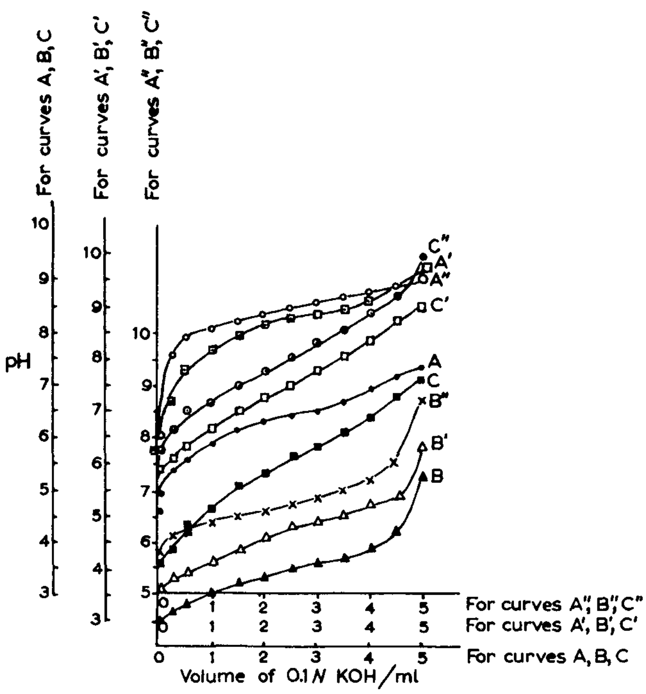

Fig 3 pH-metric titrations (A, B, C) DL-serine–TiCl$_3$, (A′, B′, C′) DL-α-alanine–UO$_2$SO$_4$, (A″, B″, C″) DL-valine VOSO$_4$.

TABLE 1

VALUES OF LOG (K_s/mol^2 l^{-2}) FOR VANADYL, URANYL AND TITANOUS AMINO ACIDS COMPLEXES OBTAINED BY TWO METHODS

Amino acids	*Vanadyl sulphate*		*Uranyl sulphate*		*Titanous chloride*	
	Theoretical	*Graphical*	*Theoretical*	*Graphical*	*Theoretical*	*Graphical*
L-Asparagine	6.95	6.90	6.88	6.85	7.25	7.20
β-Alanine	9.77	9.80	9.92	9.90	9.72	9.70
DL-α-Alanine	8.75	8.70	9.00	9.00	8.53	8.50
Glycine	× ×	× ×	8.62	8.65	8.52	8.50
L-Leucine	9.08	9.10	8.61	8.60	8.55	8.50
L-Proline	10.33	10.30	10.46	10.45	10.08	10.05
DL-Serine	7.54	7.50	6.86	6.90	7.60	7.60
DL-Valine	8.65	8.65	8.59	8.60	8.12	8.20

(b) metal salt (0.005 *M*) and (c) metal salt and amino acid (total concentration 0.005 *M* and 0.01 *M*, respectively), employing 0.1 *N* KOH as titrant. The pH-titration curves show appreciable shifts, indicating the formation of complexes with the amino acid (Fig. 3). The complex formation constant K_s was evaluated by the method modified by Albert[4].

The values of log K_s at $\bar{n}=1$, where $\bar{n}$ is the average number of molecules of amino acid bound by one atom of the metal ion, were calculated from the values of $-\log[\mathrm{Sc}]$ obtained by plotting $\bar{n}$ *vs.* $-\log[\mathrm{Sc}]$ (Fig. 2). [Sc] is the concentration of the free amino acid. The values of log K_s for various amino acids evaluated from the formation curves, and those calculated are given in Table 1.

The values of the overall stability constants log K_s obtained from the formation curves (Fig. 2), are in good agreement with those calculated.

Uranyl sulphate, vanadyl sulphate and titanous chloride form 1 : 1 complexes with various amino acids (L-asparagine, β-alanine, DL-α-alanine, glycine, L-leucine, L-proline, L-serine and DL-valine). In the vanadyl and titanous complexes the values of log K_s vary from L-asparagine (6.95, 7.25) to L-proline (10.33, 10.08), whereas in uranyl complexes the variation is from DL-serine (6.86) to L-proline (10.46). There does not seem to be any correlation between the nature of the aminoacids and the K_s values although, with a few exceptions, the latter decreases with increase in chain length of carbon atoms. The real nature of bonding in these complexes is a matter of speculation as no complex could be isolated in a sufficiently pure form.

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Spectrophotometric Studies on the Composition of V (iv)-Ethanolamines Complexes

The existing literature deals with a number of metal-ethanolamine complexes[1]), [2]), [3]) but little appears to have been done to investigate the compounds formed by the interaction of vanadyl ions with ethanolamines It was, therefore, thought worth considering to study the interaction of *V* (iv) with mono-, di and triethanolamines spectrophotometrically

Monoethanolamine and triethanolamine (Extra pure Naarden) diethanolamine (E Merck) were used for preparing the solutions and the solutions were standardized by titrating against 1 0 N HCl Vanadyl chloride (E Merck) was used to prepare the solution of the reagent and its strength was determined by titrating against $KMnO_4$ after reducing the solution in Jones' reductor Absorption measurements were done with a Beckman DU Spectrophotometer with tungsten lamp as the light source

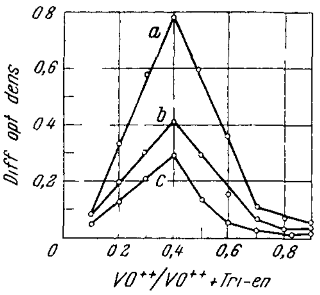

Fig 1 Concentration of vanadyl chloride and triethanolamine, *a* 2 10^{-2} M, *b* 1 33 10^{-2} M and *c* 1 10^{-2} M Ordinate Difference in optical density

Preliminary experiments provided the following information (i) the reaction was possible only in the concentration range (2×10^{-2} M to 5×10^{-3} M), at lower concentration range no reaction took place whereas at higher concentrations a turbidity was found to set in (ii) The colour of the solution (greenish yellow in colour in all cases) faded on long standing in air However, on covering the solution with a thin layer of paraffin, the solution could be kept stable for a number of days (iii) The products crystallized in well defined black crystals, which were extremely hygroscopic in nature (iv) The monoethanolamine complex was stable in the p_H range 6 4 *to 11 0 where as the di- and triethanolamine* complexes were found to be stable in the p_H range 5 0 to 11 0

Spectrophotometric investigations[4]) showed the existence of absorption maxima λ_{max} at 650 mμ, 800 mμ and 800 mμ for the mono-, di- and triethanolamines respectively Job's method of continuous variation[5]) as well as the slope ratio[6]) method gave the combining ratio of 2:3 for VO^{++} and ethanolamines respectively (typical curves given in Fig. 1).

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Amperometric Studies on the Composition of V(IV)-Ethanolamine Complexes

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Ethanolamine is known to form complexes with a number of heavy metal ions. In most cases these have been characterised by the method of chemical analysis[1-3] and little has been done to elucidate their nature and composition by physico-chemical methods. Only Michell[4] applied spectrophotometric and polarographic methods for elucidating the structures of copper complexes of triethanolamine. It was therefore thought worthwhile to extend the studies to compounds other than those formed with copper.

Earlier results[5] indicate existence of soluble complexes (greenish yellow in colour, of vanadyl chloride with mono-, di-, and tri-ethanolamines with absorption ~~peaks at 650 mμ and 800 mμ) with a combining ratio of 2:3 (Vo^{4+}: En)~~ as found by the defferent spectro-photometric-methods[6-8]. The complex was, however, found to be non-reducible at the dropping mercury electrode (d.m.e.) and therefore the polarographic method could not be employed. We were, however, able to apply the amperometric titration in this case. The results of these studies are described below.

Procedure.—Mono-(E. P., Naarden product), di-(E. Merck), and tri-ethanolamine (Naarden) were used during the experiments. Molar solutions of ethanolamines were prepared in double distilled water and were standardised *p*H-metrically against 1.0*M*-HCl. The strength of vanadyl chloride was determined[9] after reducing it on a Jones reductor and titrating it against $KMnO_4$. The titrations (*p*H-metric) were carried out with a Beckman *p*H-meter, model G, with E type glass electrodes. The amperometric titrations were made with a Fischer elecdropode in conjunction with a multiflex galvanometer (type MGF2) in the external circuit. Before carrying out the titrations, the constant potential to be applied during titration was first determined. From the plateau of the polarogram (current-voltage curve) it was found to be –1.0 volt. Electrodes used were the dropping mercury and the standard calomel. Purified nitrogen was passed to maintain an inert atmosphere. The polarographic cell was kept immersed in a Townson-Mercer water bath, maintained at 30°±0.1°. Both direct (vanadyl chloride in the cell) and reverse

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(ethanolamines in the cell) were tried. Only the direct titration curves provided sharp inflections.

