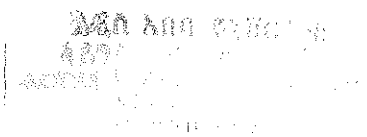
SYNTHESIS AND CHARACTERIZATION OF SUBSTITUTED $[Fe(CN)_5L]^{3-}$ COMPLEXES
(L = para and ortho nitroaniline and nitrophenol)



A Thesis presented to the
School of Graduate studies
Addis Ababa University

In Partial fulfilment of the requirements
for the degree of Master of science
in chemistry

by

MUSSIE HAGOS

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To

My father **Ato Hagos Tewelde**

My mother **w/o Letihanes G/aregawi**

My **brothers and sisters**

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Symbols and Abbreviations used.

Å = Angstrom
λmax = Maxmum wave length
ρ = Resistivity
$\acute{o}$ = Conductance
ϵ = Molar absorptivity
cm = Centimeter
s = Second
ppm = parts per million
M = Molar
m.mole = millimole
IR = Infrared
UV = Ultraviolet
Vis = Visible
NMR = Nuclear magnetic resonance
M. P = Melting point
B. P = Boiling point
en = ethylenediamine
py = Pyridine
PNP = p-nitro phenol
PNA = p-nitro aniline
ONP = o- nitro phenol
ONA = o- nitro aniline

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF SUBSTITUTED $[Fe(CN)_5L]^{3-}$ COMPLEXES (L = para- and ortho- nitroaniline and nitrophenol)

By
MUSSIE HAGOS

ADVISOR: Dr NEGUSSIE RETTA

A study is presented on the synthesis and characterization of the pentacyanoferrate(II) complexes, $Na_3[Fe(CN)_5L]^{3-}.xH_2O$ where L = p-nitroaniline, o-nitroanline, p-nitrophenol, and o-nitrophenol. The structure of the synthesized complexes were confirmed by using IR, NMR, and UV-VIS spectroscopy and cyclic-voltammetry measurements. Melting points were used to determine the purity of the synthesized complexes. Atomic absorption spectroscopy was used for the analysis of sodium and iron and results confirmed the proposed stoichiometric formula of the complexes. Cyclic-voltammetric measurements indicated the occurrence of one reversible wave for each complex. These were assigned to the oxidation of Fe(II) and reduction of Fe(III) in the reversible wave cycle. Low solid conductivity of the complexes were observed. This is related to the strength of the iron(II) - cyanide bond.

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INTRODUCTION

The pentacyanonitrosylferrates,(the nitro prussides) are of interest. Cyano complexes in general do not easily form mixed complexes by replacement of CN^- groups and, in the hexacyano complexes of iron, only one CN^- can be replaced by NH_3, H_2O, CO, NO_2(nitro) or NO (nitroso) [1]. Acidification of a mixture of $K_4Fe(CN)_6$ and KNO_2 gives first the pentacyanonitroferrate(II) ion $[Fe(CN)_5NO_2]^{4-}$.

$$Fe(CN)_6^{4-} + NO_2^- \Rightarrow [Fe(CN)_5NO_2]^{4-} + CN^-$$

and then the pentacyanonitrosylferrate(II) ion, the nitroprusside ion:

$$[Fe(CN)_5NO_2]^{4-} + 2H_3O^+ \Rightarrow [Fe(CN)_5NO]^{2-} + 3H_2O$$

The interest in reactions of pentacyanoferrate(II) ion with different ligands is mainly associated with the fact that this ion typically coordinates only one additional ligand and can be used as a probe for the binding properties of the several functional groups. The pentacyanoferrate(II) type of complexes are further important because they offer a specific site for a particular functional groups which can participate in the metal-binding process. The increasing importance of such complexes and their analogous has initiated an intensive study in the field.

The red sodium salt, $Na_2[Fe(CN)_5NO].2H_2O$, (stable crystalline starting material) is diamagnetic. Since the NO group is an odd electron group, one would expect the NO to exert paramagnetism in the complexes. However, the NO is coordinated to Fe in the form of NO^+ and results not only in the complex being diamagnetic but also the charge of the iron formally equal to +2.

Sodium pentacyanonitrosylferrate(II) [2] in 2:3 ethanol : water medium at pH 7 was used for the photometric determination of 2-mercaptobenzo thiazole by forming a coloured complex. Similarly sodium nitro prusside [2] was used for the determination of thiosulphate, thiourea, thiocyanate, ammonia, nicotine, streptomycin, urea, and fructose. Sodium nitroprusside was also used for the spectrophotometric determination of amino acids such as alanine, methionine, glycine and hydroxylamine in the concentration range of 10^{-4} - 10^{-3}M [3].

The present investigation is to synthesize and characterize, substituted pentacyanoferrate(II) complexes ($[Fe(CN)_5L]^{3-}$) with some organic ligands (L = p-nitroaniline, o-nitroaniline, p-nitrophenol, o-nitrophenol). This could provide additional analytical applications, for the Fe complex and possibly enhance stability of the " $Fe(CN)_5$" group to photodegradation.

The thesis is divided into four chapters, namely Chapter 1: Theoretical background, Chapter 2: Literature survey, Chapter 3: Experimental work, Chapter 4: Results and Discussion.

1. THEORETICAL BACKGROUND

1.1 SUBSTITUTED CYANIDE COMPLEXES.

The best known cyano complex of iron is, undoubtedly yellow potassium hexacyano ferrate(II) or ferrocyanide, $K_4[Fe(CN)_6].3H_2O$, obtained by the action of excess aqueous cyanide on any iron(II) compound[4]. The cyanide in this salt is kinetically inert with respect to substitution, as is shown by the absence of exchange with labelled cyanide; further, the salt is not poisonous. The $[Fe(CN)_6]^{4-}$ ion is, of course, a low spin d^6 system like the similarly unreactive cobalt(II) complexes. Recent structural studies[4] of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, established beyond doubt that the Fe-C distance in $[Fe(CN)_6]^{4-}$ (1.92Å), is shorter than that in $[Fe(CN)_6]^{3-}$ (1.95Å), the reverse of what is found for Fe(II) and Fe(III) hexaaquo and hexachloro complexes and is reflected in the smaller radius assigned to Fe^{3+} ion. Since the C≡N bond lengths and stretching frequencies differ very little between $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, the Fe-C bond lengths provide convincing evidence for stronger π-bonding in the lower oxidation state compound. There are many known mono substitution products of the $[Fe(CN)_6]^{4-}$ ion, the most important being the red salt sodium nitrosopentacyanoferrate (II), $Na_2[Fe(CN)_5NO].2H_2O$, commonly called sodium nitroprusside. Sodium nitroprusside, $Na_2[Fe(CN)_5NO].2H_2O$, is prepared by boiling potassium ferrocyanide with concentrated nitric acid, followed by dilution and making alkaline with sodium hydroxide. The most well known substituted pentacyanoferrate(II) complexes are nitroso, ammino, carbonyl and aquo complexes.

1.1.1. Nitroso complexes:

Sodium nitroprusside forms red rhombic crystals [5] and in freshly prepared solution, gives an intense violet coloration with alkali sulphides. This is used as a sensitive test for the sulphide ion in alkaline solution. The structure of the nitroprusside ion is such that the odd electron in NO enters the shell of the ferric ion giving a ferrous ion and leaving NO^+ with one lone pair available for coordination. This postulate is in agreement with the observed diamagnetism of the nitroprusside ion [5].

The electron in the π^* orbital of NO is relatively easily lost ($\Delta H_{ion} = 891$ kJ $mole^{-1}$)[6], to give the nitrosonium ion (NO^+), which has an extensive and important chemistry. Because the electron removed comes out of an antibonding orbital, the bond is stronger in NO^+ than in NO : the bond length decreases by 0.09Å and the vibrational frequency rises from 1840cm^{-1} in NO to about 2150 (depending on environment) in NO^+ [6].

1.1.2. Ammino complexes:

Pale yellow sodium pentacyanoamminoferrate(II), $Na_3[Fe(CN)_5NH_3].3H_2O$, may be made by the action of concentrated ammonia on the aquo compound, or by reduction of sodium nitro prusside with ammonia and sodium hydroxide [7]. Many ligands will displace ammonia to give $[Fe(CN)_5L]^{3-n}$ (n = charge of the ligand) [7]. The conductivity of the sodium salt in aqueous solution suggests that, in water, ammonia is largely displaced by the solvent[7]. With alkaline sodium nitrite, sodium sulphite, or carbon monoxide the ammonia is replaced by NO_2^-, SO_3^{2-}, or CO, respectively[41,43,46]. Oxidation of the Fe(II) ammine complex with hypobromite or sodium nitrite and acetic acid gives the dark yellow Fe(III) compound[7]. An aqueous solution of the acids $H_2[Fe(CN)_5NH_3]$ and HN_3 or HSCN, prepared in an ion-exchange column, may be converted into tetra butyl ammonium salts containing the mixed anion $[Fe(CN)_5N_3]^{3-}$ or $[Fe(CN)_5SCN]^{3-}$ [7]. The visible spectra of many of these substituted ferrocyanide ions have been reported [8].

1.1.3. Carbonyl complexes:

Carbonmonoxide reacts with potassium ferrocyanide solution at 130°C or above under pressure, forming $K_3[Fe(CN)_5CO]$ [7]. Displacement of ammonia from the amminopentacyano complex by carbon monoxide in the ammino- pentacyano complex by carbon monoxide in the presence of acetic acid also occurs[9]. These reactions suggest that the aquapentacyano complex would react with CO.

1.1.4. Aquo complexes:

Aquopentacyano complexes are obtained by the action of light on neutral or acidic solutions of ferrocyanide:

$$[Fe(CN)_6]^{4-} + 2H_2O = [Fe(CN)_5H_2O]^{3-} + OH^- + HCN$$

This process, for which the equilibrium constant is 10^{-8} [7], is retarded by alkali but promoted by nitrosobenzene (which forms a stable violet complex with the aquo pentacyanide). On a preparative scale, however, it is usual to make the sodium salt, $Na_3[Fe(CN)_5H_2O].H_2O$, from nitro prusside by the reaction

$$[Fe(CN)_5NO]^{2-} + NH_2OH + OH^- = [Fe(CN)_5H_2O]^{3-} + N_2O + H_2O$$

Iron(III) aquopentacyano complexes are obtained from ferricyanide under the influence of light, heat, or acid, by oxidation of the Fe(II) compounds with bromine water, nitrous acid, or permanganate and acetic acid[7], or by the action of chlorate on ferrocyanide or chlorine on a ferricyanide[7].

1.1.5. The chemistry of iron [10]

Iron is the first element in the first transition series which does not show its group oxidation state. Its highest oxidation state is +6 (in $[FeO_4]^{2-}$) and even this is unstable $[FeO_4]^{2-}$ is a powerfully oxidizing agent. Iron has an extensive cationic chemistry in the +2 and +3 oxidation states. This contrasts with the behaviour of ruthenium and osmium for which the higher oxidation states have a markedly greater stability.

The formation of $[FeO_4]^{2-}$ requires very strong oxidizing conditions such as the action of fused KOH and KNO_3 on iron filings [10]. The ferrate (VI) ion is tetrahedral, and the salts are isomorphous with sulphates, chromates, and manganates. In aqueous solution it is a stronger oxidizing agent than permanganate. It oxidizes ammonia to nitrogen in the cold, and acidification immediately causes liberation of oxygen from water [10].

Indeed iron(III), in its high- spin compounds at least, would no doubt be less stable with respect to its lower oxidation states were it not for the presence of the symmetrical half-filled d-shell.

Fe(II) is the most stable oxidation state for iron and is found with both the high-spin configuration and the diamagnetic t^6_{2g} configuration. Iron(II) hydroxide is quite strongly basic and gives rise to green, ionic salts with most anions. Fe(II) is mildly reducing and in this respect continues the sequence of diminishing reducing power found for first the transition series, M^{2+}. It is probably a fair generalization to say that where spin-pairing occurs (as with ligands such as CN^-), Fe(II) is the more stable, but with out spin-pairing, Fe(III) is favoured.
It is certainly noticeable that the hexacyanoferrate(II) anion, $[Fe(CN)_6]^{4-}$, is more stable than the hexacyanoferrate(III) anion, $[Fe(CN)_6]^{3-}$. In the former, the cyanide ions are so tightly bound that the complex ion is non-poisonous, whereas in the latter, dissociation renders it quite toxic.

With Fe(III) ions, hexacyano ferrate(II) gives a deep-blue precipitate (prussian blue) identical with that produced by the action of Fe(II) ions on $[Fe(CN)_6]^{3-}$. It is formulated as $[Fe^{2+}Fe^{3+}(CN)_6]^-$ and its intense colour may be associated with the presence of iron in two oxidation states and the possibility of their interconversion by charge transfer. Treatment of hexacyanoferrate(II) with 30 percent nitric acid gives dark-red crystals of the so-called nitroprussides, $[Fe(CN)_5NO]^{2-}$. Since these compounds are diamagnetic, the anion is most easily regarded as containing NO^+ coordinated to low-spin Fe(II). Although octahedral coordination is the most common geometry for Fe(II), several tetrahedral complexes are known. These are mostly halide complexes of the type $[FeX_4]^{2-}$ associated with a large cation.
Mention must be made of what is biologically one of the most important of all coordination compounds, haemoglobin[10]. This contains high-spin Fe(II) coordinated to the four planar nitrogen atoms of a porphyrin ring system, and attached also to a nitrogen atom of a protein. The sixth position may be occupied by water, which can be reversibly replaced by molecular oxygen when the molecule becomes low-spin and diamagnetic.

This is of course an over simplification, and the way in which the oxygen is bonded to the iron is not yet understood. The ability of cyanide ions and carbon monoxide to replace the oxygen and to destroy the oxygen-carrying ability is the main reason for the extremely poisonous nature of these materials.

Lower oxidation states of iron are stabilized by carbonyl and related ligands. The nobel-gas configuration is attained by five-coordination, in $Fe(CO)_5$. The molecules of $Fe(CO)_5$ have trigonal bipyramidal structures. Octahedral coordination can be achieved by dimerization. $Fe_2(CO)_9$ has three bridging CO groups and its diamagnetism implies the presence of an Fe-Fe bond.

Among the multitude of organometallic compounds of iron is the first and best-known of the "sandwich" compounds, ferrocene, $Fe(C_5H_5)_2$. The molecule is regarded as being composed of an Fe(II) ion attached to two cyclopentadienide ($C_5H^-_5$) anions [10]. If each carbon atom is considered to be sp^2 hybridized, forming bonds with the two adjacent carbons and one hydrogen, then a single electron in a p_z orbital perpendicular to the ring system remains. These p_z orbitals form five π molecular orbitals and the electrons they contain, plus the additional electron (because the ring is negatively charged) give three electron pairs occupying the three lowest molecular orbitals. Each ring may then be coordinated to the Fe(II) ion by donation of these three pairs of "aromatic" π-electrons. The iron then achieves the noble-gas configuration and is diamagnetic[11]

1.1.6. Nucleophilic substitution reaction in complexes

Reactions in which ligand-metal bonds are broken and new ones are formed, without a change in their oxidation state are called substitution reactions of metal complexes[12]. Generally nucleophilic substitution reaction are classified in to four specific types [12], ligand exchange reaction, solvent exchange reaction, acid-base catalyzed reaction and complex formation reaction. Another type that can be added is the substitution reaction promoted by a metal ion. Most of the promoter ions are soft acids like Hg(II), Pd(II), and Ag(I) which are able to abstract soft ligands like S^{2-}, CN^-, SCN^- etc. The abstracted ligand can be replaced by an incoming ligand, including water.

Pearson[13], has classified metal ions and ligands as "hard" and "soft" Lewis acids and bases and has suggested a general rule that hard acids bind strongly to hard bases and soft acids to soft bases. Hard acids are those that bind to bases which bind strongly to the proton, i.e., basic in the usual sense, while soft acids bind strongly to highly polarisable or unsaturated bases which often have negligible proton basicity, e.g. R_2S. Yet it is possible for a base to be soft and strongly binding to the proton. Such a case is the highly polarisable S^{2-} ion. Pearson's hard and soft acid defintion corresponds roughly to class (a) and class (b) metals, [13] respectively.

Jorgensen[14] has pointed out that class(b) contain three rather disparate categories:

i. metals with unusually low oxidation numbers;

iii. metals with certain high oxidation numbers;

iii. the ions Sn^{2+}, Sb^{3+}, Tl^{+}, Pb^{2+}, Bi^{3+}, which show class(b) character with heavy halides and chalcogenides but class(a) aversion to CN^{-}.

Jorgensen [14] also suggested that some metals may have class(b) character in a low and a high oxidation state yet class(a) character in an intermediate oxidation state.

The spectrochemical series of ligands is arranged according to the spectroscopic splitting parameter Δ, as given by the frequency of the lowest ligand field absorption band in a transition metal complex. The series is [14]: I^{-}, < Br^{-} < SCN^{-}, Cl^{-}< H_2O < NCS^{-} , glycine < pyridine < NH_3 < ethylenediamine ~ SO_3^{2-}~ NO_2 1,10-phenanthroline ~ 2, 2^1-bipyridyl < H^{-} < CH_3^{-} < CN^{-} < CO.

The parameter Δ is dependent on:

i. electrostatic attraction

ii. the effect of lone pairs on the ligand

iii. M→L d_π— p_π or d-d bonding

iv. L → M p_π— d_π bonding

(i), (ii) and (iii) increase Δ whereas (iv) decreases it [15]. The ligands attached to the central metal may be anionic, neutral or (less frequently) cationic. In classical coordination chemistry, the number of donor atoms (with one Lewis base electron pair per donor atom) bound directly to the central metal defines[16] the coordination number.

1.2 THE LIGANDS

1.2.1 CYANIDE LIGAND[17]

The fourteen electron diatomic ligand has unique complex forming properties. The following species belong to this particular set of ligands: CN^-, CO, NO^+, N_2.

In spite of the same electronic structure there are important differences in the reactivities and complex forming properties of these ligands. These differences stem partly from the difference of the electric charge of them and partly from the dissimilarities in the donor properties of the constituent atoms and of the π-system. Furthermore the electron accepting properties due to the empty π^* antibonding orbital are also different.

Cyano complexes of transition and post-transition metal ions form the most stable complexes. This permits the elimination of interfering effects of complex forming substances in the analytical determination of these ions. In the atomic absorption spectroscopic determination of metal ions the complex forming substances considerably interfere. This is evidently due to the fact that the atomization process of the metal are markedly, sometimes dramatically, influenced by the ligands bound to metal ions[17]. In principle this interfering effects can be eliminated by adding an extremely strong complex forming compound to the solution to be analyzed, because in such a condition the immediate environment of the metal ion is independent of the original composition of the solution. Cyanide ion appears eminently suitable for this purpose.

The elimination of interferences by applying cyanide as a masking agent, succeeded with cobalt [18], palladium [19] and ruthenium [20].

INFRARED SPECTRAL PROPERTY OF CYANO COMPLEXES

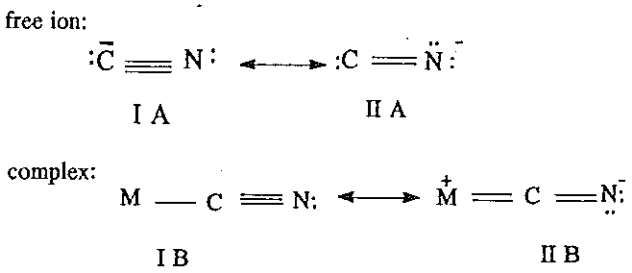
C≡N stretching bands.

Cyano complexes exhibit sharp C≡N stretching bands between 2200 and 2000cm^{-1}. The table below shows the observed C≡N stretching frequencies for a number of cyano complexes. Some complexes exhibit band splitting in the crystalline state. Polynuclear complexes give several bands. Hydrates exhibit spectra different from those of the anhydrates. The C≡N stretching frequencies of cyano complexes are generally higher than that of the free CN^- ion (2080cm^{-1} for KCN)[21].

Table1. C≡N stretching frequency in various cyano complexes in the solid state (cm^{-1})

Compound	Frequency(cm^{-1})	Reference
$K_4[Ni(CN)_4]$	1985	22
$K_2[Ni(CN)_4]$	2135	22
$K_4[Ni(CN)_6]$	2128,2079,2055	22
$K_2[Pd(CN)_4]H_2O$	2143	22
$K_2[Pt(CN)_4]3H_2O$	2150	22
$Na_3[Fe(CN)_5NH_3].6H_2O$	2036	this work
$Na_3[Fe(CN)_5H_2O].H_2O$	2043	22
$K_3[Fe(CN)_6]$	2125	22
$Na_2[Fe(CN)_5NO].2H_2O$	2152	22
$[Ag(CN)_2]^-$	2135	22
$[Ag(CN)_3]^{2-}$	2105	22
$[Ag(CN)_4]^{3-}$	2092	22

In terms of resonance structures, this result can be explained by structure IIA contributing more to the total structure of the free ion than does structure IIB to the total structures of the complex.