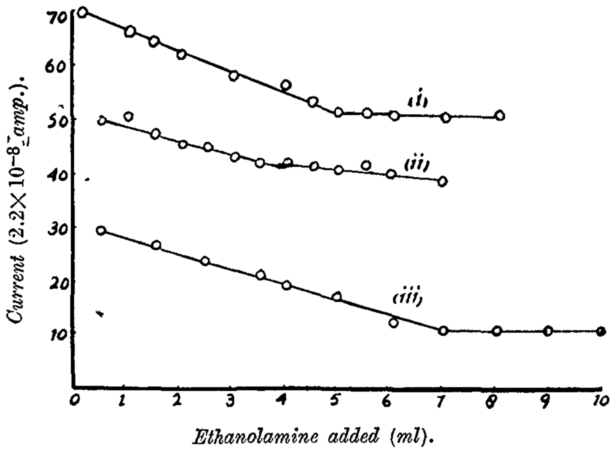

FIG. 1

(*i*) $0.05M$-$VOCl_2$ (10 ml)/$0.2M$-mono-En.
(*ii*) ,, ,, (5 ml)/ ,, -di-En.
(*iii*) ,, ,, (,, / $0.083M$-tri-En.

The sharp inflections in the amperometric titration curves show the existence of 1:2, 1:3, and 1:2 complexes for mono-, di-, and tri-ethanolamine (Fig. 1) respectively. The results here do not confirm those obtained by spectrophotometry. The discrepancy may be attributed to two factors: (*i*) the instability of complexes under ordinary atmospheric conditions; (*ii*) the existence of colloidal precipitates. Since these factors would not interfere in the amperometric titrations (especially when the reactions are carried out in an inert atmosphere), this method is likely to provide more satisfactory results than those obtained by the spectrophotometric methods.

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8-Hydroxy-7-iodoquinoline-5-sulphonic Acid (Ferron) as the Spectrophotometric Reagent for Vanadium (IV)

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8-Hydroxy-7-iodoquinoline-5-sulphonic acid (Ferron) forms with vanadyl ions a yellowish green soluble complex with an absorption maximum at 380 mμ. Based on this, a spectrophotometric method for the determination of vanadium in concentrations of the order of $1\ 0 \times 10^{-4}M$ has been developed. The results obtained by this method are comparable to those obtained by the volumetric method.

FERRON (8-hydroxy-7-iodoquinoline-5-sulphonic acid) has been employed for the detection of iron[1-3], bismuth[4], thallium[5], cobalt[6] and for the separation of plutonium from uranium[7]. The interaction of this reagent with vanadium (IV) has, however, not been studied. In the present communication, an attempt has been made to investigate the utility of the reagent for the colorimetric estimation of vanadyl ions.

Experimental Procedure

Beckman spectrophotometer (model DU) with tungsten lamp as the light source and 1 cm. corex cells was used. The *p*H meter used was Beckman model G with general purpose glass electrode. The solutions of Ferron (AnalaR) were prepared in double-distilled water-acetone (AnalaR) mixture. The solution of vanadyl sulphate (Riedel) was prepared in double-distilled water and was standardized[8] by reducing it in Jones reductor and titrating it against potassium permanganate. Universal buffer[9] was prepared by adding different amounts of sodium hydroxide ($0{\cdot}1M$) to the mixture containing phenylacetic acid, boric acid and phosphoric acid of $0{\cdot}04M$ concentrations. Analytical grade salts were used to prepare (0·1 per cent) of various ions.

Results

Determination of optimum conditions — Preliminary experiments showed that vanadyl sulphate forms a yellowish green complex with Ferron. The colour develops rapidly and is stable for several days. The complex is stable over a wide *p*H range (2·4-11·0). Vosburgh and Cooper's method[10] gave evidence for the existence of a simple complex having an absorption peak at 380 mμ (Fig. 1). Ferron and vanadyl sulphate gave absorption maxima at 430 and 750 mμ respectively. The maximum intensity of the complex was recorded at *p*H 7-7·5 (Fig 2)

Beer's law and sensitivity — The concentration range over which Beer's law is obeyed by the complex is $1{\cdot}0\times10^{-4}$ to $1{\cdot}0\times10^{-3}M$. From the molar ratio curve, it can be seen that the absorbance continues to increase and the curve is linear up to $1{\cdot}2\times10^{-3}M$ VO^{2+} (Fig. 3).

Structure of the complex — Job's method of continuous variation[12] (Fig. 4) and Harvey-Manning slope ratio method (Fig. 5) indicate an unusual 2 3 vanadyl-Ferron complex.

Effect of diverse ions — Absorption experiments were carried out with $1{\cdot}0\times10^{-4}M$ complex in the presence of about thirty metal ions, e.g Fe^{3+}, Fe^{2+}, Ti (IV), Co, Ni, Cu, Zn, Hg^{2+}, Hg^{+}, Pb, Bi, Sb, Sn^{2+}, Ag, Au, Tl^{3+}, La, Ce (IV), Cd, Cr^{3+}, Be, Pd (IV), Mo (VI), W (VI), etc , having concentration of 0·01 per cent and buffered at *p*H 7·5. Only Fe (II), Hg (II) and Ag interfere to some extent whereas in other cases an error of less than 0·3 per cent was observed

Estimation of the strength of an unknown solution of vanadyl sulphate — About 1·60 per cent solution of vanadyl sulphate was prepared in double-distilled water. The solution was standardized as described earlier. An aliquot (0·1 ml) of the solution was pipetted out with the help of a micropipette and 0·2 ml. of $1{\cdot}0\times10^{-3}M$ Ferron was added to it. The mixture was buffered at *p*H 7·5, making the total volume up to 10·0 ml. The absorption of the solution was noted and from the calibration curve (Fig. 1) the concentration of the complex was

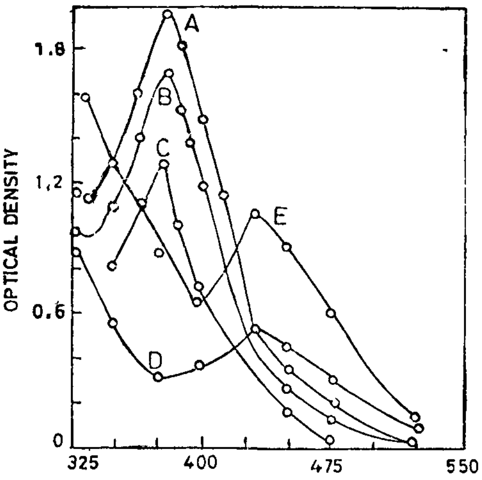

Fig 1 — Absorption curves of vanadyl sulphate and Ferron at different VOSO$_4$ Ferron concentration ratios [A, 4 6, B, 5 5, C, 6 4, D, conc of Ferron, $1{\cdot}0\times10^{-3}\ M$, and E, conc of Ferron, $1{\cdot}5\times10^{-3}M$]

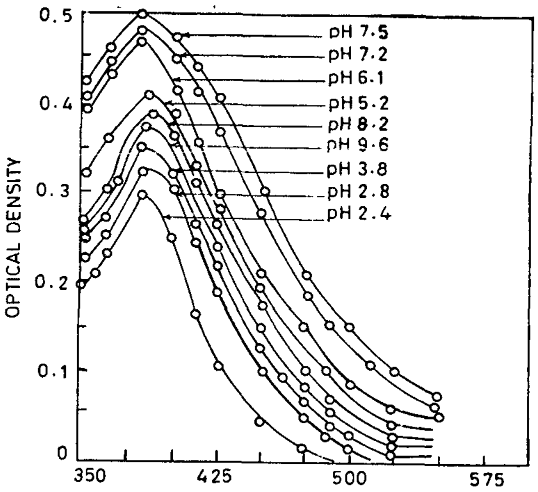

Fig. 2 — Absorption curves of vanadyl sulphate ($8 \times 10^{-5}M$) and Ferron ($1{\cdot}6 \times 10^{-4}M$) at different *p*H

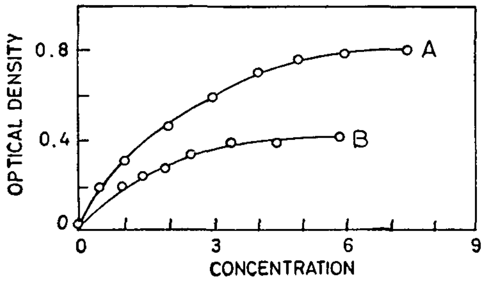

Fig. 3 — Determination of the composition of the complex by molar ratio method [A, 1 ml. of $2 \times 10^{-3}M$ VO^{2+} titrated against $2 \times 10^{-4}M$ Ferron; and B, 1 ml. of $2 \times 10^{-3}M$ Ferron titrated against $2{\cdot}0 \times 10^{-4}M$ VO^{2+}]

calculated. The concentration of the salt was found to be of the same order as that calculated from the volumetric method.

Analysis of vanadite ore — About 0·4 g. of the sample was dissolved in the smallest quantity of nitric acid (AnalaR), the solution boiled to dryness, cooled and then diluted with water and filtered. To the filtrate was added a small amount of hydroxylamine hydrochloride. The volume was then made up to 1 litre. An aliquot (1 ml.) of the solution was mixed with 0·2 ml. of $1 \times 10^{-3}M$ Ferron and buffered at *p*H 7·5, making the total volume up to 10 ml. The concentration of vanadyl ions was then determined from the calibration curve.

The amount of vanadium present was found to be 3·4 per cent whereas the amount calculated (by precipitating it as silver vanadate) was 3·2 per cent.

Discussion

The 8-hydroxyquinoline complexes, which are not water soluble can be made water soluble, without disturbing the nature and stability of the coordination bonds, if a highly dissociated sulphonic acid group which makes the resulting complex negatively charged is attached to it. The formation of a soluble complex in the present studies is, therefore, quite understandable.

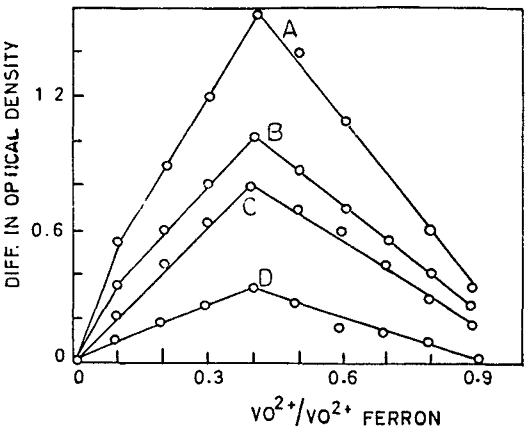

Fig. 4 — Absorption curves of vanadyl sulphate-Ferron mixture [Conc. of mixture in A, $1{\cdot}0 \times 10^{-3}M$; B, $8{\cdot}8 \times 10^{-4}M$; C, $4{\cdot}4 \times 10^{-4}M$; and D, $2{\cdot}0 \times 10^{-4}M$]

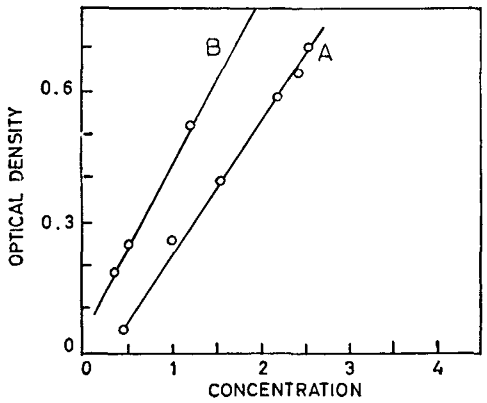

Fig. 5 — Absorption curves of vanadyl sulphate and Ferron [A, 5 ml. $VOSO_4$ of conc. $5{\cdot}0 \times 10^{-4}M$ (fixed) + Ferron $5{\cdot}0 \times 10^{-4}M$; and B, 0·5 ml. of Ferron of conc. $5{\cdot}0 \times 10^{-4}M$ (fixed) + $5{\cdot}0 \times 10^{-4}M$ $VOSO_4$]

The spectrophotometric methods employed to determine the composition of the complex give evidence for the ratio 2:3 for vanadyl ions and Ferron.

From the existing literature[13] on the analytical chemistry of vanadium it can be traced that no suitable reagent is available for the spectrophotometric determination of vanadium. Hence it was thought worthwhile to use Ferron for the spectrophotometric determination of vanadium. The stability of the complex over a wide *p*H range combined with its sensitivity for amount as low as $1{\cdot}0 \times 10^{-4}M$ justify its use as a colorimetric reagent for vanadium. The estimations are best possible in the *p*H range 7-7·5. Spectrophotometric measurements carried out with $1{\cdot}0 \times 10^{-4}M$ complex in the presence of about 30 metal ions (0·01 per cent) buffered at *p*H 7·5 showed that only Fe (II), Hg (II), Ag interfere appreciably whereas in other cases an error of less than 0·3 per cent was observed. The estimation of vanadium in alloys and ores is possible by this reagent. The method besides being rapid is quite reliable and Pb^{2+} ions (in case of vanadite ore) present do not interfere. In all these estimations the higher state of vanadium could be reduced to V (IV) by reducing agents such as hydroxylamine hydrochloride or ascorbic acid.

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Ferron as an Indicator in the Complexometric Titration of Vanadium (IV)

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A complexometric method has been developed for the estimation of vanadium (IV) employing ferron as an indicator in EDTA titration The titrations are performed in the pH range 4 5-5 5 for estimating vanadium in: (i) vanadyl sulphate, (ii) in the presence of Pb, Al, Zn, Cd, Cu, Ni and Co using KCN as the masking agent, and (iii) in vanadite ore The method is rapid and reliable compared to the existing volumetric and gravimetric methods.

DURING the course of investigations[1] on the complexes of V (IV) with 7 iodo-8 hydroxyquinoline 5-sulphonic acid (ferron), it was found out that this reagent could be used as an indicator in the titration of vanadium by EDTA So far no suitable indicator for the complexometric titration of vanadium has been reported[2] A simple method has been developed in which V (IV) can be titrated against EDTA at pH 4 5 5 5 using ferron as an indicator The results of this study are reported in this communication

EDTA (E Merck) solution (0 1M) was prepared in doubly distilled water after drying the reagent at 80° A solution of ferron (2 per cent) was prepared in water-acetone mixture (1 1) Vanadyl sulphate (Riedel) was standardized by reducing the salt in Jones reductor and titrating against permanganate Other reagents used were A R samples

Estimations were carried out in three samples containing (a) vanadium alone (b) vanadium in the presence of diverse ions, e g , Co, Ni, Cu, Cr, Zn, Al, Mg, Pb and Mn and (c) vanadium from vanadite ore For (a) 10 ml of approximately $4\ 0\times10^{-2}M$ VO^{2+} solution was diluted to 20 ml with water and buffered with ammonia-acetic acid solution (pH$\sim$5) followed by the addition of 2 ml of 0 2 per cent ferron solution The solution was titrated against 0 1M EDTA Change in colour from greenish yellow to deep green indicated the null point In the case of (b) the same procedure was employed with the only difference that hydroxylamine hydrochloride (1 0 g for 20 ml of $4{\cdot}0\times10^{-2}M$ VO^{2+}) was added to reduce the solution into V (IV) and KCN (1 0 g) for masking the interfering metal ions The resulting solution was titrated as before after warming

The ore (1 0 g) was dissolved in minimum quantity of conc nitric acid and diluted to 100 ml, filtered and hydroxylamine hydrochloride (1 g) added to 10 ml of the solution The resulting solution was titrated using 4 ml of the indicator

The probable mechanism of the titration may be as follows

VO^{2+} + ferron = VO^{2+} (ferron) yellowish green

VO^{2+} (ferron) + EDTA = VO^{2+} (EDTA) deep green + ferron

The suitability of the titrations for determining vanadyl sulphate may be adjudged by comparing the data from volumetric (Jones reduction) method