I A II A

I B II B

In metal cyano complexes,the larger the contribution of IIB, the lower the C≡N stretching frequency.

According to the El-sayed and Sheline[23], the C≡N stretching frequency of cyano complexes depends upon:

i) the electronegativity

ii) the oxidation state and

iii) the coordination number of the metal.

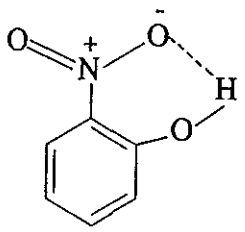
The effect of electronegativity [22, 23], is seen in the frequency order, $[Ni(CN)_4]^{2-} < [Pd(CN)_4]^{2-} < [Pt(CN)_4]^{2-}$. The electronegativity of Ni(II) is smallest and the contribution of structure IIB is largest. Therefore the C≡N stretching frequency of the Ni(II) complex is the lowest in this series[21,22]. The effect of oxidation state is seen in the frequency order, $[Ni(CN)_4]^{4-} < [Ni(CN)_4]^{2-}$. Here the larger negative charge of Ni increases the contribution of structure IIB, resulting in a lower frequency shift in the Ni complex.

The effect of coordination number is seen in the frequency order, $[Ag(CN)_4]^{3-}$ $< [Ag(CN)_3]^{2-} < [Ag(CN)_2]^-$ [23]. Here an increase in coordination number results in an increase in the negative charge on the metal which,in turn,increases the contribution of structure IIB, thus decreasing the CN frequency.

Hydration water does not influence appreciably the value of ν_{CN} (stretching frequency of CN); upon dehydration at 100-120°C, the observed frequency remains unchanged.

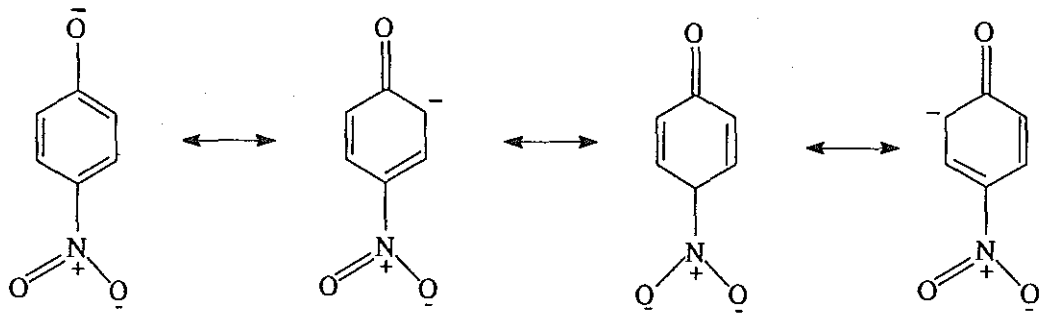
1.2.2. NITROPHENOLS:

Treatment of phenol with cold dilute nitric acid gives a mixture of ortho and para-nirto phenols, the latter predominating; oxidation products are also obtained [20]. These isomers may be separated by steam distillation. Solubility of nitrophenols in hydroxylic solvents depends on the power to form hydrogen bonds with the solvent. Phenol can form these bonds and hence a certain solubility in water can be expected. This argument [24] also applies to substituted phenols since the hydroxyl group is still present, but in o-compounds, because chelation is possible, hydrogen bonding with the solvent water molecules is hindered and hence the solubility is lowered.



Furthermore, since chelation causes the o-compound to behave as a "monomer", this isomer will be more volatile than the corresponding m-and p-isomers. Thus the effect of chelation is a lower solubility and greater volatility in the o-compounds, thereby enabling these to be separated from their m-and p-isomers by crystallisation or by chromatography. The presence of an electron donating group decreases the acidity of phenol by about 0.25 pK_a unit, or a factor of 2 [24]. The electron attracting groups increase the acidity. The para-nitro group increases the acidity of phenol by approximately 600 times.

A nitro group is powerful electron-withdrawing group, both by induction and by resonance.



The presence of additional nitro groups increases the acidity still further, so that finally 2,4,6-trinitrophenol(picric acid) has an acidity similar to that of mineral acids.
Resonance forms are effective only if the nitro group is in a position ortho or para to the hydroxyl. A meta-nitro group has a qualitatively similar effect but only from induction, so that it will increase the acidity of a phenol but not by very much.
Similarly, the effect of the nitro group in aniline tends to decrease its base strength and increase the acidity of the anilinium salt. Thus, for the salts of aniline and p-nitroaniline, the pKa's are approximately 5 and 2, respectively.
PHYSICAL PROPERTIES[24]. Both the ortho and para solids, are freely soluble in hot water, and sparingly in cold water. o-Nitro phenol is a bright yellow complex, volatile in steam, and with an odour resembling both that of phenol and of nitrobenzene. The p-nitro phenol is colourless when pure, is non-volatile in steam, and it is odourless.

o-Nitrophenol	p-Ntirophenol
M.p = 46°C	M.p = 114°C
B.p = 214.5°C	B.p = 279°C

solubility in H_2O = 0.21g/100ml at 20°C solubility in H_2O = 1.6g/100ml at25°C
An important point emerges from a comparison of the physical properties of the isomeric nitrophenols.

The lower solubility and boiling point properties of o-nitrophenol is because of intermolecular hydrogen bonding. In o-nitrophenol the nitro and phenol group are located correctly for the formation of hydrogen bonding within a single molecule. This intramolecular hydrogen bonding takes the place of intermolecular hydrogen bonding with other phenol molecules and with water molecules; therefore o-nitrophenol does not have the characteristic solubility in H_2O. It may be quite interesting to mention that in some cases the phenols having electron-withdrawing substituents in the ortho position are weaker acids than the para isomers. For instance, o-nitrophenol is weaker molecular hydrogen bonding with oxygen of nitro group. NMR spectra of ortho nitrophenol [25] shows a considerable down field shift appearing between δ10.0-12.0 for the proton of the phenolic group. This high down field shift is due to the presence of intramolecular hydrogen bonding.

1.2.3. *NITROANILINES [25]:*

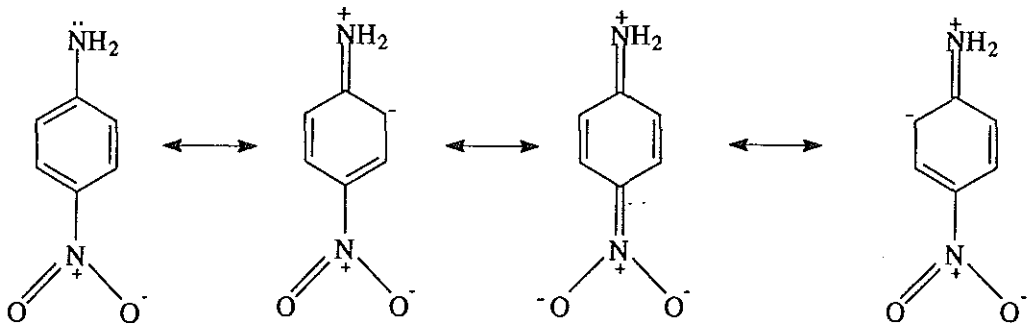
Ortho and para-nitroanilines are prepared by heating o-and p-chloronitro benzenes with ammonia.

Physical properties: All the solids are sparingly soluble in cold water and freely soluble in hot water. o-Nitroaniline is orange and volatile in steam;whch m-nitroaniline is yellow and also volatile in steam. p-Nitroaniline is yellow but non-volatile in steam.

o-Nitroaniline	p-Nitroaniline
M.P = 71^{0}C	M.P = 148^{0}C
Solubility in H_2O = 0.012g/100ml	Solubility in H_2O =0.08g/100ml

The effect of a ring substituent on basicity depends on whether the substituent is electron attracting, or releasing, its ability to enter into resonance with the amino-group, and its position in the ring. All the nitroanilines are weaker bases than aniline. The nitro group has a strong resonance effect, and ortho and para-nitroaniline are therefore more resonance stabilised than aniline itself. A meta group can not enter into resonance with the amino group, but nevertheless m-nitroaniline is a much weaker base than aniline. In this case, the explanation is that in addition to exhibiting a resonance effect when possible, the nitro- group always has a strong inductive effect.

This inductive effect tends to draw into the ring the lone pair on the nitrogen atom of the NH_2 group, with consequent decrease in basicity.



2. LITERATURE SURVEY

SYNTHESIS OF PENTACYANOFERRATE(II) COMPLEXES

The first modified synthetic method of substituted pentacyanoferrate(II) complex was given by Asperger[26]. This was based on the mixture obtained by reduction of $[Fe(CN)_5NO]^{2-}$ by hydroxylamine in strong basic solution. The methods of Asperger were abandoned after a simple method of preparation was discovered [35,36]. This more recent method is based on the generation of $[Fe(CN)_5H_2O]^{3-}$ by aquation of solid sodium pentacyanoammineferrate(II), followed by reaction with the required ligand to form a complex. The rate of release of ammonia from $[Fe(CN)_5NH_3]^{3-}$ during aquation was found to be $1.75 \times 10^{-2} s^{-1}$ [27].

The first pentacyanoferrate(II) complex containing monodentate ethylene diamine, $Na_2[Fe(CN)_5enH].6H_2O$, was first reported by Aymonino[1] but no structural properties were described. The behaviour of ethylene diamine as a monodentate ligand has also been reported in a few other cobalt and chromium complexes[1]. In all these cases the ethylene diamine molecule is protonated.

Katz[2] prepared, a new cyano-bridged binuclear complex of Fe(II), by mixing pentacyanoammineferrate(II) with 4-cyanopyridine (mole ratio 2 : 1). IR and UV-VIS spectra, together with kinetic data on ligand substitution, are consistent with the structure $(NC)_5Fe\text{-}NC\text{-}Fe(CN)_4$(4-cyano py), both in the solid state and in aqueous solution, thus demonstrating that cyanide can form a bridge between two iron atoms and stablize the complex.

Waggoner[28] has prepared, the Zn, Cd, Hg and Ag salts of $[Fe(CN)_5NO]^{2-}$. The objective of the investigation was to synthesize and study the properties of some nitro prussides of cations other than those of the alkali metals and to propose structures for the nitroprusside ions.

The infrared, UV-Vis and NMR spectra of $K_2[Co(CN)_5py].H_2O$ and $Na_3[Fe(CN)_5py].3H_2O$ were reported and discussed by Olabe[29]. In particular it was argued that the wave numbers and intensities of the IR-active CN stretching vibrations and the NMR chemical shifts of the m- and p- but not o-protons suggest greater metal to ligand back π-bonding in the Fe(II) complex than in the Co(III) complex.

Butler[30] reported reactions of pentacyanonitrosylferrate(II) with various carbonions (malonitrile, ethylmalonitrile, and dimethyl malonate). The first carbon acid selected for study was malonitrile. As hydroxide reacts quite rapidly with nitro prusside and as alkaline solutions of malonitrile are unstable, Butler used dilute NaOH solutions in his studies. In other report the course of the reactions of nitroprusside with a range of thiols studied. Thiols, RSH, (RSH = MeSH, cysteine, N-acetylcysteine, 2-methyl cysteine, N-acetyl-2-methylcysteine, penicillamine, N-acetyl penicillamine and glutathione) react with $[Fe(CN)_5NO]^{2-}$ to form coloured products[31].

Alfred[32], has prepared, the mixed ligand complexes of Fe(II) with cyanide and 2,2′ - bipyridine and with 1,10-phenenanthroline and cyanide.

Griffith[33], has prepared a pentacyanonitrosylvanadate complex by the reaction of hydroxylamine hydrochloride with potassium vanadate in the presence of excess of cyanide and hydroxyl ions. It is diamagnetic and shows a N-O stretching frequency of $1575cm^{-1}$, which is the lowest recorded for nitric oxide in an octahedral complex where the nitric oxide must be regarded as bonding as NO^+ . The reason for this unusually low N-O frequency may be due to the influence of the extent of π-bonding between the metal atom and the ligands. The factors responsible for this effect are the stereochemistry of the complex, the nature of the ligands, and the electronegativity of the metal atom.

Burgess[34] reported the synthesis and characterization of $[Fe(CN)_5(3,5\text{-}Me_2Py)]^{3-}$, $[Fe(CN)_5(3\text{-}CNPy]^{3-}$ and $[Fe(CN)_5(3\text{-}ClPy)]^{3-}$. He studied the kinetics of these complexes with CN^- as incoming ligand, in water, 40% ethylene glycol and 40% t-butyl alcohol. He found that the rates of substitution at these $[Fe(CN)_5L]^{3-}$ anions are remarkably insensitive to the composition of the mixed aqueous solvent.

Toma and Malin[35] studied the ligand exchange behaviour of pyridine, pyrazine and related aromatic nitrogen hetrocycles with sodium pentacyanoammineferrate(II). Each complex showed a strong absorption band in the visible region which was assigned to a metal-to-ligand electron transfer transition (d_π-p_π back donation).
In another studies they also reported the complexation properties of aqueous pentacyano ferrate(II) with the aromatic hetrocycles 4-methyl pyridine, pyridine, isonicotine amide pyrazine and N-methyl pyrazinium ion.In their work , they reported evidence for a limiting S_N1 mechanism of ligand exchange in aqueous solution. They also found that the optical and chemical properties of those pentacyanoferrate(II) complexes showed a striking similarity to the properties of the pentaammineruthenium(II) complexes[36].
They also studied the kinetics of formation of pentacyanoferrate(II) complexes of three amino acids, imidazole, glycine, and L-histidine in aqueous solution. The visible absorption band of pentacyano ferrate(II) complexes of imidazole, glycinato, and 1-histidine was assigned to the d-d transition from the $^1A_1$ ground state to the $^1E_1$ excited states based on a comparison with the absorption spectra of many other pentacyanoferrates. The visible absorption spectrum of the glycinato-complex was found to be similar to those of the corresponding complexes of ammonia and methyl amine, indicating the coordination of glycinato to be through the amine group [37].

Macartney and Mcauley[38] studied the kinetics of the formation and dissociation of pentacyanoferrate(II) complexes of cysteine, penicillamine, gluthathione, and 2-mercaptoethylamine. The results of a kinetic study of the formation of pentacyanoferrate(II) complexes of the indicated ligands were reported to be 330(cysteine), 370(penicillamine), 350(gluthathione), and 200 $M^{-1}s^{-1}$

(2-mercaptoethylamine), at 25°C. A correlation between the formation rate constants and the ligand charge type was observed; deviations from this relationship were discussed in terms of the location of the charges in the ligand.

Asperger[39] studied the complex formation between aqueous pentacyano ferrate(II) and various ligands such as nitroso benzene, 3-cyano pyridine, thiocyanate, nitrite, cyanide and sulphite. They found that when the entering ligand L bears no electrical charge, the K_f values are very similar and in the range 200 - 300 $l.mol^{-1}.s^{-1}$(at 25°C). For singly negatively charged anions K_f equals 40 to 60, and for the doubly charged SO_3^{2-} ion K_f equals 3.3 $l.mol^{-1}.s^{-1}$. Though the I_d mechanism can explain equally well the experimental data, they concluded that their kinetic results did not allow them to distinguish between the D and I_d mechanisms.

Murati [40] has studied the kinetics of the reaction of potassium hexacyano ferrate(II) with nitroso benzene in aqueous solution spectrophotometrically by measuring the extinction of the violet complex ion $[Fe(CN)_5C_6H_5NO]^{3-}$.
The approximate value of the activation energy for the reaction
$[Fe(CN)_6]^{4-} + H_2O \rightarrow [Fe(CN)_5H_2O]^{3-} + CN^-$
was calculated as 19.8 kcal/mole

Fluk [9] studied the bonding properties in prussian blue analogues of the type $Fe[Fe(CN)_5L].xH_2O$. All the three compounds of the type $Fe[Fe(CN)_5L].xH_2O$ (L = H_2O, NH_3 and CO) crystallise in the face centred cubic system characteristic of prussian blue analogues. The infrared absorption bands were assigned by analogy with the corresponding pentacyanonitrosylferrate(II) compounds. The energy of intervalence electron transfer bands increased with the increasing back donation of the $[Fe(CN)_5L]^{3-}$ moiety.

Davies [41] studied the stoichiometry and kinetics of the substitution-controlled oxidation of pentacyano aquo ferrate(II) species by hydrogen peroxide and by tert-butyl hydroperoxide in aqueous sodium perchlorate solution. Comparison of the kinetic data for oxidation with those for complexation by pyrazine, thiourea, isonicotin amide, acetonitrile, cyanide and nitrite under similar experimental conditions indicates that the oxidation process are limited by substitution at the iron(II) centre.

Gray and Manoharan [42] have studied the electronic structures of metal pentacyanonitrosyls. The bonding in transition metal pentanitrosyls was described in terms of a molecular orbital approach. The very strong M-NO bond dominates the over all ligand field, where M is the transition metal. Detailed molecular orbital calculations of $[M(CN)_5NO]^{n-}$ complexes give the d-level ordering to be $xz,yz < xy < x^2- y^2 < z^2$, suggesting some axial destabilization of z^2. The most important result was that the antibonding e level derived from π^* of NO is the lowest empty level in the $[M(CN)_5NO]^{n-}$ complexes and was assigned using the derived energy level scheme. The most important new result of this report was the assignment of the low energy bands as due to charge-transfer transitions from the metal-based e and b_2 levels to the unusually stable e (π^*NO) level. Agreement between the calculated and measured spin Hamiltonian parameters indicated the reliability of the derived molecular orbital approach.

Brown [43] has prepared the complex $Co_3[Fe(CN)_5CO]$ and shown it to contain a carbonyl group bonded to transition metals through both its carbon and oxygen atoms. The bond distance between the metal-oxygen atoms in $[Fe(CN)_5CO]^{3-}$ is approximately 1.9Å.

Toma [27] studied the intervalence electron transfer of several Fe(III) and Cu(II) pentacyanoferrate(II) complexes and compared the results to those of the hexacyanoferrate(II) analogues. The energies of the intervalence transitions have shown to strongly depend on the properties of the $[Fe(CN)_5L]^{n-}$ anion. Toma observed the trend of the energies of the intervalence bands to follow the sequence $NH_3 <$ py $<$ pyrazine carboxylate $<$ dimethyl sulfoxide $<$ CO. This sequence was interpreted in terms of back bonding of the low spin, iron(II) donor iron with the cyanide.

Eldik [44] studied the pressure dependence of a series of complex formation reactions of the type $[Fe(CN)_5H_2O]^{3-} + L^{n-} \rightarrow [Fe(CN)_5L]^{(3+n)-} + H_2O$ (where n = 0,1 L = imidazole, histidine, methionine, glautathione, glycine and alanine). The reaction was followed using stopped-flow techniques. The reported volumes of activation are all between +14 and +18 $cm^3\ mol^{-1}$. This is in good agreement with all the available data for the reverse ligand substitution reactions of $[Fe(CN)_5L]^{(3+n)-}$, which also occur according to a limiting D mechanism.
Eldik also studied the kinetics and mechanism of the acid catalyzed aquation and base hydrolysis of nitro pentacyanoferrate(III) in aqueous solution. The reaction were studied spectrophotometrically and kinetically in the pH ranges 0.3-2.0 and 11-13.7, respectively[45]. For the acid-catalyzed aquation, a dependence of the observed rate constant on the square of the acid concentration was found. A mechanism consisting of the acid-catalyzed aquation of a protonated nitro complex was proposed to account for those observations. Base hydrolysis was catalyzed by iron(II) species and exhibited pseudo-zero-order kinetics.

Santos [46] Studied the chemistry of the binuclear complex $[(CN)_5FepzRu(NH_3)_5]^n$ (n=0 for the II-III complex and n=-1 for the II-II complex, pz = pyrazine) in the solid state and in aqueous solution. Evidence for a mixed valence transition for the II-III complex was observed in the near infrared region. Based on infrared and resonance Raman spectra, a trapped valence or class II formulation was proposed for the complex. Cyclic voltammetry indicated the occurrence of two reversible waves at 0.48V and 0.72V, which were assigned to the oxidation of the ruthenium(II) and iron(II) centres, respectively.

3. *EXPERIMENTAL WORK*

3.1. GENERAL

3.1.1. *DETERMINATION OF WATER OF HYDRATION*

One gram of p-nitroaniline complex was heated between 100°C to 120°C, until constant weight was obtained. The change in mass (0.046g) permitted calculation of the number of moles of water of hydration in the sample to be one mole of water. This experiment was repeated with 0.5g of the p-nitroaniline complex to confirm the result. The same procedure as stated above was used, for p- nitrophenol (two mole of H_2O), for o-nitroaniline (three mole of H_2O) and for o-nitro phenol (two mole of H_2O) were obtained.

3.1.2. *DETERMINATION OF Na AND Fe BY ATOMIC ABSORPTION SPCTROPHOTOMETRY (AAS)*

The amount of sodium and iron were determined photometrically by comparing the intensities of radiation emitted by Na and Fe ions with respect to a series of standard solutions [47].

Instrumentation:

Melting point was determined by using the monos-Cop 45 apparatuse.

INFRARED SPECTROSCOPY(I.R): I.R spectra were recorded on a Perkin-Elmer 457 Spectrophotometer, in the region 400-5000 cm^{-1} as KBr disks.

VISIBLE AND ULTRAVIOLET SPECTRA: A Beckman DU-65 Spectrophotometer was used, with 1cm. standard quartz cell.

NUCLEAR MAGNETIC RESONANCE(NMR) spectra: Proton and carbon-13 magnetic resonance data were obtained by using a Jeol-FX 90Q Spectrometer.

ATOMIC ABSORPTION SPECTROMETRY: Sodium was determined by flame spectrophotometry (Gallen-Kamp) and iron by atomic absorption (Gallen-Kamp), in the soil laboratory of the Ministry of Agriculture.

Chemicals and Reagents.

Sodium nitrosylpentacyanoferrate(II) (Analar), p-nitroaniline, o-nitroaniline, p-nitrophenol, o-nitrophenol, sodium hydroxide pellets and anhydrous sodium carbonate were obtained from BDH,Analar. 35% (w/w) hydrochloric acid (BDH, Analar), 70% (w/w) nitric acid (Reidel-Dehaen), 70% (w/w) perchloric acid (Merck), Potassium hexacyanoferrate(II) (Reidel-Dehaen) were used as supplied. Acetonitrile, methanol, ethanol(absolute) and ammonia solution (28%) were from BDH and Analar. All chemicals were used without further purification. Distilled water was used throughout the experiments.

3.2. SYNTHESIS

3.2.1. SYNTHESIS OF SODIUM PENTACYANO AMMINE FERRATE(II) TRIHYDRATE

$$Na_2Fe(CN)_5NO].2H_2O + 2NH_3 + NaOH \longrightarrow Na_3[Fe(CN)_5NH_3].3H_2O + N_2 + H_2O$$

Sodium pentacyanoamminoferrate(II) trihydrate, $Na_3[Fe(CN)_5 NH_3].3H_2O$ was prepared from sodium nitroprusside $Na_2[Fe(CN)_5NO].2H_2O$ following the conventional procedure[48].

A solution of 30g (95 mmole) of $Na_2[Fe(CN)_5NO].2H_2O$ with 120 ml of water was prepared and cooled in an ice-salt mixture. Ammonia was then introduced at 10°C until saturation; the temperature during this operation did not exceed 20°C.

The solution was allowed to remain under a loose cover for 48hr, at 0°C, followed by addition of 90% alcohol to give fine, yellow needle crystals which were collected by filtration.

Yield: 24g(73%) .

SYNTHESIS OF THE COMPLEXES $[Fe(CN)_5L]^{3-}$

(L = p-nitroaniline, o-nitroaniline, p-nitrophenol, o-nitrophenol)

3.2.2. SYNTHESIS OF p-NITROANILINE COMPLEX

The product from the reaction between pentacyanoferrate(II) and p-nitroaniline was prepared in solution by direct substitution, of water, from aquated $[Fe(CN)_5NH_3]^{3-}$ ion. Sodium pentacyanoammineferrate(II) (one gram, 3mmole) was dissolved in 50 ml of distilled water. At least a three-fold excess of ligand (p-nitroaniline) was dissolved in a mixture of 15 ml of water and 25 ml of ethanol. A slight excess of ethanol was added to the ice cooled solution until a precipitate was formed. The bright-yellow needle crystals produced were separated by suction filtration, washed with distilled water and dried over $CaCl_2$ in a desiccator until no further change in weight was noted(24hr).

% yield : 60% ; M.P : 170 -172°C ; elemental analysis: found (calc.) for $Na_3[Fe(CN)_5NH_2C_6H_4NO_2].H_2O$) Na 16.9 (16.79), Fe 13.53(13.62), H_2O 4.54 (4.38)

λ_{max} : 370 nm ; ϵ_{max} : 1.86 x 10^4 $mol^{-1}.cm^{-1}$; IR (KBr disk): ν_{CN} , 2050 cm^{-1}; ν_{FeN} , 410, ν_{NH} , 3363cm^{-1}; NMR: δ(H) ($CDCl_3$) 6.02 (2H, NH_2), 6.75 (2H,Ph), 8.00 (2H, Ph); δ(C) ($CDCl_3$) 155.8 (C-4), 138.4 (C-1), 113.633 (C-3), 126.8 (C-2); Oxidation potential (E^0) of Fe(II) : 0.505 V; Conductivity ($\acute{o}$) : 1.47 x $10^{-6}\Omega^{-1}.cm^{-1}$; Resistivity ($\rho$) : 6.79 x 10^5 Ω. cm; Rate constant (K) : 1.253 x $10^{-4}s^{-1}$.

3.2.3. *SYNTHESIS OF o-NITROANILINE COMPLEX*

Following the same procedure as above, bright-orange needle crystals were separated by suction filtration, washed with distilled water and dried over $CaCl_2$ in a desiccator, until constant weight was obtained.

% yield : 55% ; M.P : 156 -158°C; elemental analysis: found (calc.) for $Na_3[Fe(CN)_5NH_2C_6H_4NO_2].3H_2O$) Na 15.30 (15.43), Fe 12.58 (12.53), H_2O 12.50 (12.10); λ_{max} : 400nm (280 nm) ; ϵ_{max} : 1.16 x10^4 $mol^{-1}.cm^{-1}$; IR (KBr disk): ν_{CN}, 2040, ν_{FeN} ,420, ν_{NH} , 3350cm^{-1}; NMR: δ(H) ($CDCl_3$) 6.66 (2H,NH_2), 7.25 (H, Ph), 7.50 (H, Ph), 7.80 (H, Ph), 8.70 (H, Ph);δ(C) ($CDCl_3$) 145.5 (C-2), 135.6(C-1), 125.9 (C-3), 118.7 (C-4); Oxidation potential (E^o) of Fe(II): 0.320 v; Conductivity ($\acute{o}$) : 2.033 x 10^{-6} $\Omega^{-1}.cm^{-1}$; Resistivity(ρ) : 4.918 x 105 Ω. cm; Rate constant (K) : 1.01x$10^{-4}s^{-1}$

3.2.4. SYNTHESIS OF p-NITROPHENOL COMPLEX

One gram (3mmole) of $Na_3[Fe(CN)_5NH_3].3H_2O$ was dissolved in 50ml of distilled water. 1.5g (10.8mmole) of p-nitrophenol was also dissolved in a mixture of 10 ml of water and 25 ml of ethanol. These solutions were mixed in a 300 ml beaker and cooled in ice-salt (about -7°C) for about 24 hr. A white yellowish fibrous precipitate was separated by suction filtration.

% yield : 54.8 % ; M.P : 163 -165°c; elemental analysis: found (calc.) for $Na_3[Fe(CN)_5OC_6H_4NO_2].2H_2O$) Na 15.90 (16.08), Fe 13.16 (13.05), H_2O 8.54 (8.39); λ_{max} : 372 nm ; ϵ_{max} : 1.11 x 10^4 $mol^{-1}.cm^{-1}$; IR (KBr disk) : ν_{CN} , 2063 , ν_{FeC}, 430, ν_{OH}, 3358cm^{-1}; NMR: δ(H) ($CDCl_3$) 9.50 (H,OH),7.06 (2H, Ph), 8.02 (2H, Ph); Oxidation potential(E^0) of Fe (II) : 0.398 V ; Conductity ($\acute{o}$) : 1.47 x 10-6 $\Omega^{-1}.cm^{-1}$; Resistivity (ρ) : 6.8 x 10^5 Ω.cm; Rate constant (K) : 2.25 x $10^{-5}s^{-1}$.

3. 2.5. *SYNTHESIS OF O-NITROPHENOL COMPLEX*

Following the same procedure as above, light-yellow crystals were separated by suction filtration and dried over $CaCl_2$ in a desiccator for about 48 hr.

% yield : 51.5 %; M.P : 145 - 147^{0}C; elemental analysis: found (calc.) for $Na_3[Fe(CN)_5OC_6H_4NO_2].2H_2O$) Na 16.0 (16.08), Fe 13.18 (13.05), H_2O 8.62 (8.39); λ_{max} : 350 nm (285 nm); ϵ_{max} : 2.04 x 10^4 $mol^{-1}.cm^{-1}$; IR (KBr disk): ν_{CN}, 2045 ν_{FeC}, 450, ν_{OH}, 3235cm^{-1}; NMR: δ(H) ($CDCl_3$) 10.50 (H, OH), 7.55 (H, Ph), 7.10 (H, Ph), 6.95 (H, Ph), 8.10 (H, Ph); δ(C) ($CDCl_3$) 155.8 (C-2), 137.3 (C-1), 124.9 (C-3), 119.9(C-4); Oxidation potential (E^0) of Fe(II) : 0.299V; Conductivity ($\acute{o}$) : 1.559 x 10^{-6} $\Omega^{-1}.cm^{-1}$; Resistivity (ρ) : 6.413 x 10^5 Ω.cm; Rate constant (K) : 1.223 x 10^{-5} s^{-1}.

4 RESULTS AND DISCUSSION

CHARACTERIZATION OF THE COMPLEXES

4.1. MELTING POINT

The melting point of the complexes $[Fe(CN)_5L]^{3-}$ were found to be :

L = p-nitroaniline, 170 -172^{0}C , L = o- nitroaniline, 156 -158^{0}C , L = p-nitrophenol, 163 - 165^{0}C, L = o - nitrophenol, 145 - 147^{0}C.

4.2. RESULTS OF FLAME SPECTROPHOTOMETRY

Table 2 Reading of flame spectrophotometry for standard solution

standard (ppm) solution	Flame photometer Reading				
	1st	2nd	3rd	4th	Average
100	17	17	17	17	17
200	38	41	41	40	40
300	56	55	55	57	55
400	76	74	75	75	75

Table 3 Reading of flame spectrophotometry for sample solutions

Sample complexes	Flame photometer reading
p-nitroaniline	31
o-nitroaniline	26
p-nitrophenol	30
o-nitrophenol	29

The calibration curve of the standard solution is given below:

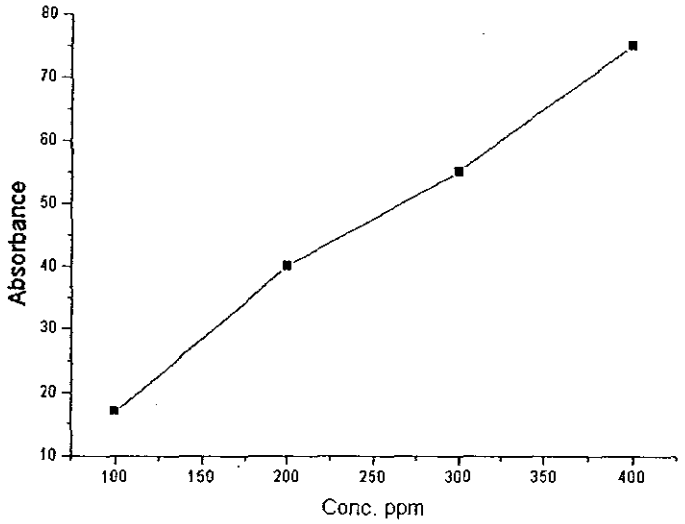


Fig .1. Calibration curve for sodium standard solution.

From the calibration curve the concentration of sodium in the complexes of the four sample were obtained as follows.

Table 4. Estimated concentration of Na from fig. 1

Complex*	Concentration of Na (ppm)
I	169
II	153
III	159
IV	160

Table 5. Analytical data for Na and Fe in the complexes

Complex*	Na%		Fe%*	
	calc.	found	calc.	found
I	16.79	16.90	13.62	13.53
II	15.43	15.30	12.53	12.58
III	16.08	15.90	13.05	13.16
IV	16.08	16.0	13.05	13.18

** Iron was determined, in soil Lab of Ministry of Agricalture.*

4.3 IR - SPECTRAL STUDY

IR spectra were obtained using thin KBr disks of the complexes, $Na_3[Fe(CN)_5L]xH_2O$, where L = p-nitroaniline, or o- nitroaniline p-nirtophenol and o-nitrophenol.
Frequencies, assignments and intensities of the major bands in the spectra of the complexes are given in table 6. The major frequency data for the free para- and ortho-nitroaniline and nitrophenol are given in table 7.

The four synthesized complexes ($Na_3[Fe(CN)_5L]xH_2O$) were numbering as following:
*I = (L is p-nitroaniline)
II = (L is o-nitroaniline)
III = (L is p-nitrophenol)
IV = (L is o-nitrophenol)

Table 6 IR frequencies (cm^{-1}) and asignments of the complexes (KBr pellets)

Complex I	* Assignment	Complex II	* Assignment
3589(vs)	ν_{H2O}(asy)	3475(s)	ν_{H2O}
3521(m)	ν_{H2O}(sy)	3350(m)	ν_{NH}
3363(m)	ν_{NH}	2040(s)	ν_{CN}
2050(s)	ν_{CN}	1629(s)	ν_{CH}
1633(s)	ν_{CH} , ν_{NO2}	1569(m)	ν_{NO2}
1301(m)	ν_{NO2}	1346(m)	ν_{NO2}
410(w)	ν_{FeCN}	420(w)	ν_{FeCN}

Complex III	* Assignment	Complex IV	* Assignment
3480(s)	ν_{H2O}	3415(s)	ν_{H2O}
3358(m)	ν_{OH}	3235(m)	ν_{OH}
2063(s)	ν_{CN}	2045(s)	ν_{CN}
1632(s)	ν_{CH}	1615(s)	ν_{CH}
1590(m)	ν_{NO2}(asy)	1587(m)	ν_{NO2}
1299(m)	ν_{NO2}(sy)	1350(m)	ν_{NO2}
430(w)	ν_{FeCN}	450(w)	ν_{FeCN}

(ν : designates the stretching vibrations β : designates the bending vibrations)
** Assingments are assigned based on K. Nakamota [22] system.*
Intensities in parenthesis (vs = very strong, s = strong, m = medium, w = weak)

Table 7 IR-Frequencies (cm^{-1}) and asignments for the free ligands (KBr pellet)

p-nitroaniline	* Assignment	o-ntroaniline	* Assignment
3450(s)	ν_{NH2}	3448(s)	ν_{NH2}
1640(m)	β_{NH2}(sy)	3333(m)	ν_{NH2}
1470(w)	ν_{NO2}	1613(s)	β_{NH2}
1450(s)	ν_{CH}	1563(s)	ν_{NO2}
1320(m)	ν_{NO2}	1493(m)	ν_{CH}
1110(m)	β_{NH2}(asy)	1333(vs)	ν_{NO2}
840(w)	β_{CH}	960(w)	β_{CH}

p-nitrophenol	* Assignment	o-nitrophenol	* Assignment
3330(s)	ν_{OH}	3250(m)	ν_{OH}
3130(s)	ν_{CH}	1180(s)	β_{OH}(asy)
1590(s)	ν_{NO2}	1250(s)	β_{OH}(sy)
1330(vs)	ν_{NO2}	1320(s)	ν_{NO2}(asy)
1110(s)	ν_{CH}	1340(s)	ν_{NO2}(sy)
860(m)	β_{NO2}	1250(vs)	ν_{CH}
760(vs)	β_{NO2}	860(m)	β_{NO2}

(ν : designates the stretching vibrations β :designates the bending vibrations)
** Assignments are assigned based on K. Nakamota [22] system*
Intensities in parenthesis (vs =very strong, s = strong, m = medium, w = weak)

DISCUSSION

Fe - CN stretching bands

In addition to the C ≡ N stretching bands, the cyano complexes exhibit Fe - C (410 - 450cm^{-1}) stretching, Fe - C ≡ N and C -Fe - C bending bands in the lower frequency region.

The M - CN stretching frequencies in $[Fe(CN)_6]^{3-}$, $[Mn(CN)_6]^{3-}$, and $[Fe(CN_6)]^{4-}$, are reported [22] to be 505cm^{-1}; 514 cm^{-1} and 584cm^{-1} respectively. The IR spectra of the synthesized complexes are given in table 6, the Fe-C stretching frequencies are higher for compounds II (420cm^{-1}) compared to compound I (410 cm^{-1}) and IV (450cm^{-1}) compared to compound III (430cm^{-1}) This might be due to the precesence of " low Fe-L π-bonding".

N - H STRETCHING BANDS

The N-H stretching band of the aromatic amine appears in the 3235 - 3363 cm^{-1} region of the spectrum in all the pentacyano ferrate(II) complexes of para and ortho nitro anilines.

The N - H stretching band of the p-nitroaniline complex (3363cm^{-1}) absorbs at higher frequency than the N - H of the o-nitroaniline complex (3350cm^{-1}). The N-H stretching band of p- nitrophenol complex (3358cm^{-1}) is higher than o-nitrophenol complex (3235cm^{-1}). This may be due to the presence of a hydrogen bond between the ortho nitro and the neighbouring NO_2 group . Peaks at 1569 - 1590cm^{-1} region were asigned to symmetric deformation of N - H bond.

WATER BANDS

The spectra of the samples with different degree of hydration appeared similar. The position and shapes of 3589cm^{-1}, 3475cm^{-1}, 3480cm^{-1}, and 3415cm^{-1} bands in the spectra and the splitting observed in all the complexes might be due to existence of strong hydrogen bonding and due to the presence of non-equivalent numbers of water molecules in each crystal.

Water in inorganic salts may be classified either as lattice water or coordinated water [22]. There is, however, no definite border line between the two. The former denotes water molecules trapped in the crystal lattice either by a weak hydrogen bonds to the anion or by weak coordinate bond to the metal, or by both, whereas the latter denotes water molecules in the first coordination sphere of the metal.

In general, lattice water absorbs at 3550 - 3200 cm^{-1} (antisymmetric and symmetric O - H stretching modes) and at 1630 - 1600 cm^{-1}(H-O-H bending mode) [22, 21]. If the spectrum is examined under high resolution, the fine structure of these bands is observed. For example Katz and Ben Altabef[2] found eight peaks between 3500 - 3400cm^{-1} in $CaSO_4 \cdot 2H_2O$. Such a result may indicate the presence of an interaction between the water molecules through hydrogen bonding. The OH stretching frequency of the lattice water was observed at 3415-3589cm^{-1} for the para and ortho nitroaniline and nitrophenol complexes. The bending vibration frequency of
O-H, N-H and the stretching frequency of C-H of the ring were overlap in the region between 1750cm^{-1} and 1450cm^{-1}.

The C ≡ N stretching vibration in $[Fe(CN)_5L]^{3-}$ moieties:

Bands in the region of 2040-2063cm^{-1} (most intense peaks) are assigned to the cyanide stretching vibration. The frequencies and the relative intensities are similar to the corresponding hexacyanometallates[22]. The C-N stretching vibration in complexes such as $[Fe(CN)_5L]^{3-}$, (where L = NH_3, H_2O, py, and pz) are not much affected by the replacement of CN^- by other ligands in the hexacyanometallates [49].

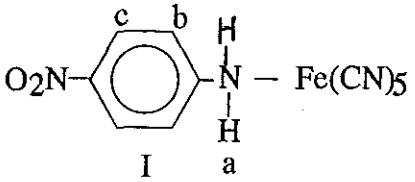
In fact, the C-N stretching wave numbers are not very sensitive to the nature of the sixth ligand because these wave numbers fall in most cases between 2040-2063cm^{-1}.

The hexacyano ferrate(II) anion, for instance, has its most intense ν_{CN} stretching mode at 2050cm^{-1} in the sodium salt [50].