Sample	Present method	Volumetric method
1	$3\ 80\times10\ {}^{2}M$	$3\ 80\times10\ {}^{2}M$
2	$1\ 47\times10\ {}^{2}M$	$1\ 50\times10\ {}^{2}M$
3	$3\ 03\times10\ {}^{3}M$	$2\ 96\times10\ {}^{3}M$

The above results indicate that the percentage error increases with dilution

Titrations in the presence of other metal ions could be satisfactorily performed after masking them with KCN Solutions of conc range $5\times10^{-1}M$ to $1\ 0\times10^{-2}M$ containing 1 mg of the foreign ion could be estimated by this method

The efficacy of the method for the estimation of vanadium in vanadite is self evident from the following results

Sample	Vanadium in the ore %	
	Present method	Gravimetric method
1	3 1	3 2
2	3 2	3 4

The method proposed above is rapid and reliable compared to volumetric or gravimetric methods It has an added advantage that foreign ions do not affect the titration value

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STUDIES ON VANADYL SULPHATE COMPLEXES WITH HETEROCYCLIC AMINES

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involving the elimination of SiH_4 from solvated polysilicon units It would have to be assumed that these reactions were fast enough to allow fairly rapid formation of $KSiH_3$ according to Morrison and Ring's second stage (equation (2)) It seems equally possible, however, that the most important base-catalyst for the elimination of SiH_4 is SiH_3^- initially produced as suggested by Morrison and Ring Neither of these suggestions accounts for the observed combining ratio and the end-point of 4 1 for Si KH The experiments with GeH_4 and with SnH_4, taken with the conductivity data in the table, suggest to us that the anionic species present in solution is probably more complicated than indicated by the formula MH_3^- (M=Si Ge, or Sn)

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Studies on vanadyl sulphate complexes with heterocyclic amines

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DURING the last two decades, extensive work has been carried out on Oxovanadium (iv) complexes [1, 2] Complex formation with Nitrogen containing ligands is of more recent discovery but a large number of papers have appeared on V(iv)-heterocyclic amine complexes [3–6] These studies are mainly concerned with the spectral and magnetic interpretation of ligand field splitting [7, 8]

The present communication deals with the composition and structure of complexes formed by the interaction of $VOSO_4$ with heterocyclic amines

EXPERIMENTAL

Vanadyl sulphate (B D H) was used Solutions of the salt were prepared in doubly distilled water or methanol VO^{2+} was estimated by precipitating vanadium as mercurous vanadate and weighing as V_2O_5 [9]

Pyridine (py), 2-picoline (2 pic), 3-picoline (3 pic), 4-picoline (4 pic), 2,4-Lutidine (2, 4 L), 2,6-Lutidine (2, 6 L), Quinoline (Q), and Isoquinoline (I Q) were all E Merck products and were distilled before being used Acridine (Ac) (B D H product) was purified by crystallising it from acetone

The potentiometric measurements were made with the help of a Tinseley potentiometer type 3387B in conjunction with a lamp and scale outfit using platinum and calomel as indicator and reference electrodes respectively

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The conductometric titrations were performed employing a Philips Conductivity Bridge Model PR 9500 with a dip type conductivity cell (cell constant 1 482)

Infrared spectra were recorded with a Perking-Elmer infra cord model 137B for the range 3–15 μ using KBr pellets whereas the spectra in the range 15–27 μ were recorded on Beckman IR 5A fitted with a CsBr prism using nujol mull as a mulling agent

Preparation of the complexes

About 0 5 g of $VOSO_4$ was dissolved in 5 ml of methanol (A R) with slight warming and subsequent addition of about 20 ml of tetrahydrofuran (T H F) The solution was treated with an excess of the amine in T H F when a precipitate formed The precipitate was centrifuged, washed several times with T H F and finally dried in vacuum desiccator over CaO

Analysis of the complexes

1 VO(py)SO_4 Calcd for VO(C_5H_5N)SO_4 V, 21 1, N, 5 8, SO_4, 39 7, C, 24 8 Found V, 21 0, N, 5 7, SO_4, 40 0, C, 24 7

2 VO(2 pic)SO_4 Calcd for VO(C_6H_7N)SO_4 V, 19 9, N, 5 5, SO_4, 37 5, C, 28 1 Found V, 19 9, N, 5 4, SO_4, 37 9, C, 29 0

3 VO(3 pic) SO_4 Calcd for VO (C_6H_7N)SO_4 V, 19 9, N, 5 5, SO_4, 37 5, C, 28 1 Found V, 20 0, N, 5 8, SO_4, 38 0, C, 29 3

4 VO(4 pic) SO_4 Calcd for VO(C_6H_7N)SO_4 V, 19 9, N, 5 5, SO_4, 37 5, C, 28 1 Found V, 19 5, N, 5 6, SO_4, 37 9, C, 28 8

5 VO(2,4 L)SO_4 Calcd for VO(C_7H_9N)SO_4 V, 18 9, N, 5 2, SO_4, 35 6, C, 31 2 Found V, 18 9, N, 5 1, SO_4 35 8, C, 30 9

6 VO(2,6 L)SO_4 Calcd for VO(C_7H_9N)SO_4 V, 18 9, N, 5 2, SO_4, 35 6, C, 31 2 Found V, 18 8, N, 5 1, SO_4, 35 9, C, 31 2

7 VO(Q)SO_4 Calcd for VO(C_9H_7N)SO_4 V, 17 5, N, 4 8, SO_4, 32 8, C, 37 0 Found V, 17 3, N, 4 6, SO_4, 32 8, C, 37 2

8 VO(I Q)SO_4 Calcd for VO(C_9H_7N)SO_4 V, 17 5, N, 4 8, SO_4, 32 8, C, 37 0 Found V, 17 3, N, 4 7, SO_4, 32 9, C, 36 0

9 VO(AC)SO_4 Calcd for VO($C_{13}H_9N$)SO_4 V, 14 9, N, 4 0, SO_4, 28 1, C, 45 6 Found V, 14 9, N, 3 9, SO_4, 28 6, C, 46 0

DISCUSSION

Vanadyl sulphate form 1 1 complexes with all these amines All the complexes are bluish-green except that of Acridine complex which is yellow Except those of quinoline and isoquinoline all the complexes are water soluble and hydrolysed on standing

Both direct and reverse conductometric titrations were performed between vanadyl sulphate and the amines Ratios of 1 1 and 1 2 for VO^{2+} to amines were obtained in all cases, except acridine, where a ratio of 1 2 was obtained in each titration

The potentiometric titrations were carried out by utilising $VO^{2+} \rightleftharpoons VO^{3+} + e$ couple, the pH of the vanadyl sulphate soln was maintained at 2 7 On the basis of the potentiometric studies formation of 1 1 complexes for lutidines and 1 2 complexes for pyridine, picolines and the other amines was infered

The difference in the composition of complexes by conductometric and potentiometric methods and from chemical analyses of the solids must be due to the lower solubility of the 1 1 complex in the medium used The extra energy required for coordination of VO^{2+} to one more tertiary nitrogen (strong σ donor) of amine is probably compensated by solvation energy

The important data regarding the metal-amine coordination are obtained by considering the regions where ring CC, CN stretching vibrations (1450–1650 cm^{-1}) and CH out of plane deformation vibrations (700–800 cm^{-1}) take place[10–11] In the region 1450–1650 cm^{-1} it is found that two distinct changes occur on coordination, namely, a reduction in the number of bands, with no appreciable changes in frequencies, and an increase in intensities of the bands In the region 700–800 cm^{-1} the bands are shifted to higher frequencies and there is an increase in intensities

The changes in the ring (CC, CN) stretching vibrations and CH out of plane deformation vibrations

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on coordination may be explained on considering the electron densities around the heterocyclic nitrogen of the amines The electron density on the heterocyclic nitrogen increases with 2 and 4 monosubstitution and 2,4 and 2,6 disubstitution, on coordination there is a change in distribution around the metal and the heterocyclic nitrogen (strong σ donor and weak π acceptor) resulting in the increase in intensities and reduction in the number of bands From the i r studies it may be infered that the greater the electron density on the heterocyclic nitrogen, on coordination, the greater is the increase in the intensities and reduction in the number of bands and stronger is the metal-nitrogen band

The strong band observed at 965 cm^{-1} in all the coordinated amines is assigned to V–O stretching vibrations[12] The constant position of the band may be due to constant charge distribution around the metal coordinated to the tertiary nitrogen of the heterocycline amine