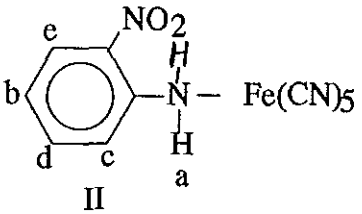
Multiplicity of peaks found in the low wave number region of $[Fe(CN)_5L]^{3-}$ (L = para- and ortho-nitroaniline and nitrophenol) when compared with the $[Fe(CN)_6]^{4-}$ ions [5] may be due to the lower symmetry of the $[Fe(CN)_5L]^{3-}$ complexes and also the influnce of the Fe-L moieties. The ν_{CN} stretching band of complex I and II are 2050 cm^{-1} and 2040 cm^{-1} respectively. The higher CN frequency in complex-I might be due to the strong π-bonding between Fe(II) and the amine of the p-nitroaniline. In complex II, the possible steric effect may decrease the degree of bonding between Fe(II) and the nitrogen of the ortho-nitroaniline. The ν_{CN} frequency of the p-nitrophenol complex (2063cm^{-1}) is higher than the o-nitrophenol complex (2045cm^{-1}). This is an indication of low π-bonding between iron (II) and oxygen of the o-nitroaniline ligand compared to the p-nirtoaniline ligand.

4.4. *NMR SPECTRAL RESULTS*

^{1}H and ^{13}C NMR spectra of the free ligands and complexes.



I



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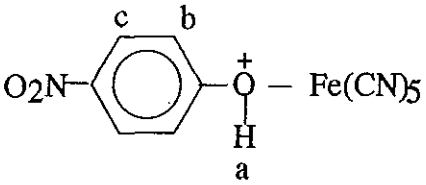
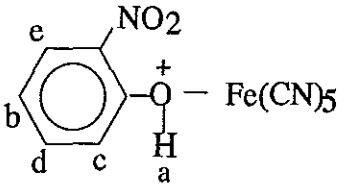


III



IV

Table 8 NMR spectral data

^{1}H NMR of the complexes, δ(ppm) in $CDCl_3$

proton	I	II	III	IV
a	6.02	6.66	9.50	10.55
b	6.75	7.25	7.06	7.55
c	8.00	7.50	8.02	7.10
d	-	7.80	-	6.95
e	-	8.70	-	8.10

Table 9 ^{1}H NMR of free ligands, δ(ppm) in $CDCl_3$

proton	I	II	III	IV
a	6.67	6.25	9.32	10.40
b	6.79	6.67	7.06	7.51
c	8.09	6.85	8.15	7.00
d	-	7.35	-	6.90
e	-	8.08	-	8.00

^{13}C NMR of the complexes, δ(ppm), in $CDCl_3$

Complex I	Complex II	Complex IV
155.89 (C-4)	145.50 (C-2)	155.86(C-2)
138. 47 (C-1)	135.60(C-1)	137.34(C-1)
113.65 (C-3)	125.90(C-3)	124.94(C-3)
126.86(C-2)	118.70 (C-4)	119.92(C-4)
		133.00(C-5)

The ^{1}H NMR spectral data of the complexes show down field shift for the aromatic protons; but for the amine proton the shift is slightly up field. This may be due to the higher electron density shift from the metal to the ligand by back donation through nitrogen atom. The most deshielded proton in benzene ring is the ortho proton in the nitro group; this is expected due to the high electron withdrawing behaviour of the nitro group; where the electron density around the ortho proton is made low. In the ortho nitro complexes compound II and IV, the para-proton is more shielded than the meta-proton. This is probably due to the effect of resonance , the ortho and para positions have slightly higher electron density than the meta proton.

From the ^{13}C NMR spectral data of the complexes we may assign the most deshielded carbon as the one attached to the nitro group(electron withdrawing group). The chemical shift of C-4 in the o-nitroaniline complex of compound II (155.89 ppm) is less than the p-nitroaniline complex I (145.50 ppm) this may be because of the chelating effect of the nitro group with the amine group on the ortho-position. The presence of the electron withdrawing group in the ortho-position increases the electron density around the C-1 and C-2 atoms in the aromatic ring by withdrawing electron density from the nitrogen-iron bond. Since the $[Fe(CN)_5]^{3-}$ moiety has negative charge, the electron density may be drawn by the nitro group in the ortho-position.

4.5. ULTRAVIOLET AND VISIBLE SPECTRAL RESULT S

The absorption of pentacyanoamine ferrate(II) with the concentration of $5x10^{-5}$m in H_2O had a maximum at the wavelength 400nm. The λ_{max}: 277nm, 232nm, 228nm, and 272nm for the ligands p-nitroaniline, o-nitroaniline, p-nitrophenol and o-nitrophenol respectively, in methanol were similar to the literature data[43]. The ligands absorb at shorter wave length, compared to the starting material, pentacyanoamine ferrate(II) and the products.

The observed data of wave lengths (λ_{max}), and molar absorptivity of the ligands and the complexes are given in table 10 and 11 .

Table.10. UV-VI. absorbances of the ligands.

Ligands	Conc.(mol.)	λ_{max}(nm)	Molar absorbitivity($mol^{-1}cm^{-1}$)
p-nitroaniline	$2.3x10^{-2}$	277	5000
o-nitroaniline	$6x10^{-3}$	232	16,000
p-nitrophenol	$1x10^{-1}$	228	7510
o-nitrophenol	$2x10^{-2}$	272	15000

Table.11. UV. VIS absorbance of the complexes.

Complexes	Conc.(mol)	λ_{max}(nm)	Absorbance	Extinction cofficient ($mol^{-1}.cm^{-1}$)
I	$1x10^{-4}$	370	1.86	18600
II	$1x10^{-4}$	400 (280)	1.16	11600
III	$1x10^{-4}$	372	1.11	11100
IV	$1x10^{-4}$	350 (285)	2.04	20400

Complexes $[Fe(CN)_5L]^{3-}$

I = *p*-nitro aniline complex

II = *o*-nitro aniline complex

III = *p*-nitro phenol complex

IV = *o*-nitro phenol complex

In order to compare the electronic spectra of the synthesized complexes with other $[Fe(CN)_5L]^{3-}$ complexes, the electronic spectral data for some complexes of the type $[Fe(CN)_5L]^{3-}$ are given below.

Table.12. Absorption maxima for anions $[Fe(CN)_5L]^{n-3}$

L	H_2O	NH_3	$BuNH_2$	NH_2OH	NH_2OMe	Py	enH
λ_{max}(nm)	394	400	394	434	365	402	402
Reference	51	51	51	51	52	52	40

The position and intensity of the absorption peaks of $[Fe(CN)_5L]^{3-}$ (L = para- and ortho- group of nitroaniline and nitrophenol) are in good agreement with peaks found for other pentacyanoferrate (II) complexes [51, 52] as shown in Table 12. This absorption has been assigned to $^1A_1 \rightarrow {}^1E^a$ electronic transition [51] in the axially distorted $[Fe(CN)_5L]^{3-}$ species (symmetry assumed: C_{4v}[23,40]). Most probably, this band also includes the transition to the second level (^1A) arising from the spliting of the octahedral $^1T_{2g}$ term[23].

Aromatic compounds show a number of bands, e.g.,benzene absorbs at 184 nm (ϵ = 60,000), 240 nm (ϵ = 740) and 254 nm (ϵ = 200). All are $\pi \rightarrow \pi^*$ transitions, and the 254nm band is called the benzenoid band. Hetrocyclic compounds such as pyridine to a large extent have UV spectra similar to those of the analogous benzenoid compounds[46].

Therefore, it is reasonable to compare the UV spectra of nitroaniline- and nitrophenolpentacyanoferrate(II) complexes with the spectra of pyridine pentacyano-ferrate(II) complex. As we can see from the reported spectra of pyridine complex (402nm) and the spectra of the p-nitroaniline (370nm) o-nitroaniline (400nm) p-nitrophenol (372nm) and o-nitrophenol(350nm) complex of this work, there is good agreement showing a slight bathochromic effect for the disubstituted benzene ligand complexes. Substituents on benzene have a bathochromic effect.

In the spectrum of the complexes there is a d-d transition, which is responsible for the colour of the complexes. Peaks at 370 nm for p-nirtoaniline complex, 400nm and (280 nm) for o-nitroaniline, 372 nm for p-nitrophenol and 350 nm (285 nm) for o-nirtophenol complexes may be due to the strong absorption of charge transfer. The high molar absorptivity of the peaks at the observed λ_{max} in the complexes is due to charge transfer , involving a d_{π} metal orbital and a low π^*orbital of ligands.

Shoulders on these absorptions are observed and this may be due to the vibrational components of a π-π^* intra-benzene charge transfer band. Such observation have also been noted in other investigations[4].
Solvents used in, the UV-VIS studies were methanol, water and ethanol. These were selected, because they do not absorb strongly in the spectral region of interest.
Water (λ_{max} < 200nm), methanol (λ_{max} = 210 nm) and ethanol (λ_{max} = 205 nm).

The complexes were scanned after a week, and no appreciable change in absorbance was observed. This is probably an indication of their stability. The spectral data of the complexes at different time interval are given in the appendix.

4.6. CYCLIC VOTAMMETRY MEASUREMENTS

Reversible cyclic votammograms were obtained at sweep rates varying from 50 to 200mV/s, using platinum wires as the auxiliary and working electrodes. All of the measurements were carried out under nitrogen, with millimolar solutions of the penta cyano ferrate(II) complexes, using 10^{-2}M n-tetrabutylamminelithium perchlorate as supporting electrolyte in acetonitryl(solvent). The electonic properties of the compounds can often be probed by examining their electro chemical properties. One electro chemical technique that is particularly useful in establishing the presence of an electroactive species is cyclic votammetry. Cyclic voltammetry is very useful in providing a convenient way of determining (qualitatively) how many reducible species are present, with an indication of their reversibility.

Creutz and Toma[54] have measured formal oxidation potentials(E°) for complexes of the pentacyano ferrate(II) with a number of unsaturated ligands by cyclic voltammetry and potentiometry. For comparison purposes, the data are included here.

Table.13. Oxidation potentials for pentacyanoferrate(II) complexes.

L in$[Fe(CN)_5L]^{n-}$	Oxidation potentials $E^{\circ}(V)$	Reference
H_2O	0.39	54
imidazole	0.35	54
γ-picoline	0.45	54
pyridine	0.48	54
isonicotinamide	0.50	54
pyrazine	0.55	54
N-methyl pyrazinium	0.79	54
Dimethyl sulfoxide	0.89	54
carbonyl	1.18	54
p-nitroaniline	0.505	this work
o-nitroaniline	0.320	this work
p-nitrophenol	0.398	this work
o-nitrophenol	0.299	this work

The oxidation potential obtained for the para- and ortho-nitroaniline and nitrophenol complexes are within the range of related $[Fe(CN)_5L]^{3-}$ complexes as shown in Table 13. The oxidation potential data given in the Table 13 indicate that the oxidation potentials of mononuclear$[Fe(CN)_5L]^{n-}$ complexes are very sensitive to substituent effects on the ligand L, as well as on the nature of the metal-ligand bond.

The plot of current versus potential (see appendix) shows that current is flowing as the potential oxidation (or reduction) is approached and increases until the concentration of electroactive species in the immediate vicinity of the electrode is depleted. At this point the current drops to a constant value that is maintained by diffusion of the electroactive species from the solution. The oxidation-reduction process of the complexes may be represented by the reversible equation as follows:

$$[Fe(CN)_5L]^{3-} \rightleftarrows [Fe(CN)_5L]^{2-} + e^-$$

$$\text{i.e} \quad Fe^{2+} \rightleftarrows Fe^{3+} + e^-$$

4.7. RESISTIVITY AND CONDUCTIVITY MEASUREMENTS

The resistivity and conductivity of the complexes were determined by measuring the resistance of defined pellets of the solid complexes.

Table.14. Observed electrical parameters of the pellets of the complexes.

$[Fe(CN)_5L]^{3-}$ L =	thickness(mm) of pellets	capacitance(pF)	resistance(KΩ)	Impedance(KΩ)
p-nitroaniline	0.53	3.145	27.01	26.65
o-nitroaniline	0.85	2.15	31.35	31.45
p-nitrophenol	0.545	2.26	27.79	27.89
o-nitrophenol	0.55	2.16	26.45	26.65

Diameter of pellets = 13.028mm, Voltage = 0.45V, Current = 0.002mA

The resistivity and conductivity of the pellets of the complexes were calculated by the formula[55] ($\rho = RA/\ell$) and ($\acute{o} = 1/\rho$) where ρ = resistivity, R = resistance, A = cross sectional area, ℓ = length (thickness of the pellets), $\acute{o}$ = conductivity

Table.15. Electrical conductivity and Resistivity

$[Fe(CN)_5L]^{3-}$	ρ Resistivity (Ω.cm)	Conductivity($\Omega^{-1}.cm^{-1}$)
p-nitroaniline	6.796×10^5	1.470×10^{-6}
o-nitroaniline	4.918×10^5	2.033×10^{-6}
p-nitrophenol	6.800×10^5	1.47×10^{-6}
o-nitrophenol	6.413×10^5	1.559×10^{-6}

Electrical conduction of a body is the tendency of electrical charged particles (or current carriers) to flow when an electrical potential difference is applied to the body and is an important property of many materials. The potential difference measures the electrical pressure driving the charges through the body.

Thus conductivity and resistivity of the complexes are related to the strength of the metal - ligand bond. The degree of movement of the charged metal ion in the complex is descriped by the conductivity property of the complex. The resistivity of a body depends partly on the material from which it is made and partly on the shape of the body. As the observed data of resistivity of the complexes indicate (table 15), the syntheszed complexes are semi-conductors. Materials known as semi - conductors have resistivity of the order 10^{-5} - 10^{7} Ω. m at 25^0C [55-60]. In order to compare the resisting or conducting powers of different types of solid materials it is necessary to compare their resistivity or conductivity at a given temperature since these properties are temperature dependent. The only thing that can be said here about the complexes is that they are insulators with a small conductivity by a trace effects or perhaps semi - conductors. This shows that the ligands are bonded to the metal strongly. As other reports on the stablity of pentacyanoferrate(II) complexes [18,19,20] show, they are stable complexes, and the observed low conductivity property of the complexes is thus related to a strong bond between ligands and the Fe(II) ion.

4.8. *Rate constant determination of the formation of the complexes* $Na_3[Fe(CN)_5L].xH_2O$

The rate constants of the reactions of $[Fe(CN)_5OH_2]^{3-}$ with ortho and para group of nitroaniline and nitrophenol were studied. In all the cases, the absorption characteristics of the complexes in the 350 - 375nm region were different from the reactants. The ligands absorb in the U.V region and the aquated pentacyano ferrate(II) absorbs in the region 400 - 450nm. Hence the kinetics of the reactions was followed by monitoring at λ_{max} of the $[Fe(CN)_5OH_2]^{3-}$ at regular time intervals without interference from the products. The range of concentrations of $[Fe(CN)_5OH_2]^{3-}$ and the entering ligands were chosen by trial and error to optimize various factors like rate, range and sensitivity of measurable absorbances etc.. In general, the reactions were all carried out under pseudo first order conditions.

Since the rates were mostly measured under pseudo first order condition, a first order rate equation was applicable. Under these condition, the rate of formation could be written as

$$dp/dt = -dc/dt = kc$$

$$\text{or} \quad dx/dt = k(C_o - x)$$

Where: the integral form of the latter equation is $\ln(C_o/C_o - x) = kt$

Since C_o and $C_o - x$ are proportional to $(A_\infty - A_o/A_\infty - A_t)$, $\ln [(A_\infty - A_o/A_\infty - A_t)]$ versus time gives the pseudo first order rate constant.

The rate constant of the complexes were determined by ploting the observed absorbance data based on the above equation. The results are as follows.

Table.16. Rate constant of the complexes

Complexes $Na_3[Fe(CN)_5L]xH_2O$	k (rate constant) s^{-1}
L = *p*-Nitroaniline	1.253×10^{-4}
L = *o*-Nitroaniline	1.010×10^{-4}
L = *p*-Nitrophenol	2.250×10^{-5}
L = *o*-Nitrophenol	1.223×10^{-5}

As the rate constant results show, the p-nitroaniline and *p*-nitrophenol ligands have more affinity to form a bond with the metal, than their corresponding *o*-nitroaniline and o-nitrophenol ligands. This low affinity of the ortho ligands to form a complex, was also observed in their percentage yield. So this may confirm that the lone pairs of nitrogen and oxygen in NH_2 and OH group respectively,are withdrawn more to the nitro group in the ortho position than that of the para position. The presence of chelate formation in ortho groups may retard the affinity. Steric factor may also be important.

The rate constant of nitroaniline ligands is greater than the nitrophenol ligands. This can be explained by the degree of basicity of the ligands. From the point of view of a nucleophile substitution reactions; strong bases can enter to the nucleophilic substitution reaction, faster than the less basic ligands. Since the nitroanilines are more basic than nitrophenols.

5 CONCLUSION

The result of analytical analysis of Na and Fe by atomic absorption agrees with calculated value in the proposed formulas. The % yield of the p-nitroaniline complex is higher than the rest of the complexes. This may show that the p-nitroaniline ligand has a better bond formation potential than the corresponding ortho isomer (o-nitroaniline) and nitrophenol ligands. Both ^{1}H and ^{13}C NMR spectra are also consistent with the proposed structure.

The IR spectra shows the presence of representative functional groups in the compounds. The stretching vibration frequency of CN group in the four synthesized complexes show slight shift from the CN stretching vibration frequency in hexacyanoferrate(II) complex. This shows that the stretching vibration frequency of CN group does not depend much on the entering (sixth) ligand.

The cyclic voltammogram of the complexes shows a reversible potential of the central iron ion which is comparable to other related pentacyano ferrate(II) complexes. The difference in oxidation potential for the four complexes show the dependence of iron(II) oxidation potential on the type of the ligand.

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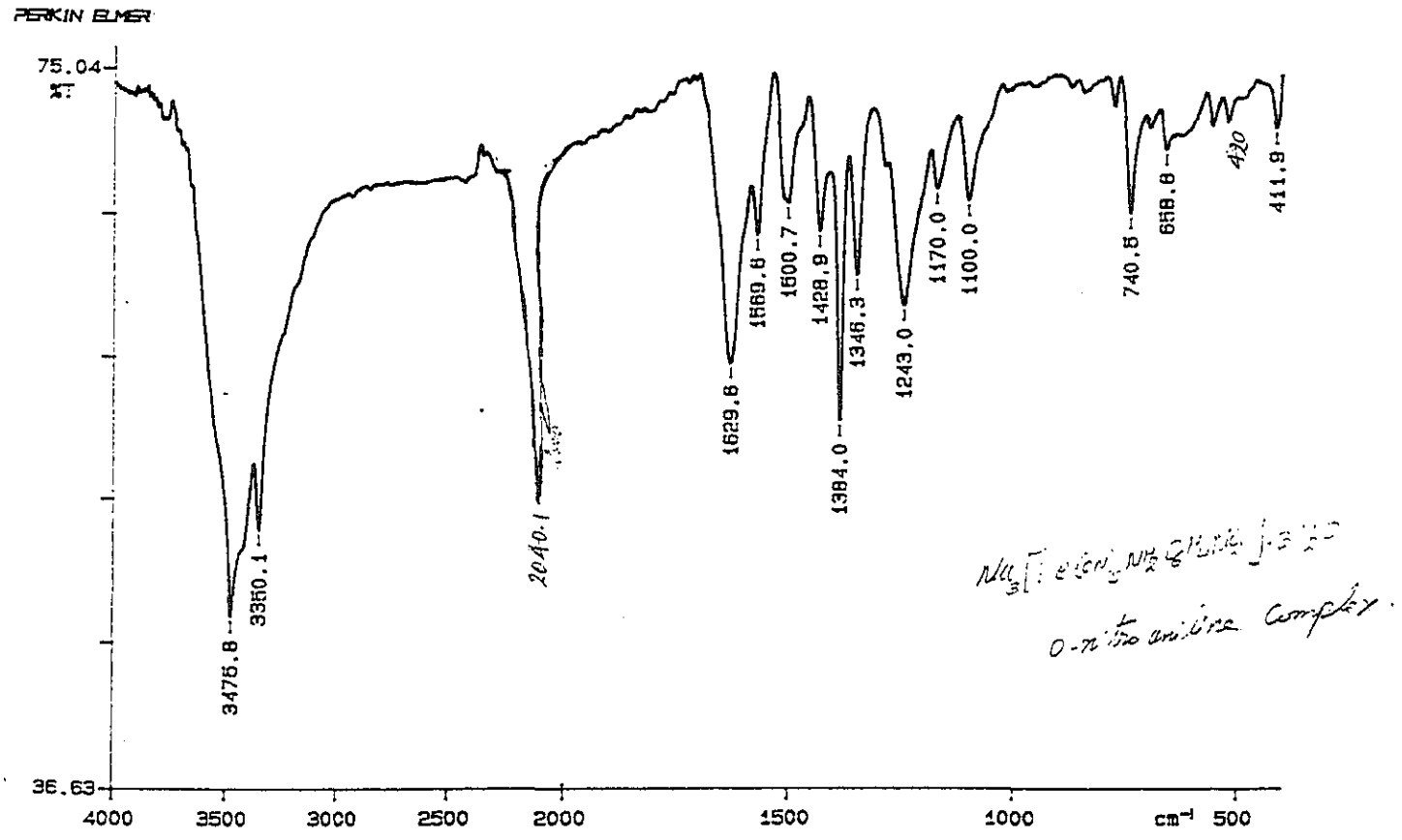
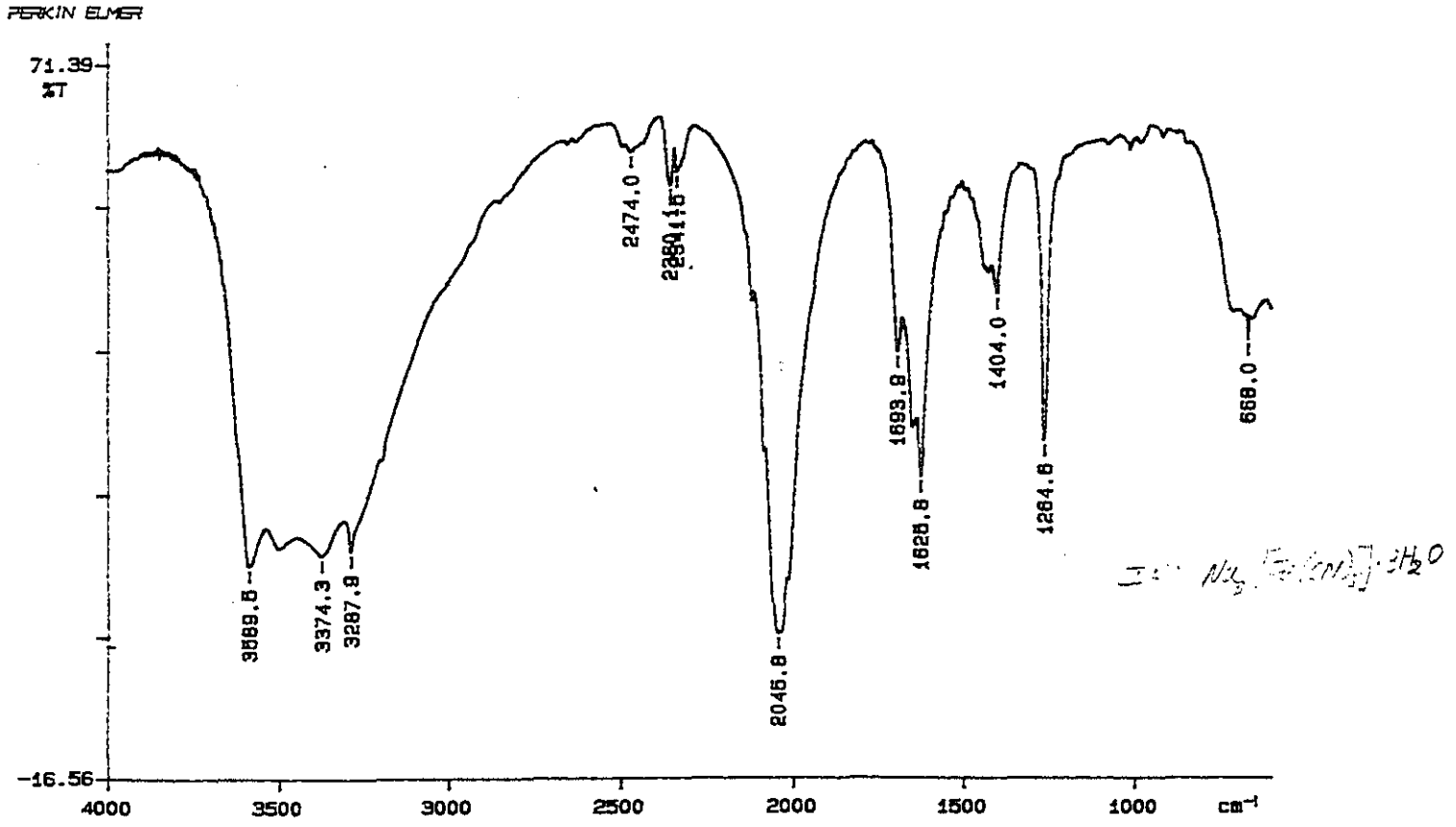
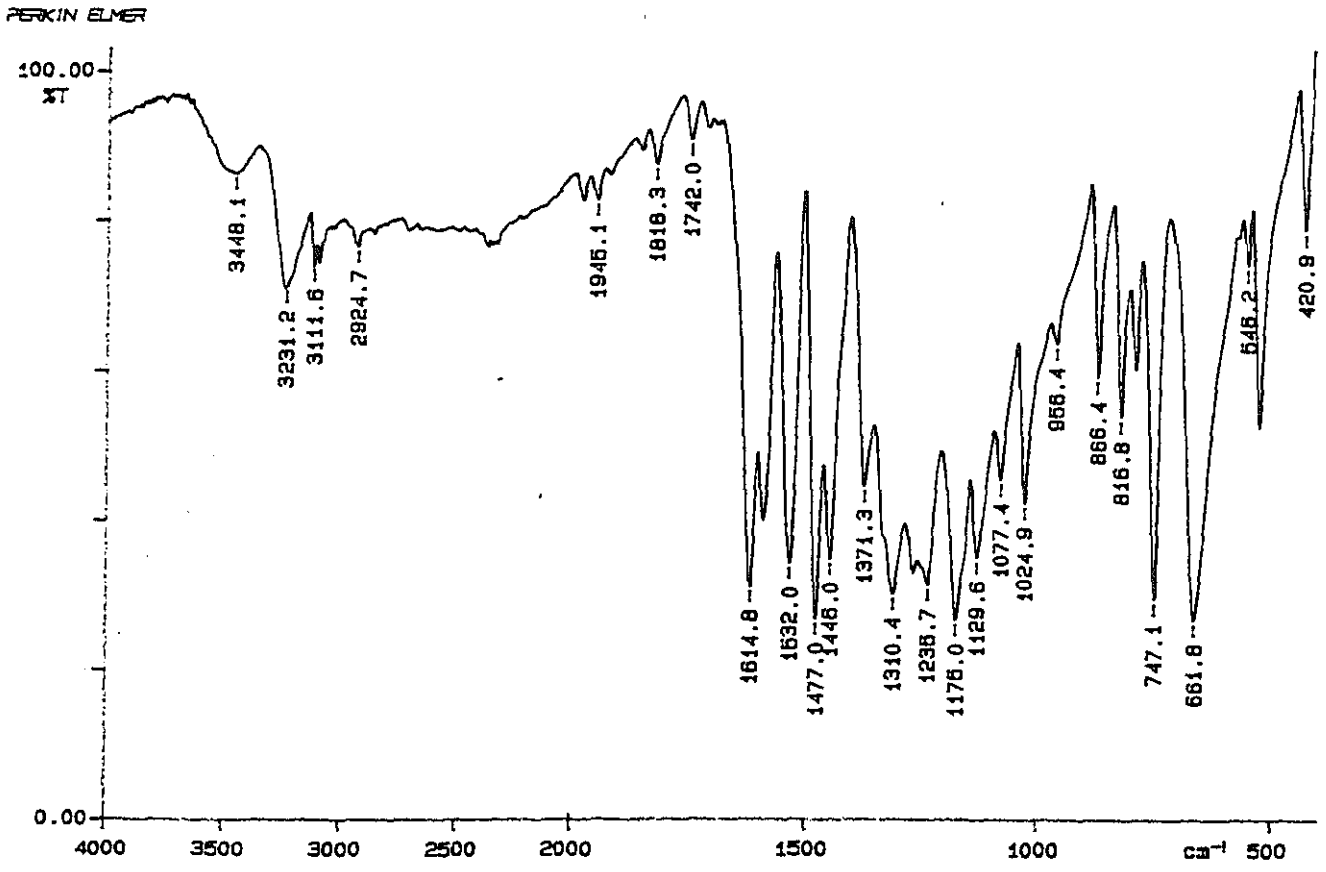


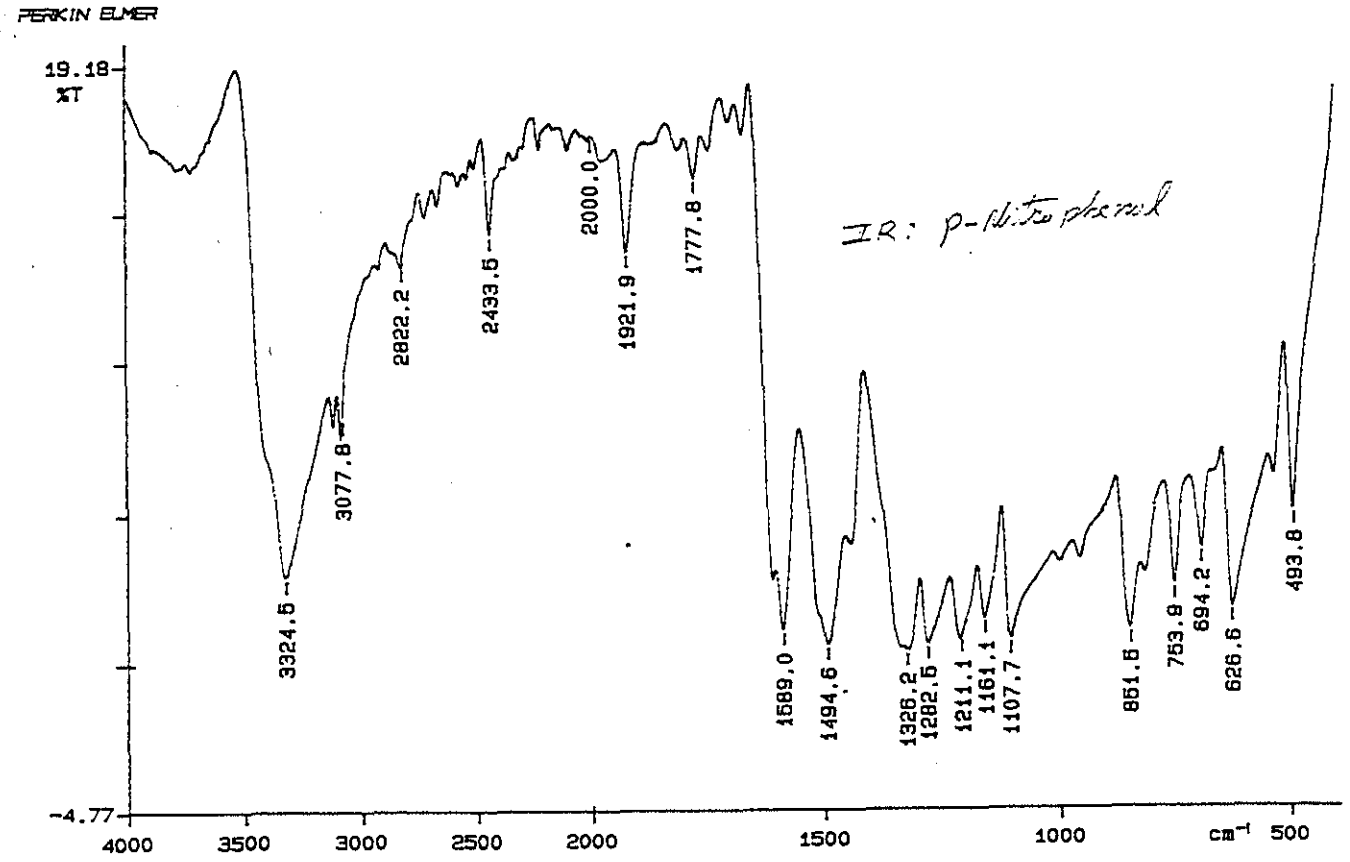
95/03/19 04:45 Beniam K.
X: 4 scans, 4.0cm-1, flat, smooth
O-nitro aniline



94/12/15 10:16 Beniam K.
Y: 4 scans, 4.0cm-1, apod weak, smooth
Na3 (Fe (CN) 5NH3) 3H20