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A re-assessment of the isomeric cross-section ratio in ^{75}Ge

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THE MEASUREMENT of the isomeric cross-section ratio is important from a number of points of view It can be used to study both the transfer of angular momentum in nuclear reactions and the spin dependence of the nuclear level density in the final nucleus via the spin cut-off parameter[1] Secondly, neutron-excited nuclear isomers may be useful for the measurement of neutron energy when used as threshold detectors In this laboratory we are interested in the measurement of the cross-section ratio for fairly short-lived isomers having half lives between a few seconds and 1 min One such isomer is ^{75m}Ge, which can be formed by the ^{75}As(n, p)^{75m}Ge reaction using 14 MeV neutrons There have been two reported measurements of this isomeric ratio for 14 MeV neutrons which disagree considerably The first measurement is by Fukuzawa[2], who obtains a value of 0 40±0 11, and the second by Okumura[3], who obtains a value of 0 855±0 074 It is the object of the present work to obtain an independent value of the cross-section ratio

Samples of a few grams of spectrographically pure arsenic trioxide were irradiated with fast neutrons from the D-T reaction produced by a 150 keV S A M E S accelerator, the neutron flux being monitored by the associated particle technique The experimental arrangements were such that the samples were irradiated with neutrons of energies between 14 3 and 14 7 MeV A simplified decay scheme of ^{75m}Ge is shown in Fig 1

Measurements of the induced γ-ray activities were made with a scintillation spectrometer having a 3"×3" NaI(Tl) crystal The 136 keV isomeric transition γ-ray was measured after an irradiation

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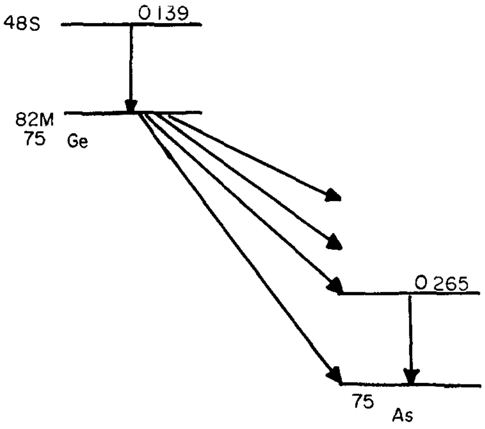

Fig 1 Simplified decay scheme for ^{75}Ge

of 2 min and the 264 keV γ-ray arising in the ground state transition after a 30 min irradiation The ratio of the efficiences of the counter for the two γ-ray energies was evaluated from the calculations of Vegars *et al* [4] and the information on the decay scheme and the internal conversion of the isomeric transition was obtained for the compilation of Lederer *et al* [5] A small correction was also made for the different absorption of the two γ-rays in the samples and the crystal container

These measurements gave a value of 0 82 ± 0 08 for the ratio of the cross-section for the production of the isomeric state to the total (n, p) cross-section The main uncertainties in this isomeric ratio were in the decay scheme data, the different absorption of the γ-rays in the source, the efficiences in the NaI crystal and in the variation of neutron flux during the irradiation These uncertainties were combined in quadrature

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Structure of potassium antimony tartrate

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POTASSIUM antimonyl tartrate (KSbT) is a well-known water soluble compound of antimony However, its structure is still a matter of speculation

Before 1931, it was thought to be a salt of tartaric acid whose two acidic hydrogens have been replaced by a K$^+$ ion and by a SbO$^+$ radical In 1931, the work of Reihlen and Hezel[1] clearly indicated that KSbT is a complex of Sb$_2$O$_3$ and K monotartarate Recent X-ray crystallographic studies [2] of the salt in the solid state confirm such a view In the present investigation, an attempt has been made to elucidate the structure of (KSbT) from solution properties as such, and more so, from the

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of the complexing agents provide evidence for one electron transfer whereas $E_{1/2}$ against pH plots indicate that two hydroxyl groups take part in complex formation

Another interesting fact emerges from the spectrophotometric study of Cu(II)-chromotrope 2B, viz the possible colorimetric estimation of Cu(II) with the help of this reagent Preliminary results have revealed that estimation of copper is possible in the concentration range 2×10^{-4}–1×10^{-6} M and over a wide pH range 7 0–11 5

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On the composition and stability of Cu(II) complexes of 1:8 dihydroxy naphthalene 3:6 disulphonic acid (chromotropic acid) and p-Nitrobenzene azo chromotropic acid (chromotrope 2B)

(*Received* 11 *June* 1963, *in revised form* 17 *September* 1963)

Several metals, such as Fe(III)(1), Ti(IV)(2), U(VI)(3), Cr(II)(4), Tl(III)(5) and Th(IV)(6), are known to form stable complexes with chromotropic acid and chromotrope 2B. Little work has, however, been done of the Cu(II) complexes, although Martell and coworkers(7) have studied the complexes by the Bjerrum method. In the present communication the spectrophotometry of the complexes and their reduction at a dropping mercury electrode are reported.

Cupric chloride (Analar), chromotropic acid sodium salt (E. Merck) and chromotrope 2B (B.D.H.) were used for preparing the respective solutions. Phosphate buffer solutions in the range pH 5·5–11·0 were prepared from A.R. products. The pH's were tested by a Beckman pH meter model G.

Spectrophotometric measurements were carried out with a Beckman DU Spectrophotometer using a 1 cm Corex cell and a tungsten lamp as the light source. A Fischer Electropode with multiflex galvanometer (Type MGF 2) in the external circuit was used for the polarographic measurements. The electrodes used were a dropping mercury and a saturated calomel. Purified nitrogen was used for maintaining the inert atmosphere inside the polarographic cell.

The absorption spectra of Cu(II)–D.N.S. complex, chromotrope 2B and Cu(II)-chromotrope 2B were measured(8) in the spectral range 400–650 mμ. The $\lambda_{\max}$ of the species were 525 mμ, 525 mμ and 560 mμ respectively.

The composition of the complex was determined by the Job and slope ratio methods.(9,10) In both the cases 1 : 1 complexes were found to exist. The Cu(II)-complex was stable in the pH range 6·0–11·0 whereas the Cu(II)-chromotrope 2B complex was found to be stable in the pH range 7·0–11·5. They were, however, unstable in the lower pH range. The formation constant(11) were found to be 2·8 × 10^5 and 2·11 × 10^6 for the D.N.S. and chromotrope 2B complexes respectively.

Polarographic studies (using methyl red as maximum suppressor and KCl as the supporting electrolyte) were carried out with about 40 samples of Cu(II)-D.N.S. complex in the pH range 6·0–11·0. In all the cases reversible waves involving one electron transfer reaction were obtained.(12) The $E_{1/2}$ values were found to depend upon the concentration of the complexing agent and the pH of the medium. On plotting $E_{1/2}$ values against log concentration at one particular pH and $E_{1/2}$ against pH at one fixed concentration of the complexing agent, straight lines with slopes 0·065 and 0·0350 respectively were obtained indicating the combination of one atom of copper and the inclusion of two hydroxyl groups in the formation of the complex.(13)

The Cu(II)-chromotrope 2B also showed a similar behaviour at the dropping mercury electrode.

The polarographic studies reveal that Cu(II)-D.N.S. and Cu(II)-chromotrope 2B complexes are reversibly reducible at the dropping mercury electrode. The plots of $E_{1/2}$ against log concentration

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Spectrophotometric and potentiometric investigations on Mn (iii)–1:8 dihydroxy naphthalene 3:6 disulphonic acid chelate

(*Received* 29 *April* 1963)

IN RECENT years the complexes of 1:8 dihydroxy naphthalene 3:6 disulphonic acid (chromotropic acid) have received considerable attention since many of them find uses in analytical chemistry. SCHWARZENBACH[1] made a detailed study of the Fe(iii) chelate while SOMMER[2] and coworkers carried out an extensive study of the Ti(iv) complexes and they have been used for the colorimetric estimation of Ti(iv). WARE[3] suggested the use of this reagent for the determination of uranium.

Little has been done on the interaction of unstable oxidation states with chromotropic acid. In the present communication the results of the interaction of chromotropic acid with Mn(iii) described employing spectrophotometric and potentiometric methods.

Experimental

Manganic sulphate was prepared by a modification of UBBLEHODE's method[4] and the solution was stored in dark coloured bottles and the strength determined by titrating potentiometrically against ferrous ammonium sulphate. E. Merck reagent grade chromotropic acid (sodium salt) was used.