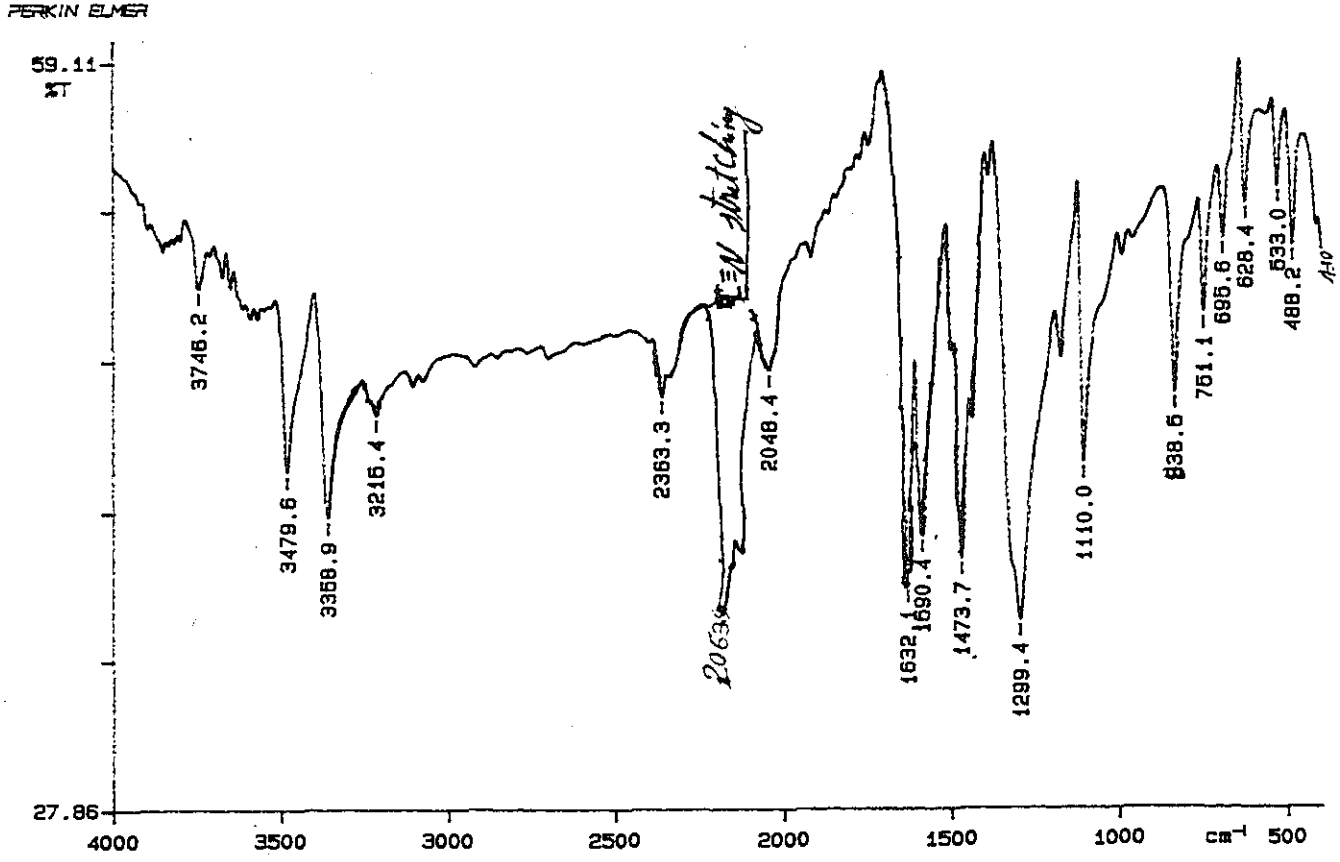


95/05/14 07:08 Kidane F.
X: 4 scans. 4.0cm-1. flat. smooth. abex
O-Nitrophenol

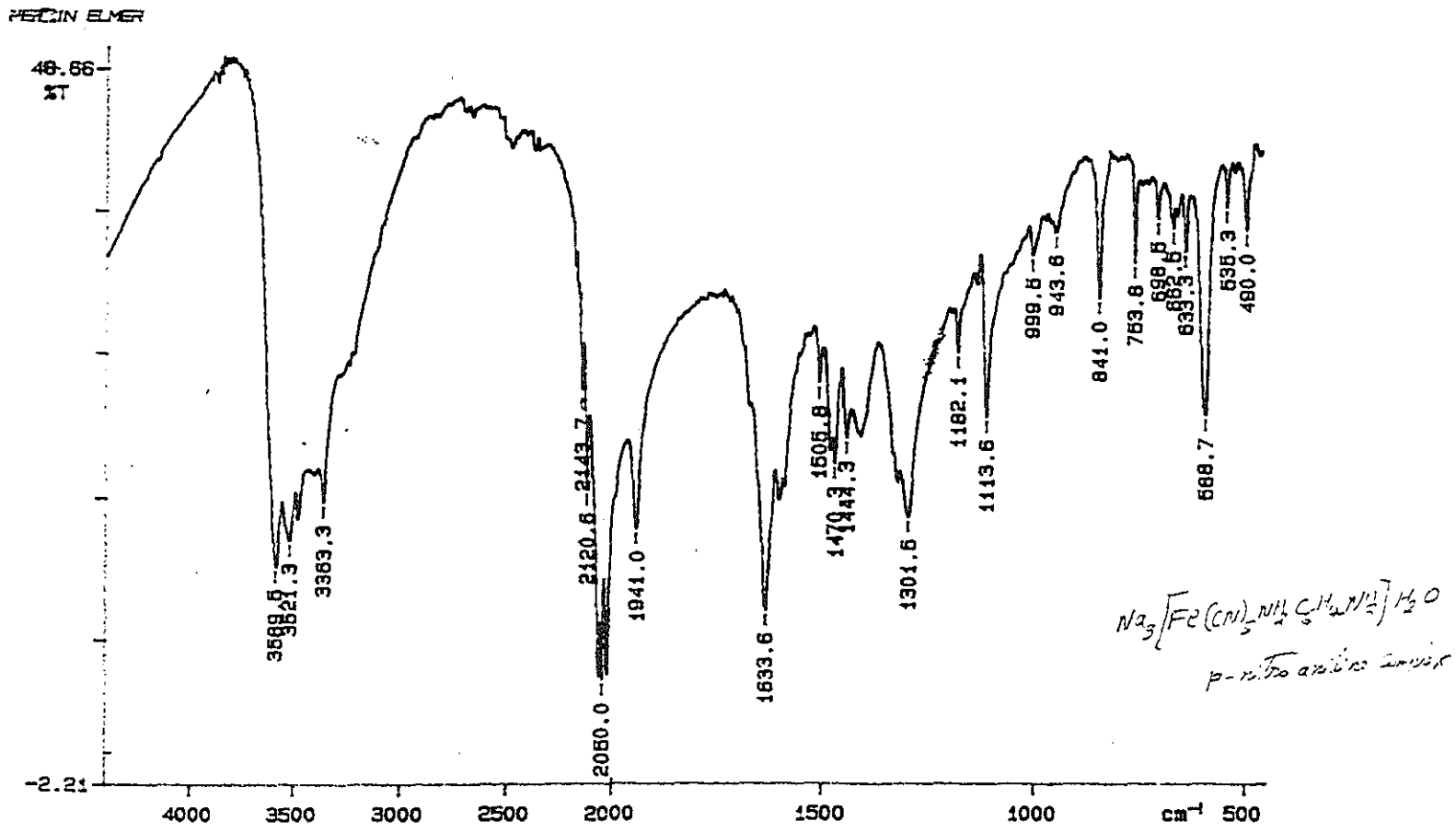


95/02/21 05:27 Kidane F.
X: 4 scans, 4.0cm-1, flat, smooth
P-nitro phenol

Mussie Hagos



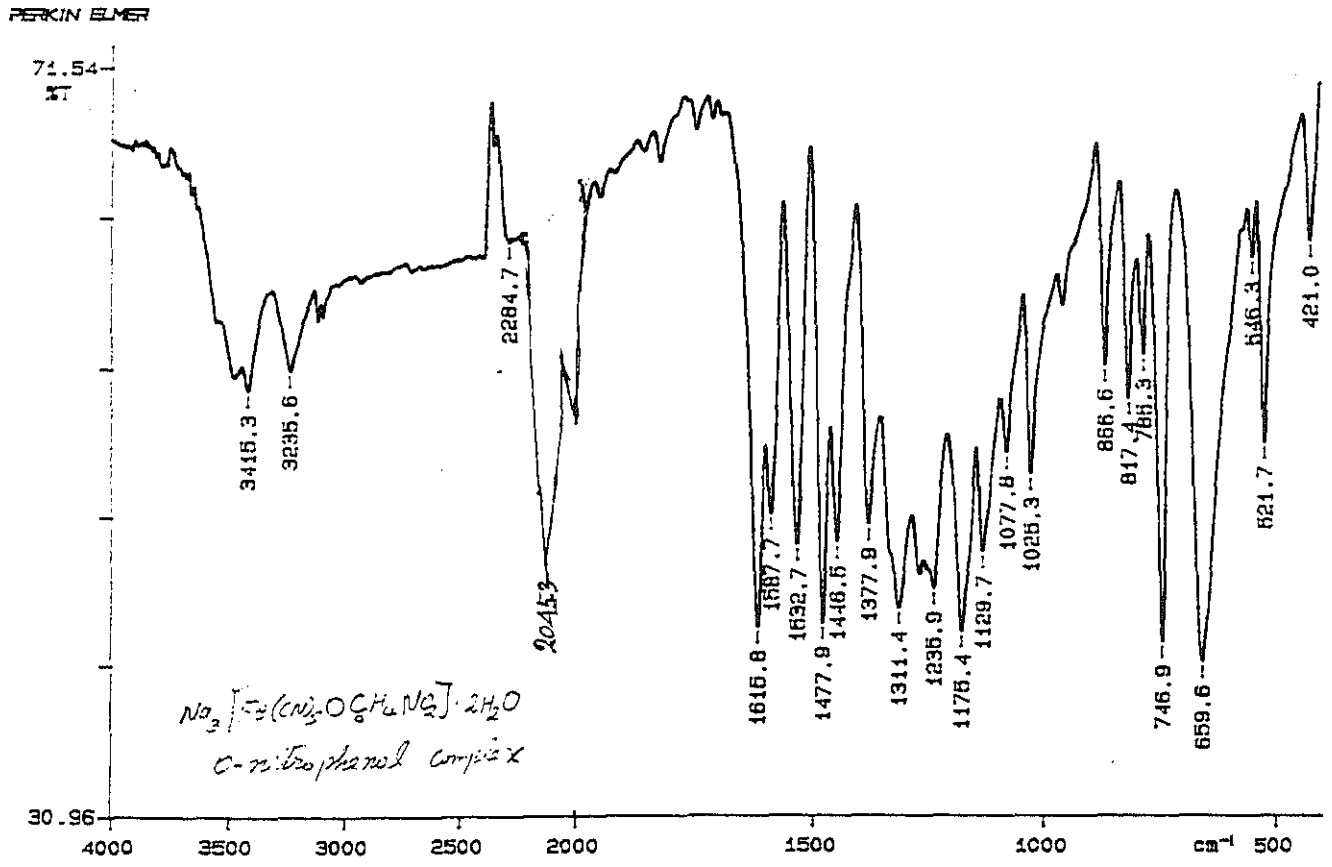
95/02/07 15:16 Beniam K.
X: 4 scans, 4.0cm-1, apod weak, flat, smooth
B



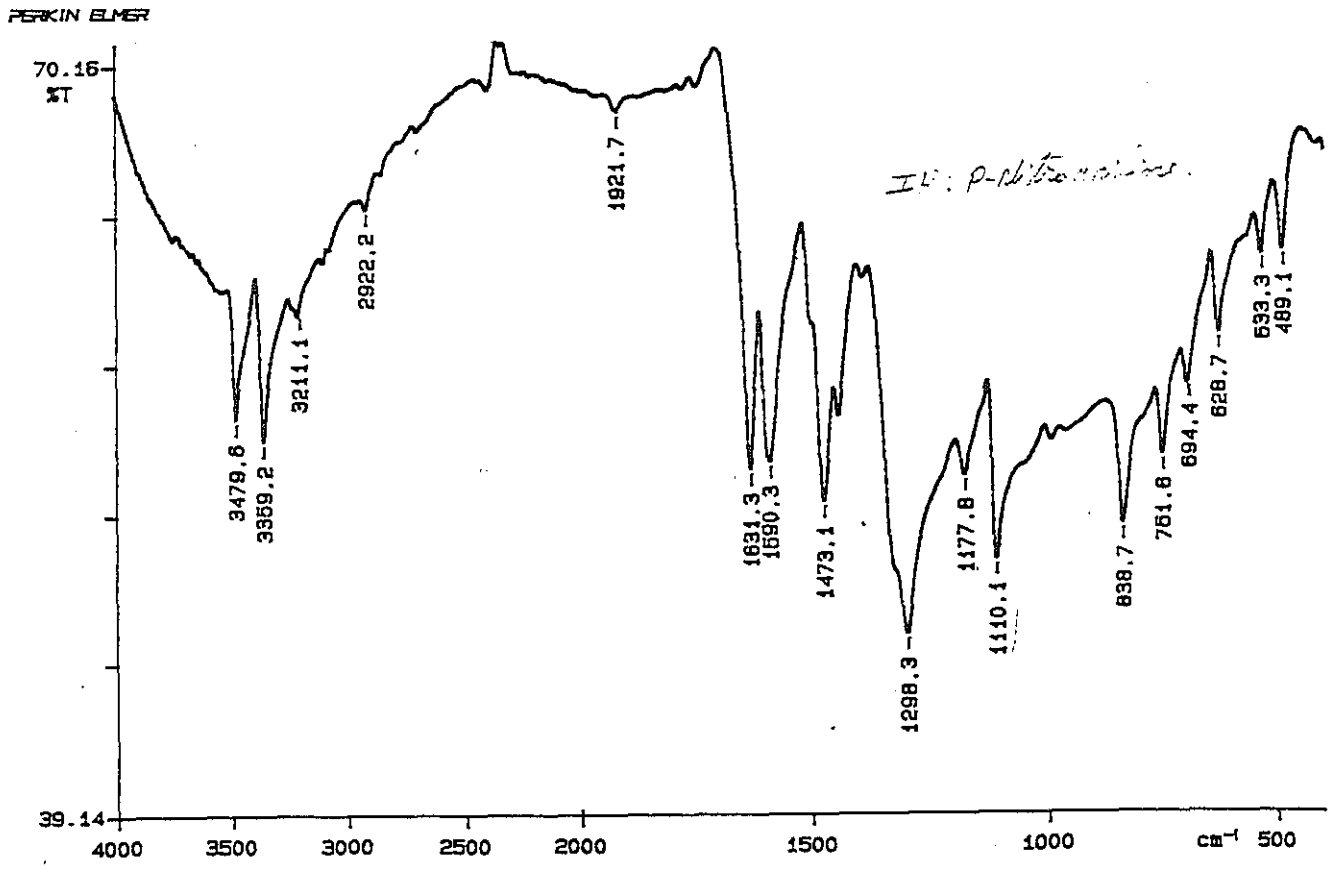
$Na_3[Fe(CN)_5NH_2C_6H_4NH_2]\,H_2O$

p-nitro aniline sample

95/02/12 16:31 Beniam K
X: 4 scans, 4.0cm-1, flat
C



95/03/19 05: 11 Beniam K.
Z: 4 scans, 4.0cm-1, flat, smooth
O-nitro phenol Complex

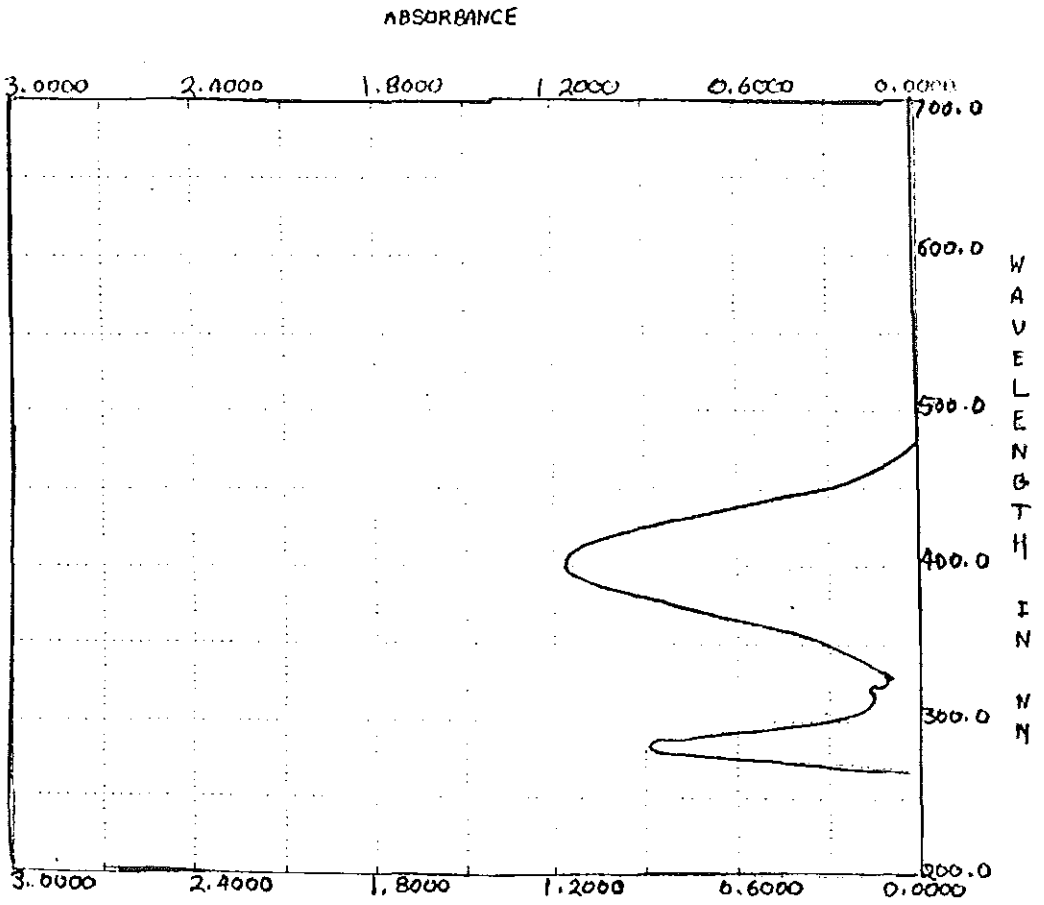


IL: p-Nitroaniline.

Mussia Hagos

BECKMAN

DU-65 SPECTROPHOTOMETER



Scan Speed: 750 nm/min

Electronic spectra of o-nitroaniline complex.

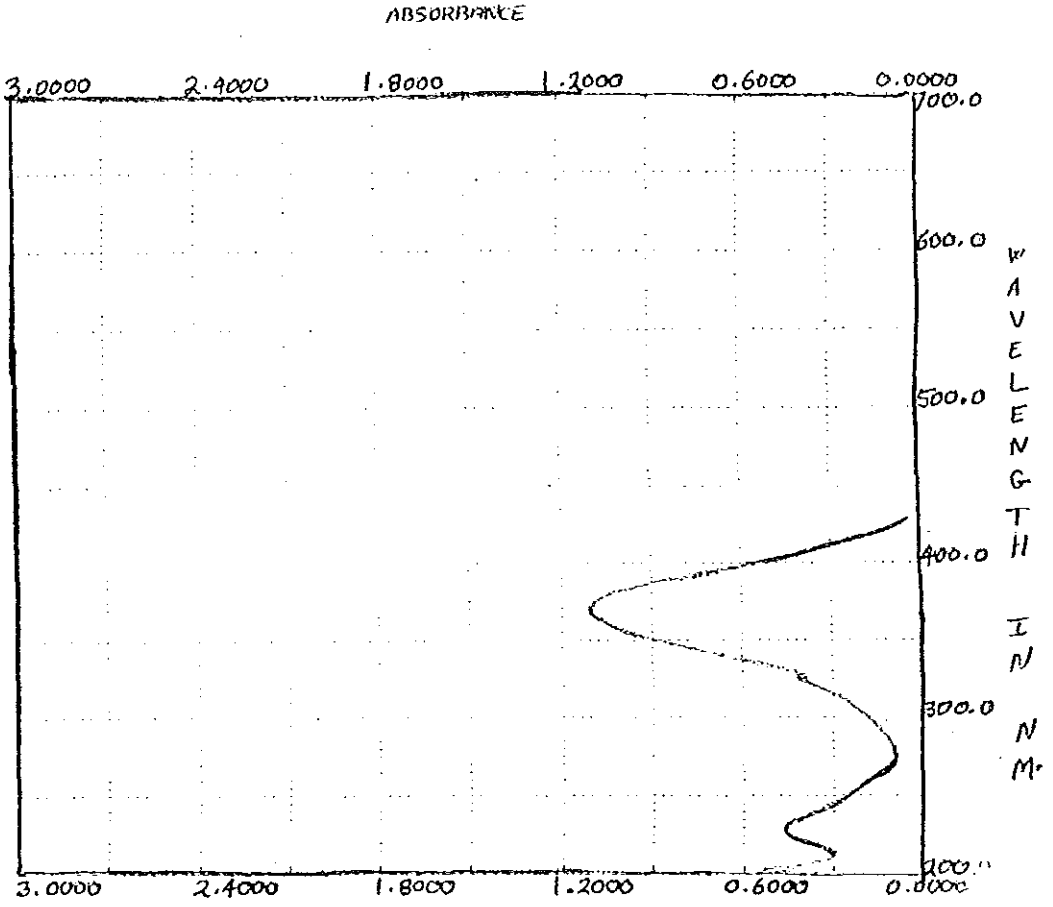
$Na_3[Fe(CN)_5 \cdot NH_2C_6H_4NH_2] \cdot 3H_2O$

Conc: 1×10^{-4} M

Solvent: methanol

BECKMAN

DU-65 SPECTROPHOTOMETER

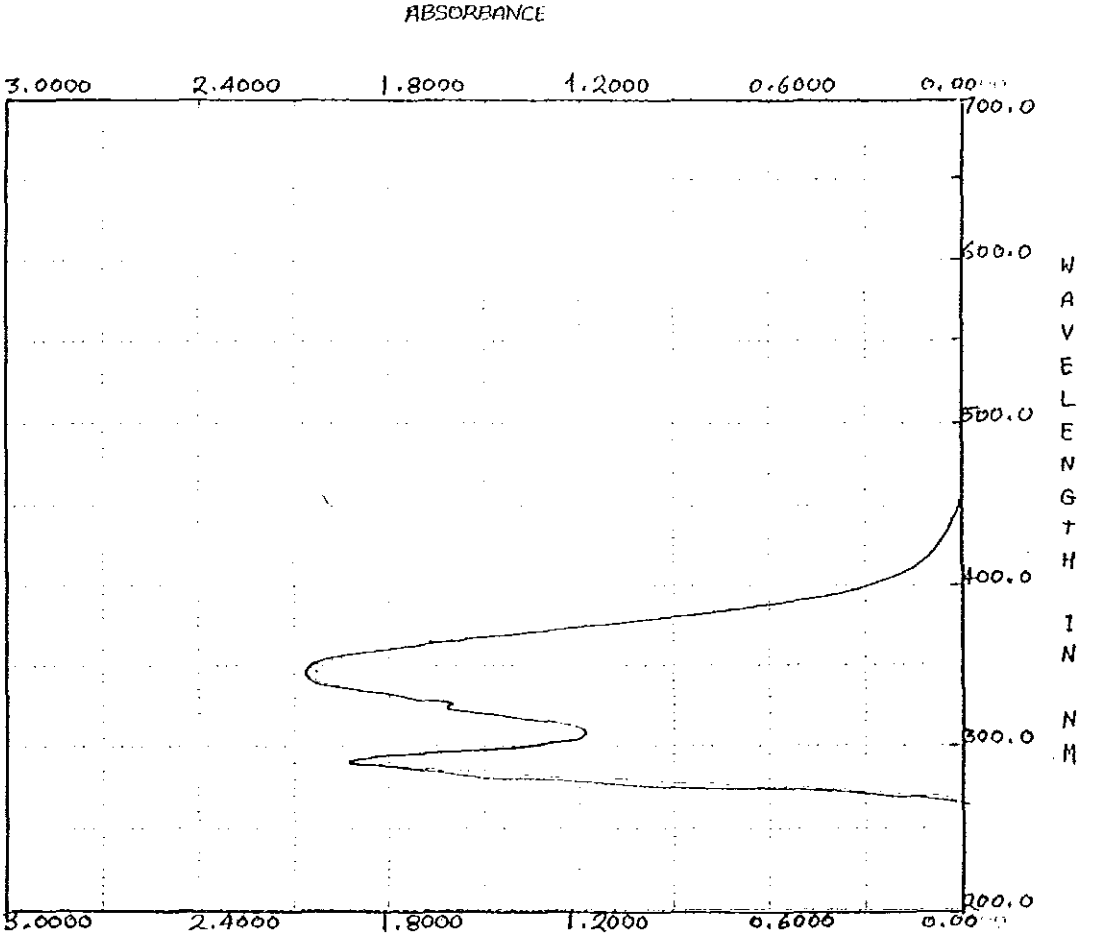


Scan Speed: 750 nm/min

Electronic spectra of $Na_3[Fe(CN)_5OC_6H_4]\cdot 2H_2O$
p-nitrophenol complex.
Conc: 1×10^{-4} M
Solvent: methanol.

BECKMAN

DU-65 SPECTROPHOTOMETER



Scan Speed: 750 nm/min

$Na_3[Fe(CN)_5OC_6H_4NO_2]\cdot 2H_2O$

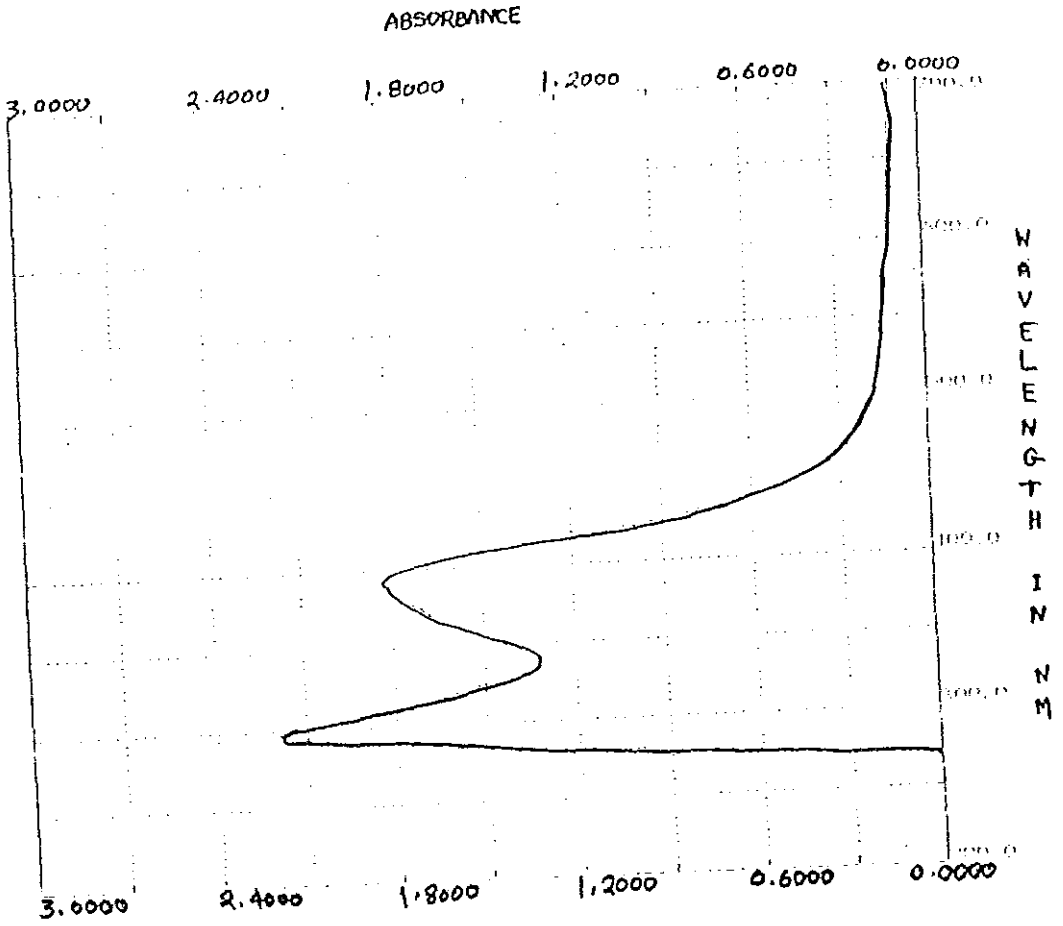
∴ Spectra of o-nitro phenol complex

Conc: 1×10^{-4} M

Solvent: methanol

BECKMAN

DU-65 SPECTROPHOTOMETER



Scan Speed: 750 nm/min

Sodium pentacyanoammine ferrate (II) complex.

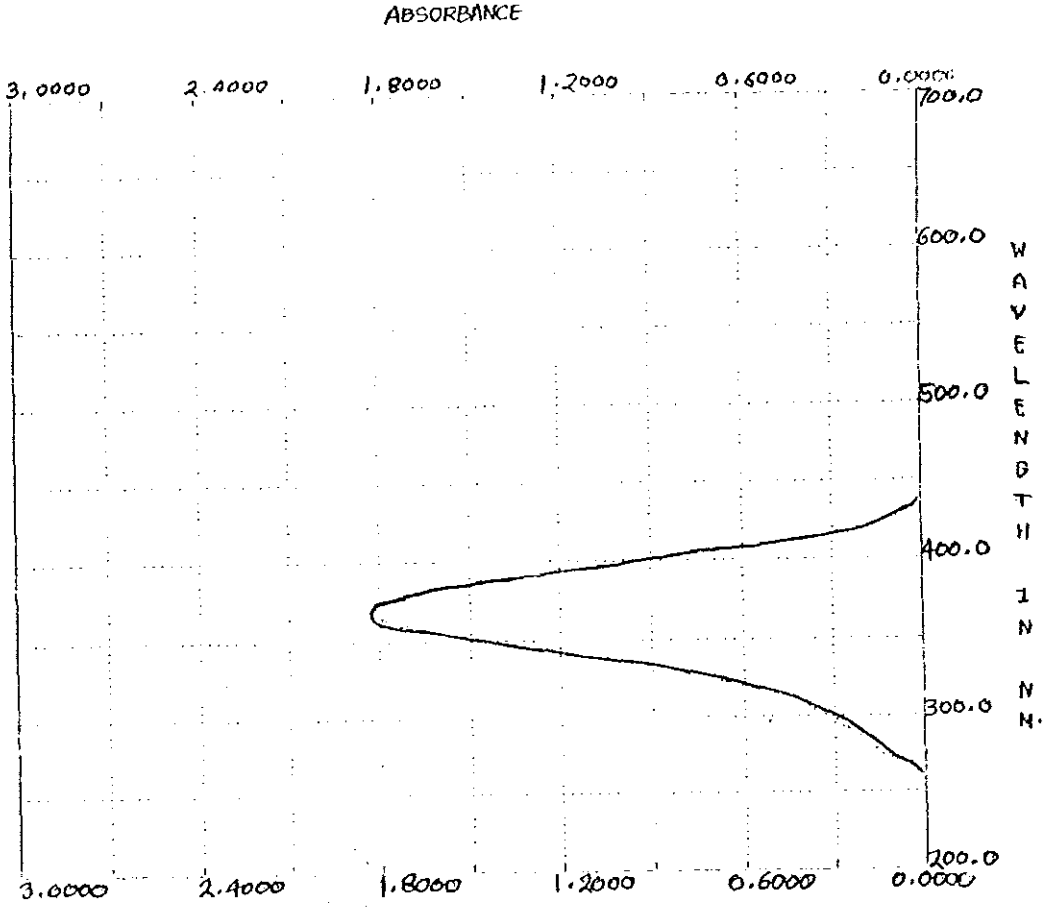
$Na_3[Fe(CN)_5NH_3] \cdot 3\frac{1}{2}H_2O$

Conc: 5×10^{-5} M

Solvent: water

BECKMAN

DU-65 SPECTROPHOTOMETER



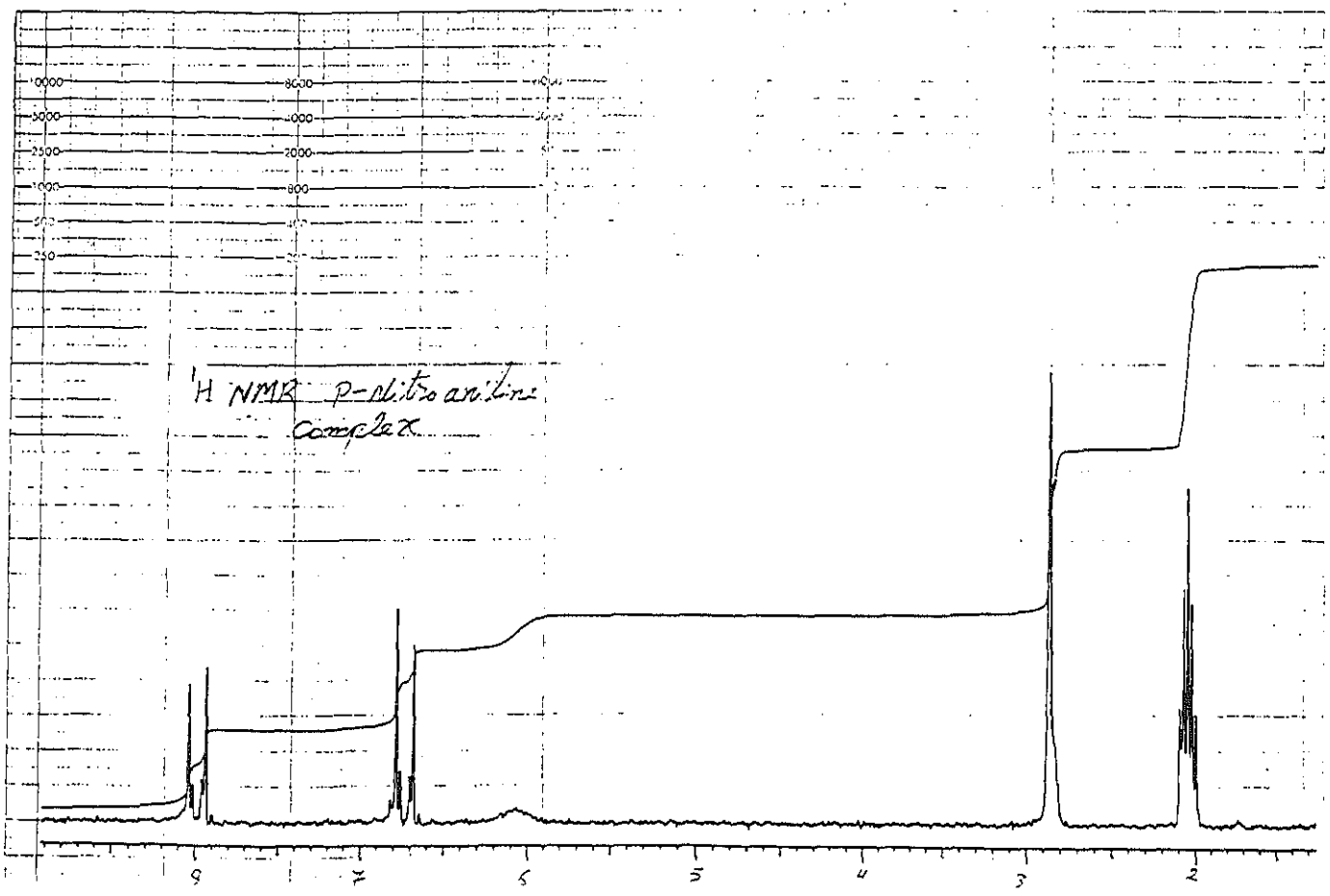
Scan Speed: 750 nm/min

Fig. $Na_2[Fe(CN)_5NH_2C_6H_4NO_2].1\frac{1}{2}O$

p-nitroaniline Complex

Conc. 1×10^{-4} M

Solvent: methanol



Addis Ababa University
Department of Chemistry

NMR Laboratory
Jeol FX-90Q Spectrometer

Spectrum No. MDS-2 V

Sample Code A
Sample Source

Lock 2D/INT
Nucleus
^{1}H (89.6 MHz)
^{13}C (22.5 MHz)

Solvent
Amount in mg
Reference
No. of Pulses
Spectral Width Hz
Amplitude

Saved on File Name
Operator

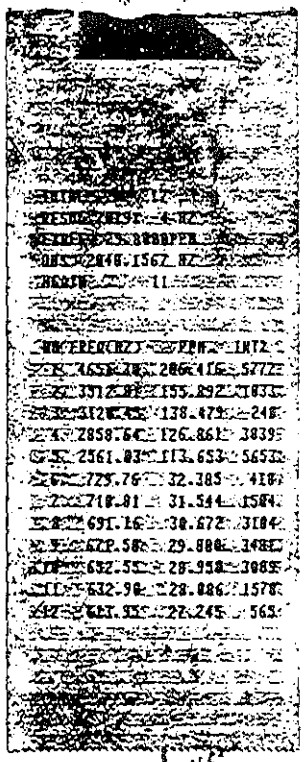
Day Month 199

Suggested structure/Remarks

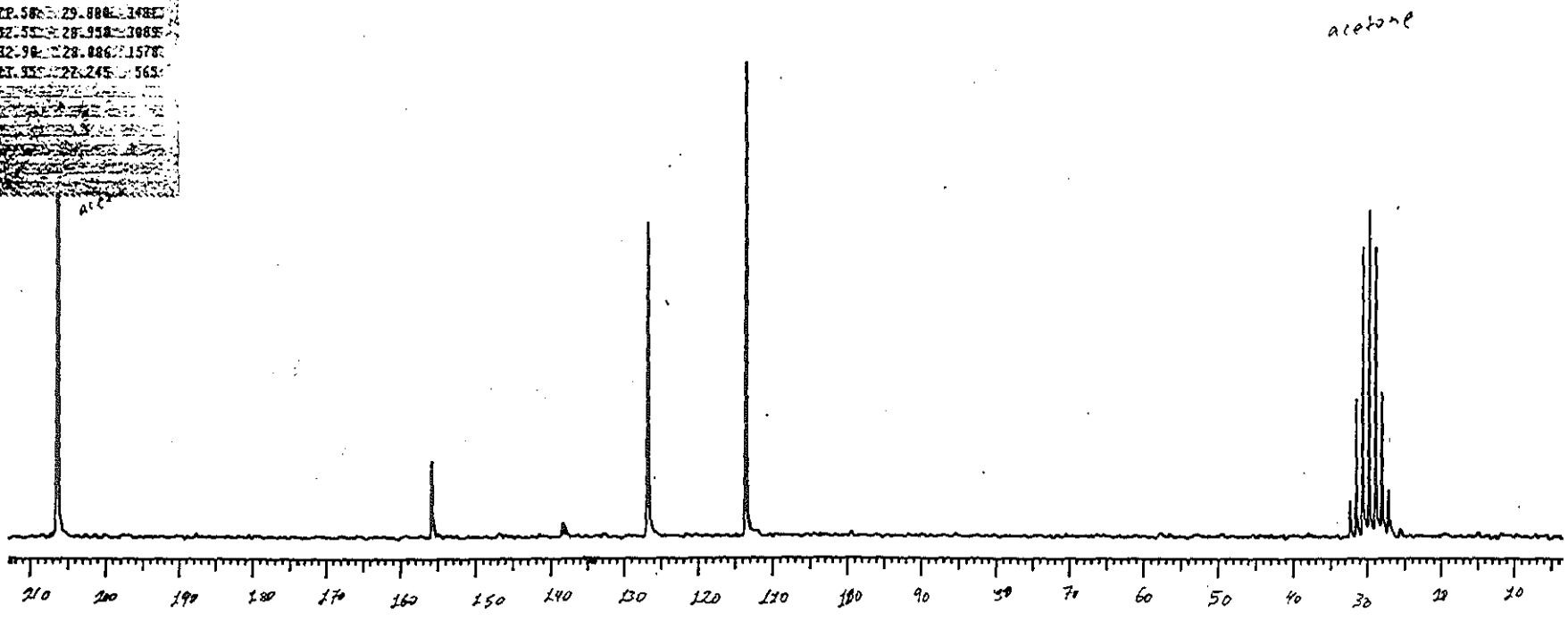
Musie Hagos

^{13}C NMR

Dr Negussie



^{13}C NMR P-nitroaniline complex



Addis Ababa University
Department of Chemistr

NMR Laboratory
Jeol FX-90Q Spectrome

Spectrum No. Musie H.

Sample Code A
Sample Source

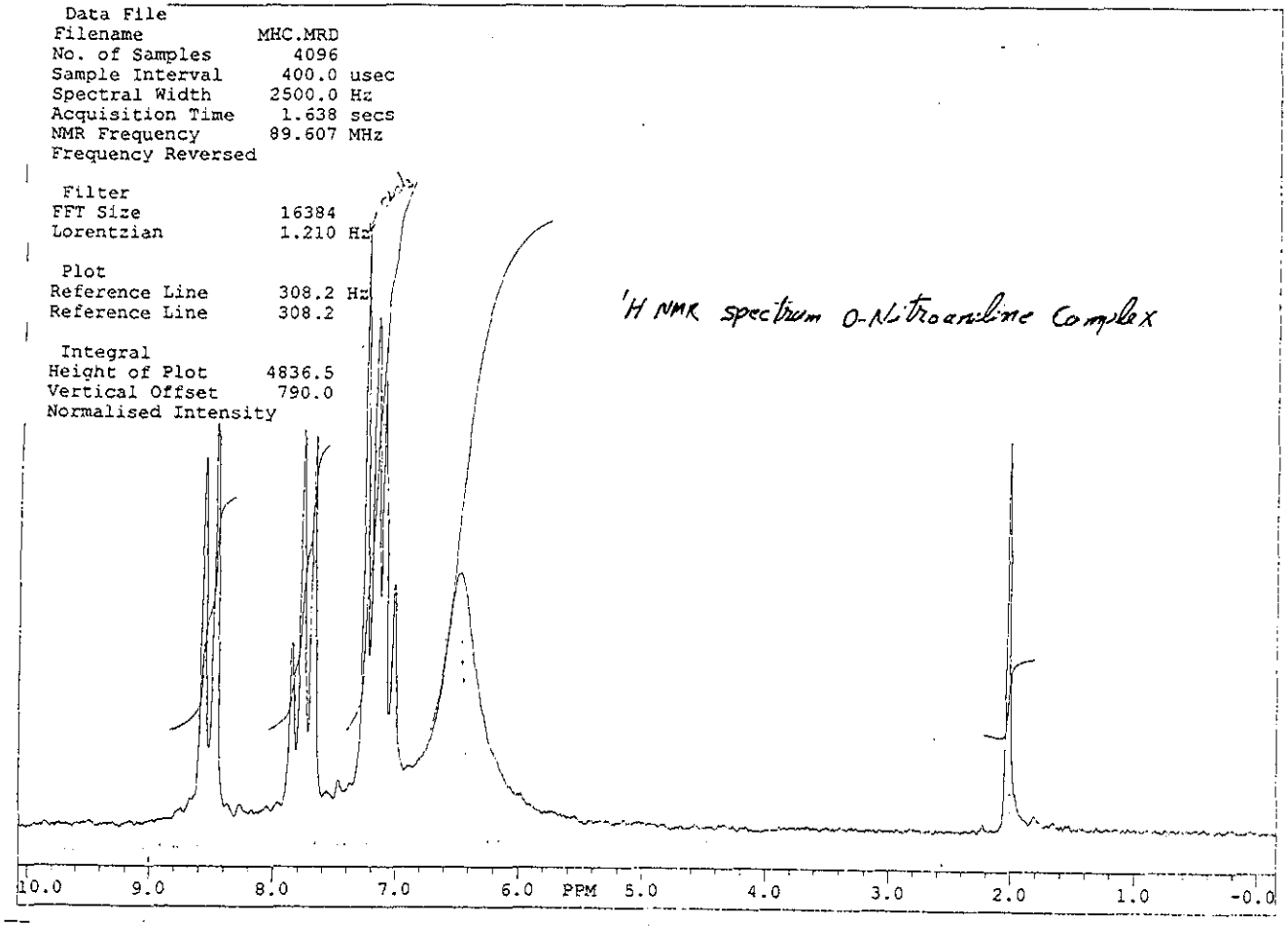
Lock 2D/INT
Nucleus
^{1}H (89.6 MHz
^{13}C (22.5 MHz

Solvent Acetone d_6
Amount in mg
Reference 29-8 11m
No. of Pulses 5000
Spectral Width 5750
Amplitude 19x168