The spectrophotometric measurements were made with a BAUSCH and LOMB Spectronic "20", while the potentiometric measurements were carried out with a PYE precision potentiometer (type 7568) using saturated calomel and platinum electrodes.

The absorption spectra of the Mn(iii) solution and Mn(iii)–D.N.S. complex were measured[5] in the wave length range 350–600 mμ. Mn(iii) sulphate shows a single absorption peak at 515 mμ whereas the $\lambda_{\max}$ of the chelate was found to lie at 430 mμ.

The composition of the complex was determined by (a) JOB's method of continuous variation[6] and (b) Slope ratio method.[7] It was found that the complex was formed in the molar ratio Mn(iii): D.N.S. as 1:1. It was observed that above pH 1, the colour of the complex was completely destroyed, hence the extinction measurements could only be made in the presence of dilute sulphuric acid.

The formation constant for the chelate was determined by the method recommended by MUKERJI and DEY.[8] For two mixtures having the same optical density (0.20), the value of K came out to be 1.8×10^5 and the calculate value of ΔF° was found to be 3.11 K Cal.

The reaction of Mn(iii) sulphate with chromotropic acid was further investigated by potentiometric titration. D.N.S. solutions of varying concentration (1×10^{-2} M to 2×10^{-3} M) were titrated with 1×10^{-2} M Mn(iii). The breaks in the curves agree with the ratio 1:1 for the complex. The reverse titrations, however, did not prove successful since there were no significant breaks in the curves.

Discussion

The complex may be represented as Mn$^{\mathrm{III}}$(DNS) which may be formulated as a chelate complex. The strong tendency of hydroxyl groups to form stable coordination complexes with metal is well known. In the present case the development of a stable colour supports this viewpoint and the possibility of chelate ring structure being formed, is indicated.

Potentiometric titration confirmed the conclusion arrived at by spectrophotometry.

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The formation of a stable coloured complex between Mn(III) and DNS in the highly acidic may be advantageously employed for the colorimetric determination of Mn(III) in small amounts Further work is in progress

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Ein Jahrbuch für Wasserchemie und Wasserreinigungstechnik
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Über die komplexometrische Bestimmung des in Wasser gelösten Sauerstoffs

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Neben der allgemein bekannten Methode nach *Winkler* (1) zur Bestimmung des im Wasser gelösten Sauerstoffs ist eine Anzahl neuer physikalischer und rein chemischer Methoden zur Bestimmung des gelösten Sauerstoffs vorgeschlagen worden. Die Veröffentlichungen von *Pieters* und *Hansen* (2) (spektrophotometrisch), *Todt* und *Todt* (4) (polarographisch), *Alcock* und *Coates* (5) (Indigo- und Carmin-Methode), *James* und *Stephen* (6), *Barbi* und *Sandroni* (7) (coulometrisch) und *Buchoff* (8) (colorimetrisch) stellen interessante Beispiele der Forschungsarbeiten auf diesem Gebiet dar.

In der vorliegenden Arbeit wird über eine neue Methode zur Bestimmung des im Wasser gelösten Sauerstoffs berichtet, die auf der Titration des Dinatriumsalzes des Mn^{3+}-Äthylendiamintetraessigsäure-Komplexes gegen Ferroammoniumsulfat beruht. Die Ergebnisse wurden durch potentiometrische Titrationen überprüft.

Lösungen und Geräte

0,1 m Dinatriumsalz der Äthylendiamintetraessigsäure (E. D. T. A.)

0,01 m Ferroammoniumsulfat-Standardlösung (hergestellt aus analysenreinen Substanzen)

0,1 m Mangansulfat p. a.

1 m Natronlauge

4 n Schwefelsäure p. a.

Alle Reagenzien wurden in luftfreiem destilliertem Wasser gelöst.

Die potentiometrischen Titrationen wurden mit Hilfe eines PYE Präzisionspotentiometers Typ 7568 unter Verwendung von Platin als Meßelektrode und Kalomel als Bezugselektrode durchgeführt.

Methodik

Zu 100 ml der Wasserprobe, die sich in einem Erlenmeyerkolben mit Glasstopfen befindet und mit einer dünnen Schicht Toluol besprüht ist, werden 4 ml 0,1 m $MnSO_4$-Lösung zugefügt. Dann gibt man 100 ml 1 m Natronlauge zu und rührt die Lösung gründlich durch. Die Mischung wird weiterhin mit 10 ml 0,1 m E. D. T. A. und 2—3 Tropfen 4 m Schwefelsäure versetzt, so daß man einen pH-Wert von 2,5 erreicht. Bei dieser Behandlung stellt sich ein Farbumschlag von farblos zu violett ein, der auf der Bildung des Mn^{3+}-E. D. T. A.-Komplexes beruht. Die Lösung wird anschließend sofort mit Ferroammoniumsulfat bis zum Farbumschlag von violett nach farblos titriert.

Auswertung

Je 1 ml 0,01 m Ferroammoniumsulfat entspricht 1,6 mg Sauerstoff/l.

In Parallelproben wurde der Sauerstoff außerdem durch die *Winkler*-Methode bestimmt.

Ergebnisse

Temp. 18° C	Sauerstoffgehalt nach der	
	Winkler-Methode	neuen Methode
Probe I: dest. Wasser	6,5 mg/l	6,5 mg/l
Probe II: Leitungswasser	4,8 mg/l	4,4 mg/l

Temp. 25° C	zugegebene Ionen	O_2-Gehalt nach der vorgeschl. Methode
Probe 1	Cl^-	4,32
Probe 2	SO_4^{--}	4,32
Probe 3	NO_3^-	4,30
Probe 4	CO_3^{--}	4,30
Probe 5	NO_2^-	2,74
Probe 6	F^-	4,31
Probe 7	Ca^{++}	4,32
Probe 8	Na^+	4,32
Probe 9	K^+	4,32
Probe 10	—	4,32

Potentiometrische Titrationen

Die potentiometrischen Messungen wurden mit Platin als Meßelektrode und Kalomel als Bezugselektrode durchgeführt. 100 ml der Wasserprobe wurden in einen Kolben gefüllt und die Reagenzien entsprechend den obigen

Angaben zugegeben. Ein Strom gereinigten Stickstoffs wurde eingeleitet, um die Mischung durchzurühren. Geringe Mengen von 0,01 m Ferroammoniumsulfatlösung wurden mit Hilfe einer Mikroburette zugegeben. Am Äquivalenzpunkt konnten scharfe Knickpunkte beobachtet werden.

Temp. 18° C

	Sauerstoffgehalt nach	
potentiometrischer Methode	*Winkler* Methode	titrimetrischer Methode
6,16 mg/l	6,50 mg/l	6,20 mg/l

Eine typische Kurve zeigt die Abb. 1.

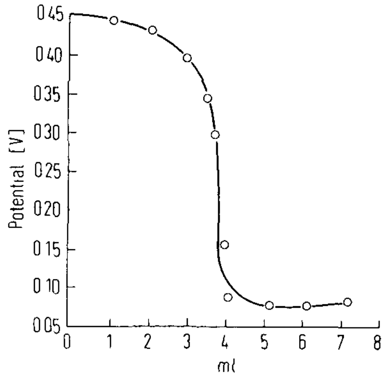

Abb. 1

Zugefügte Ferroammoniumsulfat-Lösung

Bereits *Prebil* und *Horacek* (9) zeigten, daß Mn^{3+} durch Titration gegen Ferroammoniumsulfat oder Natriumthiosulfat bestimmt werden kann. Ionen: wie Cu, Fe, Al, Mg, Pb, Zn, Cl, NO$_3$ stören die Bestimmung nicht. Da solche Verunreinigungen gewöhnlich in Abwasser, Kesselspeisewasser und Flußwasser vorkommen, kann die oben beschriebene Methode gut zur Bestimmung von Sauerstoff in derartigen Wassern verwendet werden. Die Methode ist zuverlässiger als die *Winkler* Methode, da der gebildete violette Komplex stabil ist und die Entfärbung bei der Titration einen scharfen Endpunkt erkennen läßt.

Die potentiometrischen Titrationen, bei denen mit der Platin-Elektrode das Gleichgewicht Mn^{++} $\rightleftarrows$ Mn^{+++} + e^{-} gemessen wurde, ergaben einen scharfen Knick, der die Eignung dieser Methode zur Bestimmung von Sauerstoff auf Grund der Bildung des Mn^{+++}-E.D.T.A.-Komplexes zeigt. Auch hier lagen die Werte in derselben Größenordnung wie die der *Winkler*-Methode und der titrimetrischen Methode, die im Vorangegangenen besprochen wurden.

Folgende Punkte sind bei der vorgeschlagenen titrimetrischen Methode zu berücksichtigen:

1. Die Lösung muß in einer Bürette aufbewahrt werden, die zur Adsorption des atmosphärischen Sauerstoffs ein Adsorptionsröhrchen mit alkalischer Pyrogallol-Lösung besitzt.
2. Die Titration sollte in einem Kolben mit Glasstopfen durchgeführt werden.
3. Eine dünne Schicht Toluol muß auf die Wasserprobe gespritzt werden.
4. Alle Reagenzien müssen mit luftfreiem dest. Wasser angesetzt werden.
5. Es darf nur gerade so viel Schwefelsäure angewandt werden, als zur Erreichung eines pH-Wertes von 2,5 notwendig ist. Durch einen Überschuß an Säure wird die Farbe des Komplexes völlig zerstört.

Weitere Untersuchungen über die Anwendbarkeit der beschriebenen Methode zur colorimetrischen Bestimmung des in Wasser gelösten Sauerstoffs sind noch im Gange.

Zusammenfassung

Eine neue Methode zur Bestimmung des im Wasser gelösten Sauerstoffs, die auf der Titration des Mn^{+++}-E. D. T. A.-Komplexes gegen Ferroammoniumsulfat beruht, wurde beschrieben. Die Methode ist recht zuverlässig, da der gebildete violett gefärbte Komplex sehr stabil ist und bei der Entfärbung ein scharfer Endpunkt festzustellen ist. Die potentiometrische Titration ergibt ebenfalls einen scharfen Knick am Äquivalenzpunkt.

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fate complex of benzimidazole precipitated. The suspension of the complex was cooled to 25°C and 2 g of potassium iodide were added, the colour changed to bluish violet. After about 3 hr, the complex was filtered on a Buchner funnel, rapidly washed thrice with small amounts of ice cold water, dried by rapid suction and finally over P_2O_5 in vacuum. The complex was then washed several times with chloroform to remove any excess of the ligand, dried and analysed.

The copper was estimated iodometrically after decomposing the complex with a mixture of nitric, sulfuric and perchloric acids. Iodide was estimated by Volhard's method and nitrogen by Kjeldahl's method. *Anal.* Calcd. for Cu(benzimidazole)$_4$I$_2$: Cu, 8·054; I, 32·19; N, 14·19. Found: Cu, 8·079; I, 31·84; N, 14·56.

Methods and apparatus. The magnetic susceptibility of the complex was determined at 25°C by the Gouy method, using Hg[Co(NCS)$_4$] as the calibrant. Diamagnetic corrections were applied to the susceptibility using Pascal's constants. The i.r. spectrum of the solid compound in Nujol mull was recorded on a Carl Zeiss UR 10 spectrophotometer using LiF, NaCl and KBr optics. The electronic spectrum of the powdered complex in Nujol mull was taken on a Unicam recording spectrophotometer, SP 700.

RESULTS AND DISCUSSION

Cuprous iodide in the presence of imidazole is oxidised to the cupric state in water[2]. On the other hand, a large excess of benzimidazole (metal: ligand = 1 : 10) is required to prevent the reduction of aqueous cupric ions to the cuprous state in the presence of iodide. Because of the tendency of benzimidazole to loose a proton in water to form a neutral copper(II) benzimidazolato complex, the reaction medium had to be maintained at pH 5·5 with acetic acid to prevent the ionisation of benzimidazole. Under the conditions used for the preparation of the complex, the aqueous suspension of Cu(benzimidazole)$_4$I$_2$ is not stable towards heating. However, by further addition of the ligand, the complex is stabilised even at 85°C. In the presence of polar non-aqueous solvents like alcohol, acetone, etc., the complex decomposes liberating iodine. The compound, however, is not affected by nonpolar solvents like benzene, chloroform, ether, etc. The solid complex melts with decomposition at 152°C.

The i.r. spectrum of Cu(benzimidazole)$_4$I$_2$ in the region 4000 to 400 cm^{-1} was compared with that of Cu(benzimidazole)$_4$Cl$_2$[3]. The spectra were almost identical showing similar ligand environment.

The magnetic moment of the complex is 1·87 B.M., which is comparable with that of other similar copper(II)-benzimidazole complexes.

The *d-d* transition in the complex occurs at 17,800 cm^{-1}, giving an asymmetric peak. The band position is below that of [Cu(benzimidazole)$_4$](ClO$_4$)$_2$ but near that of the corresponding copper nitrate and copper thiocyanate complexes[3], in which weak coordination of the anion is suggested. A tetragonal structure with weakly bonded iodide ions along the tetragonal axis, as in the corresponding imidazole complex[2] is suggested.

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Complexes of rare-earth with some substituted thioureas

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MUCH of the published work on rare earth complexes is concerned with nitrogen and oxygen ligated complexes, very little refers to complexes with sulphur containing ligands. This is perhaps due to the high charge on the rare earth metal ion which could be stabilized only by highly electronegative atoms e g , nitrogen and oxygen These anions transfer the charge by σ type coordinate bonds and have the capacity to donate more charge by π donor bonds involving another pair of electrons Sulphur, on the other hand is less electronegative having weak σ donor, but strong π acceptor properties, is more suitable for the stabilisation of lower valency states

DISCUSSION

Rare earth(III) ions react with substituted thioureas to form water soluble complexes These are generally colourless or light coloured and extremely hygroscopic Attempts were made to prepare the entire series of rare earth complexes with Naphthyl thiourea (N T U) Diphenyl thiourea (D P T U) Di-isopropyl thiourea (D I P T U) Allyl thiourea (A T U) and *O* Tolyl thiourea (T T U) but with limited success, and only a few complexes could be isolated in sufficiently pure form The formation of 1 1 complexes in Sm–DIPTU and Er–DPTU 1 2 complexes in Sm–ATU Gd–T T U and Er–NTU 1 4 complexes in Gd–DIPTU and Sm–DPTU 1 6 complexes in case of Dy–T T U is well established on the basis of chemical analyses of the isolated products

The i r spectra of the substituted thioureas and respective rare earth complexes were studied in the region 5–15 μ The main features of the spectra of the complexes in this region are (i) the strong bands near 1600 cm^{-1} resulting from NH_2 bending modes remain unchanged on coordination (D I P T U and D P T U do not show any band in this region due to the absence of NH_2 groups) (ii) The N–H deformation and C–H antisymmetric stretching vibrations near 1500 cm^{-1} shifted to higher frequencies to the extent of ~ 30 cm^{-1} in all cases (iii) The bands near 750 cm^{-1} assigned to C–S stretching with a small contribution from C–N stretching modes are shifted to lower frequencies by ~ 20 to 30 cm^{-1} in all cases except D P T U where the bands are almost unshifted

An interesting feature of the substituted thioureas is the decrease in N–H deformation and C–N antisymmetric stretching vibration frequencies with decrease in nucleophility[2] of the compounds as shown in Table 1

Table 1

	γ(CN, NH) (cm^{-1})	δ(CS) (cm^{-1})
DIPTU	1570	705
ATU	1540	725
TTU	1500	765
NTU	1490	770
DPTU	1510	760

This shows the strengthening of C–S double bond or decrease in coordination ability of S as we move from D I P T U to D P T U

On the basis of these affects in the 1500–1600 cm^{-1} region it seems certain that the coordination in these rare earth complexes does not take place through nitrogen and this conclusion is strengthened by the lowering of the frequencies of the C–S stretching vibrations indicating thereby a weakening of the C=S and strengthening of the C—N bond[2]

Preparation of the complexes

To an aqueous solution of the rare earth chloride (about 1 per cent) in an Erlenmeyer flask was added an excess of 2% substituted thiourea solution in acetone The resulting solution was then warmed slightly to dissolve any precipitating reagent and refluxed for about one hour After evaporation the dried product was extracted with about 10 ml of water and heated for about a ½ hr filtered and the filtrate crystallised The products were recrystallised from water

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1 Gd(DIPTU)$_4$Cl$_3$ Colorless crystals Calc for $C_{28}H_{64}N_8S_4GdCl_3$ C 37 1, H 7 1, N 12 3, S 14 05 Found C, 36 4 H 7 7 N 12 5, S 14 1

2 Sm(DIPTU)Cl$_3$, light yellow crystal Calc for $C_7H_{16}N_2S$ $SmCl_3$ C, 20 1, H, 5 6, N, 7 2, S, 8 2 Found C 20 1, H 5 7, N 7 1 S 8 1

3 Dy(DPTU)$_4$Cl$_3$ light yellow crystals Calc for $C_{52}H_{48}N_8S_4$ $DyCl_3$ C 52 8 H 4 1, N 9 4, S 10 8 Found C 54 3, H 4 3 N 9 2, S 10 7

4 Dy(TTU)$_6$Cl$_3$ – Light yellow products Calc for $C_{48}H_{60}N_{12}S_6$ $DyCl_3$ C 45 6, H 4 7, N 13 2, S 15 1 Found C 46 1, H 5 1 N 13 4, S 15 4

5 Sm(ATU)$_2$Cl$_3$ Light pink crystals Calc for $C_8H_{16}N_4S_2SmCl_3$ C 19 6 H 3 2, N 11 4, S 13 1 Found C 20 0, H 3 5, N 11 5, S 12 8

6 Er(NTU)$_2$Cl$_3$ Buff coloured product Calc for $C_{22}H_{20}N_4S_2ErCl_3$ C 38 8, H 2 9, N 8 2, S 9 4 Found C 38 4, H 2 6 N 8 1 S 9 5

7 Gd(TTU)Cl$_3$ Light pink product Calc for $C_{16}H_{20}N_4S_2VdCl_3$ C, 32 2, H 3 2, N 9 3, S 10 7 Found C, 31 1, H, 2 9, N 9 3, S, 10 7

8 Er(DPTU)Cl$_3$ buff coloured product Calc for $C_{13}H_{12}N_2SErCl_3$, C 31 2, H 2 4, N 5 6 S 6 5 Found C 30 8, H 2 5 N 5 6, S 6 5

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The reactions of dimethyl sulphoxide with sulphur tetrafluoride and tungsten hexafluoride

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IT HAS been reported that the main product from the reaction of dimethyl sulphoxide (DMSO) with iodine pentafluoride is $CH_2FS(O)H$ and the spectroscopic properties of this compound have been described[1] We find that a compound with similar properties is a major product from the reaction of DMSO with sulphur tetrafluoride at 20° and is also produced in small yield from the reaction of DMSO with tungsten hexafluoride at 0° The compound is a colourless liquid, readily volatile at 20° and although it has not been possible to obtain analytical and molecular weight data due to its ready decomposition we suggest that it is bis(monofluoromethyl)ether CH_2FOCH_2F

Mass measurement of the prominent peaks in its mass spectrum gives the following relative intensities in parentheses, $m/e = 81$ (35) 81 01514, $m/e = 63$ (15) 63 02427, $m/e = 33$ (100), 33 01398, $m/e = 31$ (18) 31 01833 Calculated masses $C_2H_3F_2O^+$ 81 01518, $C_2H_4FO^+$ 63 02460, CH_2F^+ 33 01404, CH_3O^+ 31 01838 No peak due to $C_2H_4F_2O^+$ is observed but the ions are all plausible fragments of CH_2FOCH_2F The compound s ^1H and ^{19}F NMR spectra are characteristic of the $X_2X'_2$ and AA parts of an $AA'X_2X'_2$ system and an analysis of the ^1H spectrum by the method of Harris[2] gives the following coupling constants $J(HF) = 54$, $J(HF') = 0 8$, $J(FF') = 11$, and $J(HH') = 0$Hz The ^1H and ^{19}F chemical shifts are -5 34 and $+157$ 8 ppm from Me_4Si and CCl_3F respectively The spectra indicate that the molecule is symmetrical and the coupling constants are reasonable for CH_2FOCH_2F by analogy with other hydrofluorocarbon compounds[3] A complete analysis of both

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spectra has been performed by Dr N M D Brown, University of Glasgow, and will be published elsewhere The compound's i r spectrum in the region 4000–400 cm^{-1} consists of peaks at 3010m, 2938m (CH stretches), 1438m (CH_2 def), 1268m (HCF def), 1005s (CF stretch) arising from the CH_2F groups, and peaks at 1184s and 1090mbr which may be due to COC stretching modes, although coupling with other vibrations will occur

CH_2FOCH_2F has been prepared from the reaction of α-polyoxymethylene, $(CH_2O)_x$, with SF_4[4] and a sample of CH_2FOCH_2F from the reaction of SF_4 with *sym*-trioxan, $(CH_2O)_3$ has physical properties mass, i r and NMR spectra identical with those described above The spectra appear almost identical to those reported for the DMSO, IF_5 product[1], and we believe they cast doubt on its formulation as $CH_2FS(O)H$

The other products from the reaction of SF_4 with DMSO are difluoromethane thionyl fluoride and an involatile liquid which is a mixture of compounds containing CH_2F- and CHF_2-groups The major product from the reaction of WF_6 with DMSO is a yellow, viscous oil and its ^{19}F NMR spectrum in CD_3CN shows that at least two species are present A single peak at − 144 ppm from CCl_3F, with partially resolved satellite peaks due to ^{19}F-^{183}W coupling of 40Hz, is assigned to a WF_6 complex, possibly WF_6-$OSMe_2$, by analogy with other WF_6 base complexes[5] The other signals are a doublet (relative intensity 8) at − 63 ppm with satellite peaks corresponding to J(FW) = 71 Hz and a nonet at + 145 ppm J(FW) = 50 Hz The doublet and nonet splittings are both 58 Hz Similar signals have been observed as impurities in the spectra of WF_6 complexes in SO_2[5] and in solutions containing tungsten oxytetrafluoride and the oxopentafluorotungstate (VI) anion[6] They are thought to be due to a dimeric fluorine bridged anion $(OF_4WFWF_4O)^-$

HF is a product from the reactions of both SF_4 and WF_6 with DMSO therefore the origin of some of the reaction products is uncertain and it is possible that there are additional products to those identified The formation of CH_2FOCH_2F is unexpected but may be explained by analogy with the reactions of DMSO with BCl_3, $SiCl_4$[7] and $Nb(Ta)X_5$, (X = Cl, Br) [8], in which oxygen abstraction occurs to give an oxyhalide complex, or oxide, and Me_2SX_2 Me_2SBr_2 can be isolated but Me_2SCl_2 decomposes to give CH_2ClSCH_3 and HCl A similar reaction between SF_4 and DMSO would give SOF_2 and Me_2SF_2, which readily decomposes[9] Some evidence for the formation of CH_2FSCH_3 exists in the mass spectrum of CH_2FOCH_2F, as weak peaks due to $C_2H_5FS^+$, and CH_2FS^+ are present Found *m/e* = 80, 80 00953, *m/e* = 65, 64 98675 Calculated masses 80 00960 and 64 98612 α-Fluorosulphides decompose at room temperature[10] and CH_2FOCH_2F could result either from attack on the glass, or from a further reaction with DMSO A similar series of reactions appears to occur between WF_6 and DMSO but to a smaller extent The main reaction appears to be the formation of a complex similar to those formed by NbF_5 and TaF_5[11]

EXPERIMENTAL

All operations were carried out in a high vacuum system using standard techniques NMR spectra were recorded at 33° using a Perkin-Elmer R 10 spectrometer at 60 0 MHz for ^1H and 56 4 MHz for ^{19}F Me_4Si and CCl_3F were used as internal references I R spectra were recorded using a Perkin-Elmer 257 spectrometer and mass spectra using an A E I MS9 spectrometer at 70V

DMSO (B D H spectroscopic grade) was refluxed over CaH_2 and fractionally distilled under vacuum before use SF_4 (Peninsular Chem Research) and WF_6 (Allied Chemical Co) were purified by low temperature trap to trap distillation over NaF

Reaction of DMSO *with* SF_4 A vigorous exothermic reaction occurred when a mixture of DMSO and SF_4 in a 2 1 mole ratio was allowed to warm slowly from − 196° to 20° The volatile products were partially separated by distillation at − 120° to give a mixture of CH_2F_2 and SOF_2, identified by their i r

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