Saved on EDS File Nar
Operator Getahun A

Day 20 Month March

Suggested structure/Rem

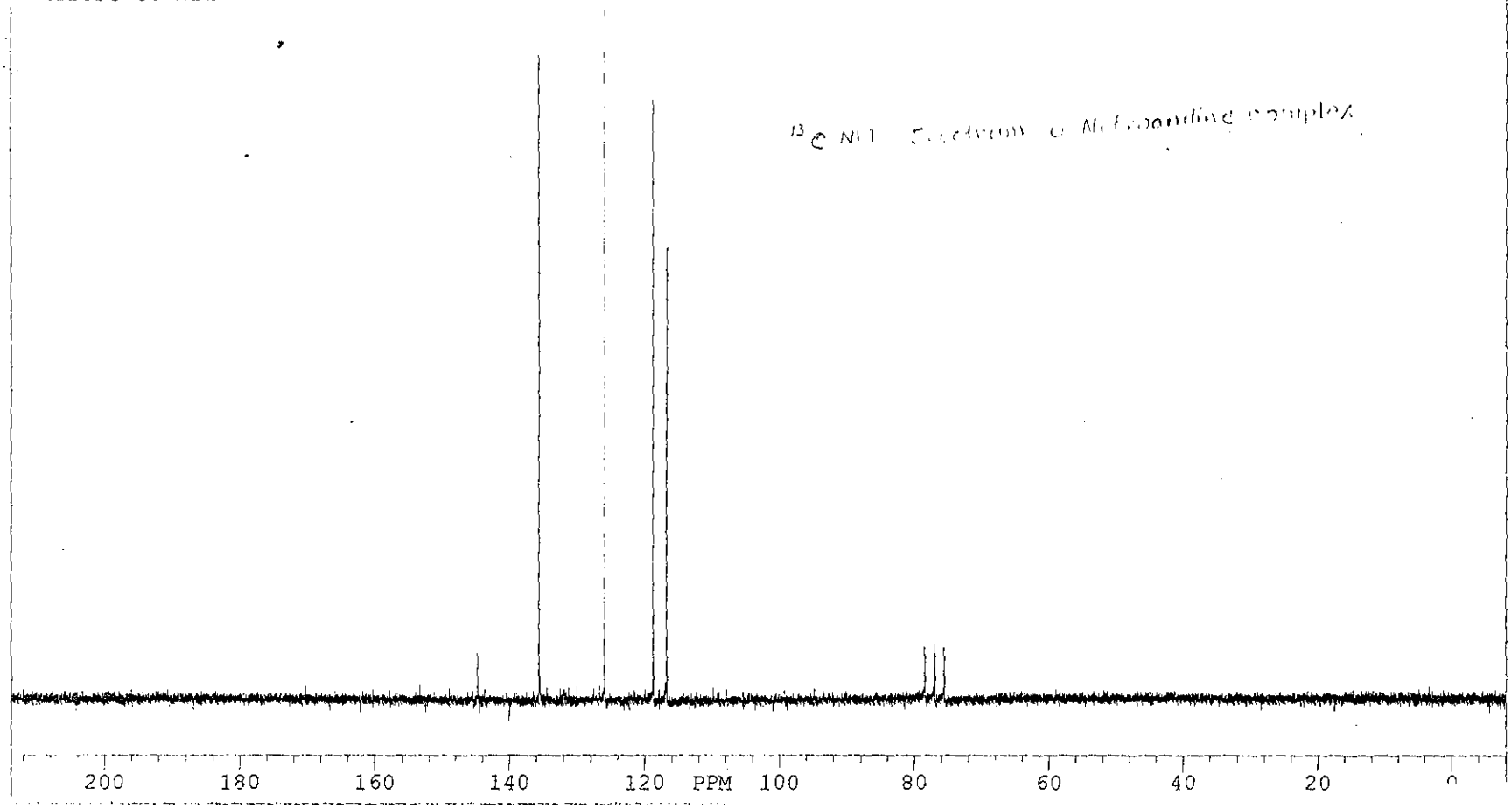


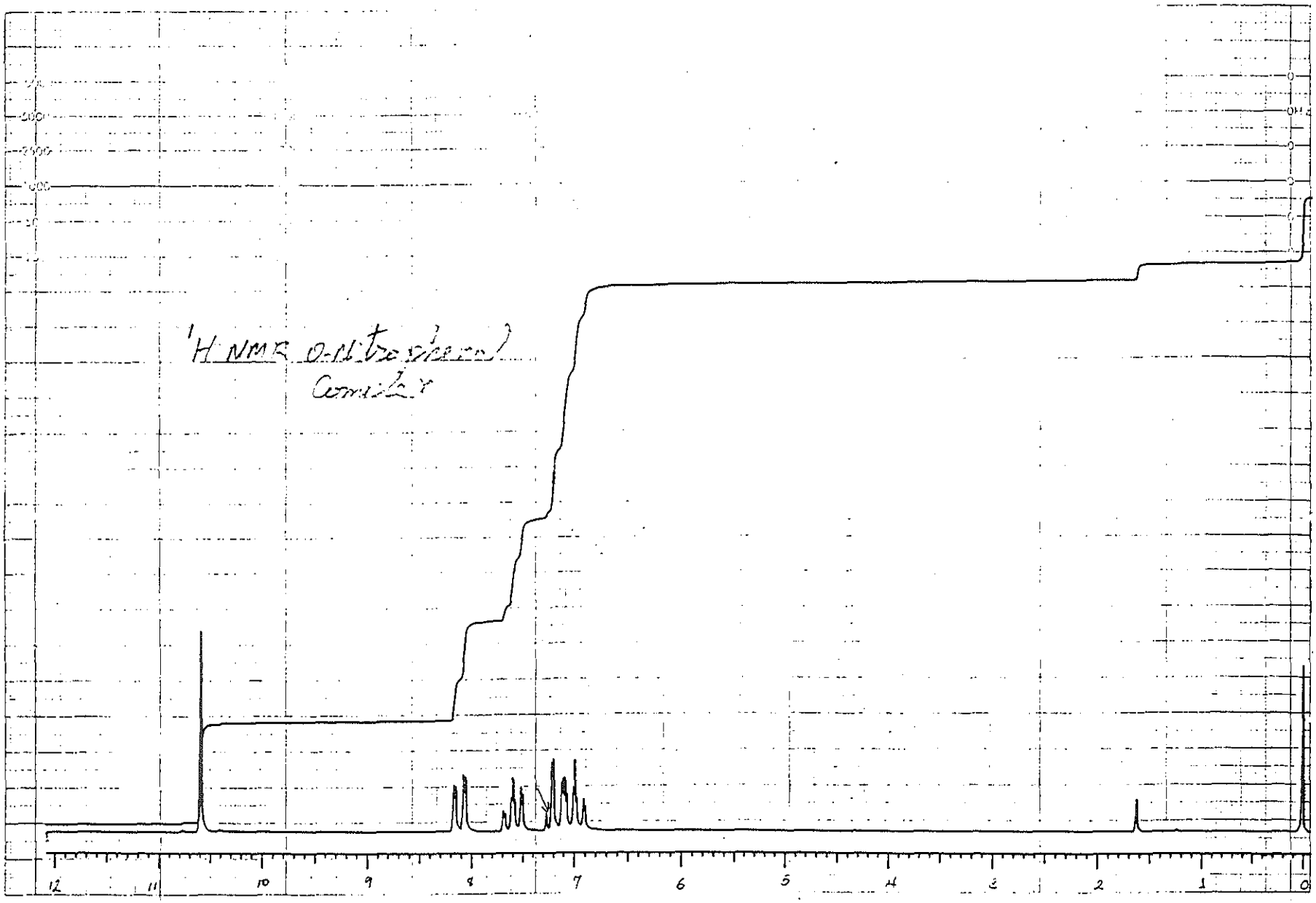
^1H NMR spectrum O-Nitroaniline Complex

Data File
Filename MHCC.MRD
No. of Samples 16384
Sample Interval 200.0 usec
Spectral Width 5000.0 Hz
Acquisition Time 3.277 secs
NMR Frequency 22.534 MHz
Frequency Reversed

Plot
Reference Line -580.7 Hz
Reference Line -580.7

^{13}C NMR Spectrum of Mn(I) complex





Addis Ababa University
Department of Chemistry

NMR Laboratory
Jeol FX-90Q Spectrometer

Spectrum No. Hussie Ha

Sample Code Hussie-
Sample Source

Lock 2D/INT
Nucleus
^{1}H (89.6 MHz)
^{13}C (22.5 MHz)

Solvent $CDCl_3$ + TMS
Amount in mg 15 mg
Reference TMS 0.0 ppm
No. of Pulses 32
Spectral Width 1 900 H
Amplitude 16 x 2dB

Saved on ED-1 File Name
Operator Sue

Day 29th Month March 1

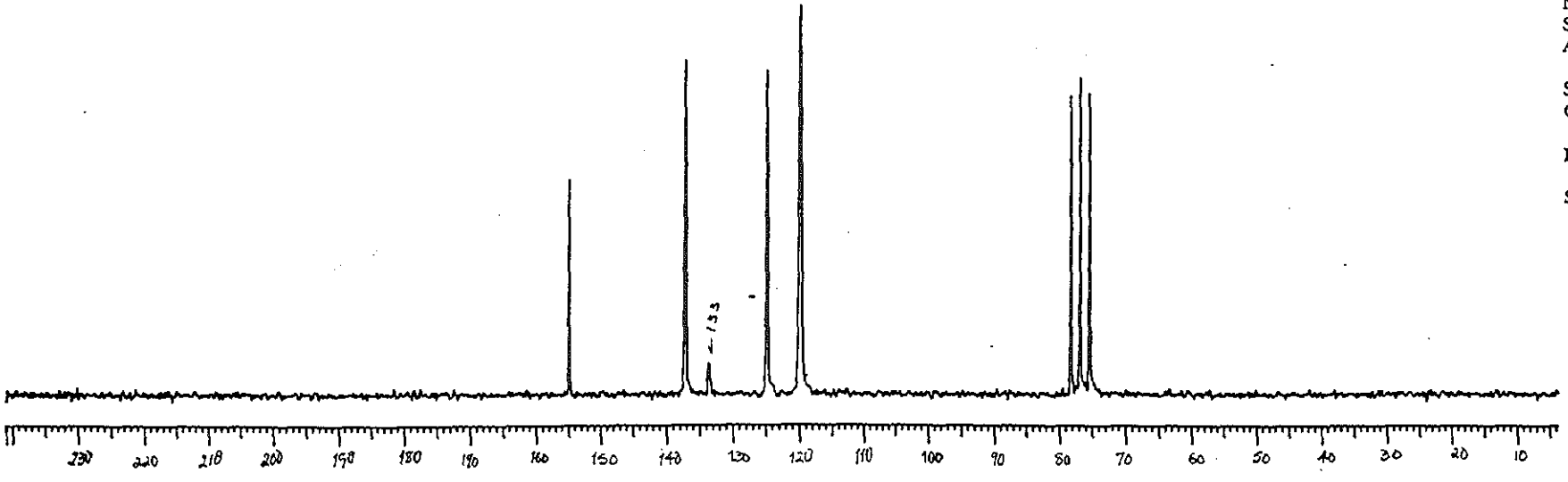
Suggested structure/Remar

O-nitrostyrene

TOTAL 7
RESOL 7819± -4 HZ
EXREF 77.0000PPM
OBS 1882.3364 HZ
MGAIN 12

NO	FREQ(HZ)	PPM	INT%
1	3494.87	155.859	4828
2	3094.69	137.336	6182
3	2815.33	124.938	5984
4	2702.32	119.923	7189
5	1766.68	78.481	5521
6	1735.18	77.080	5847
7	1702.81	75.567	5562

^{13}C NMR o-Nitrophenol Complex



Addis Ababa University
Department of Chemistry

NMR Laboratory
Jeol FX-90Q Spectrometer

Spectrum No. Mubie Hag

Sample Code Mussie-3
Sample Source

Lock 2D/INT
Nucleus
^{1}H (89.6 MHz)
^{13}C (22.5 MHz)

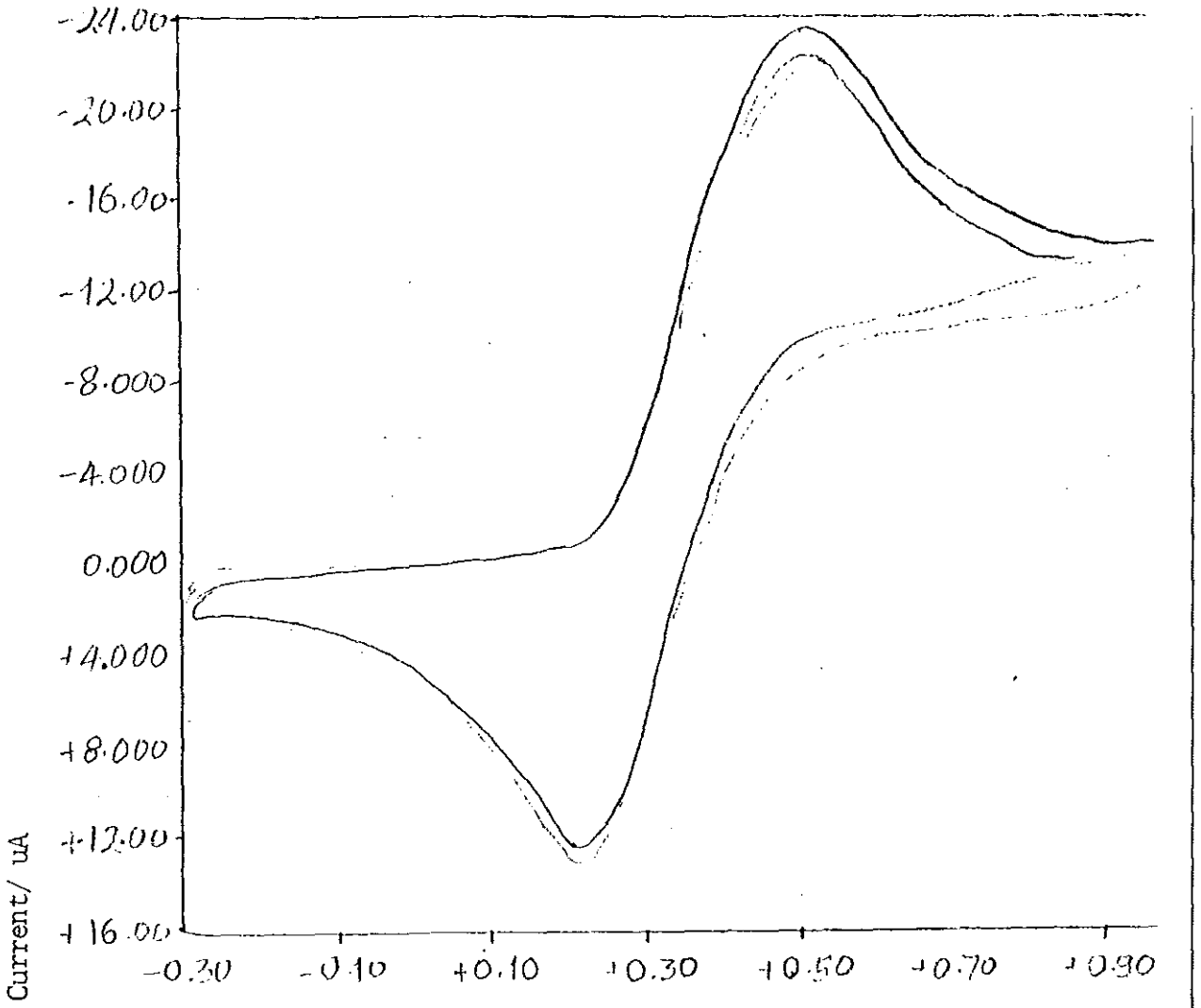
Solvent cocl3
Amount in mg 75
Reference 77 ppm
No. of Pulses 30000
Spectral Width 5750 Hz
Amplitude 19x3dB

Saved on FDG File Name
Operator NMR / GA

Day 29th Month March 19

Suggested structure/Remark

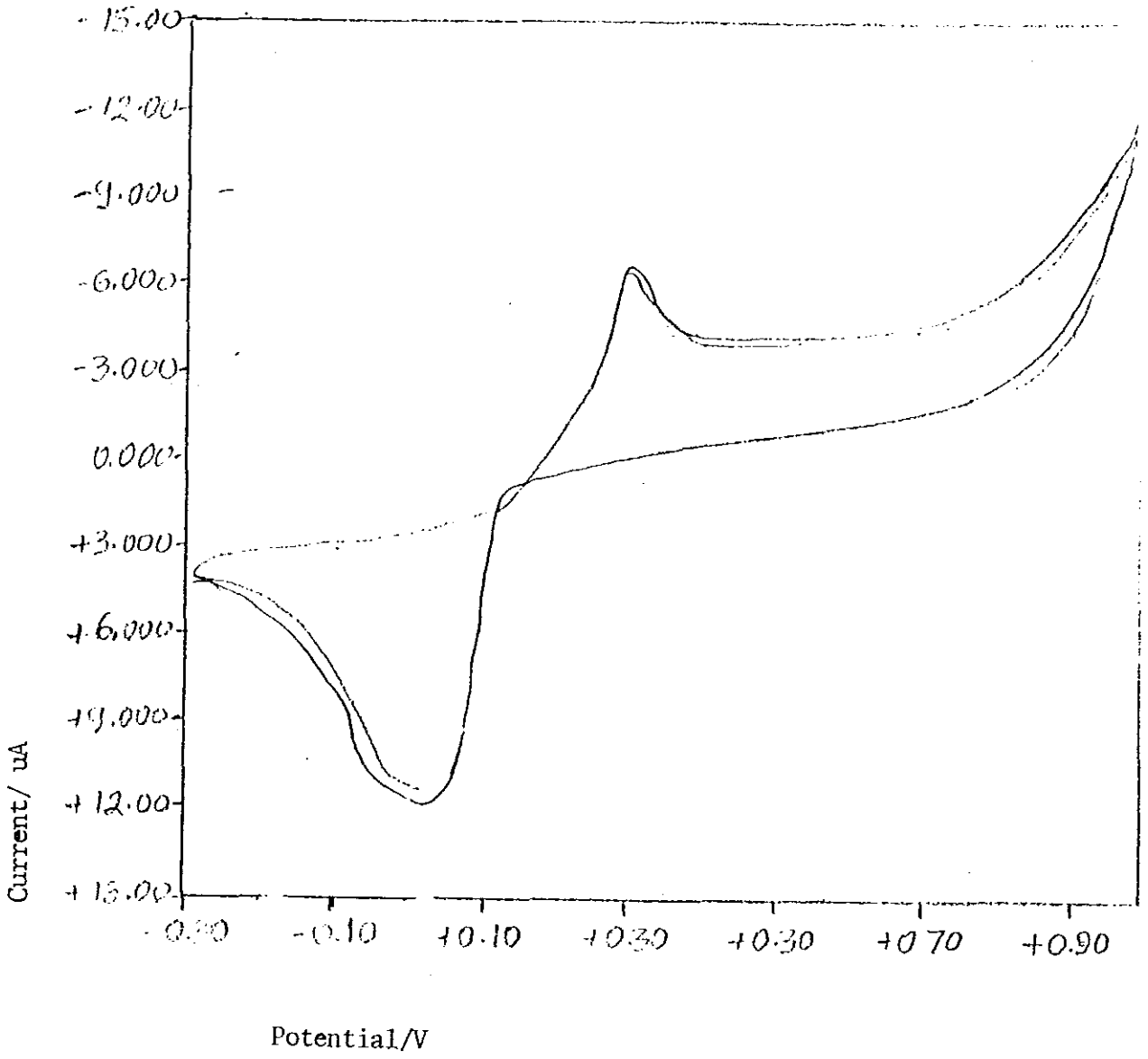
$Na_2[Fe(CN)_5OC_6H_4$
o-nitrophenol ...



CYCLIC VOLTAMMOGRAM OF $[Fe(CN)_5L]^{3-}$
(L = O-nitro~~phenol~~aniline)

CONCE: 0.001M

SCAN RATE: 50mV/s

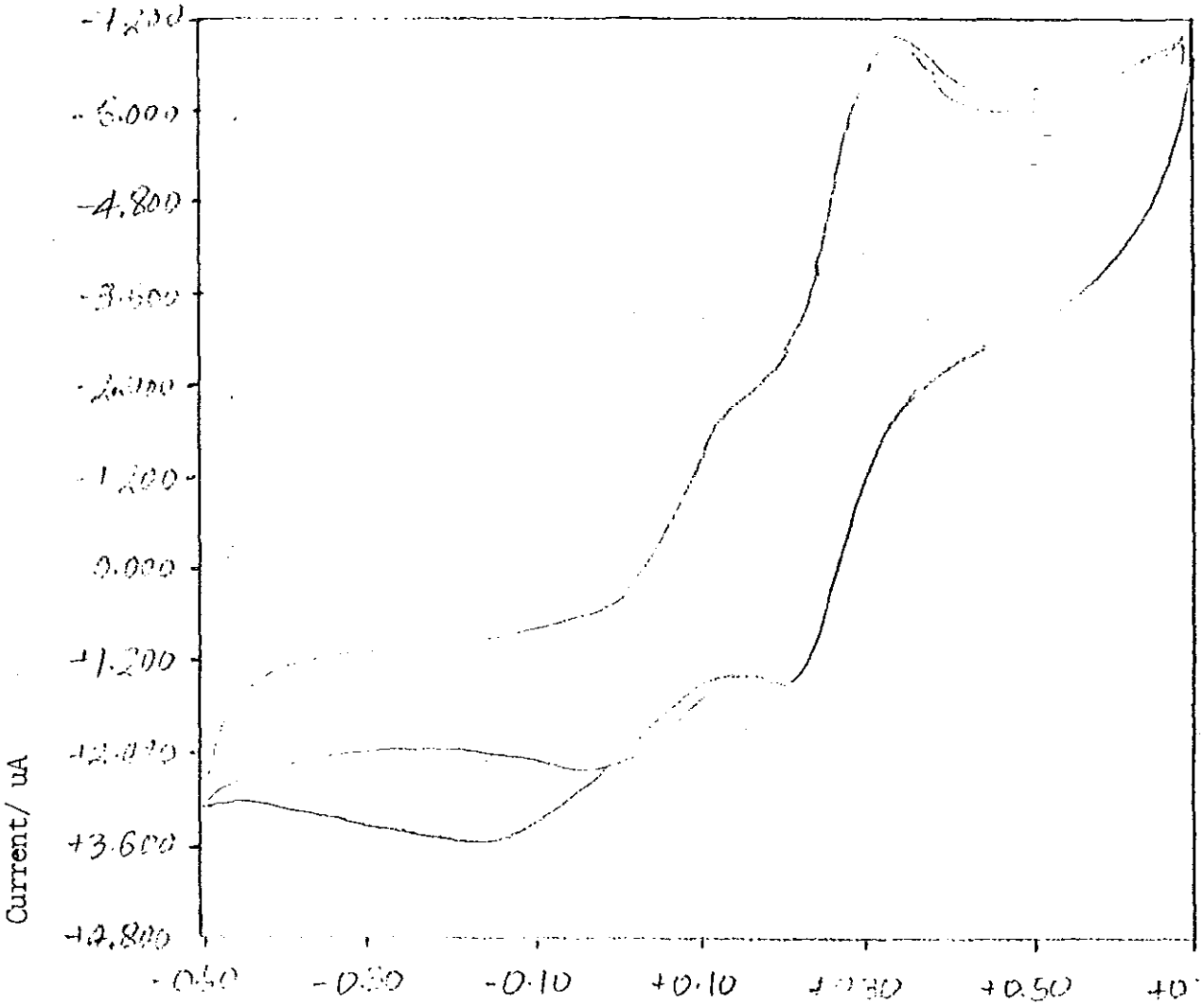


CYCLIC VOLTAMMOGRAM OF][Fe(CN)$_5$L]$^{3-}$

(L = P-nitroaniline)

CONCE: 0.001M

SCAN RATE: 50mV/s

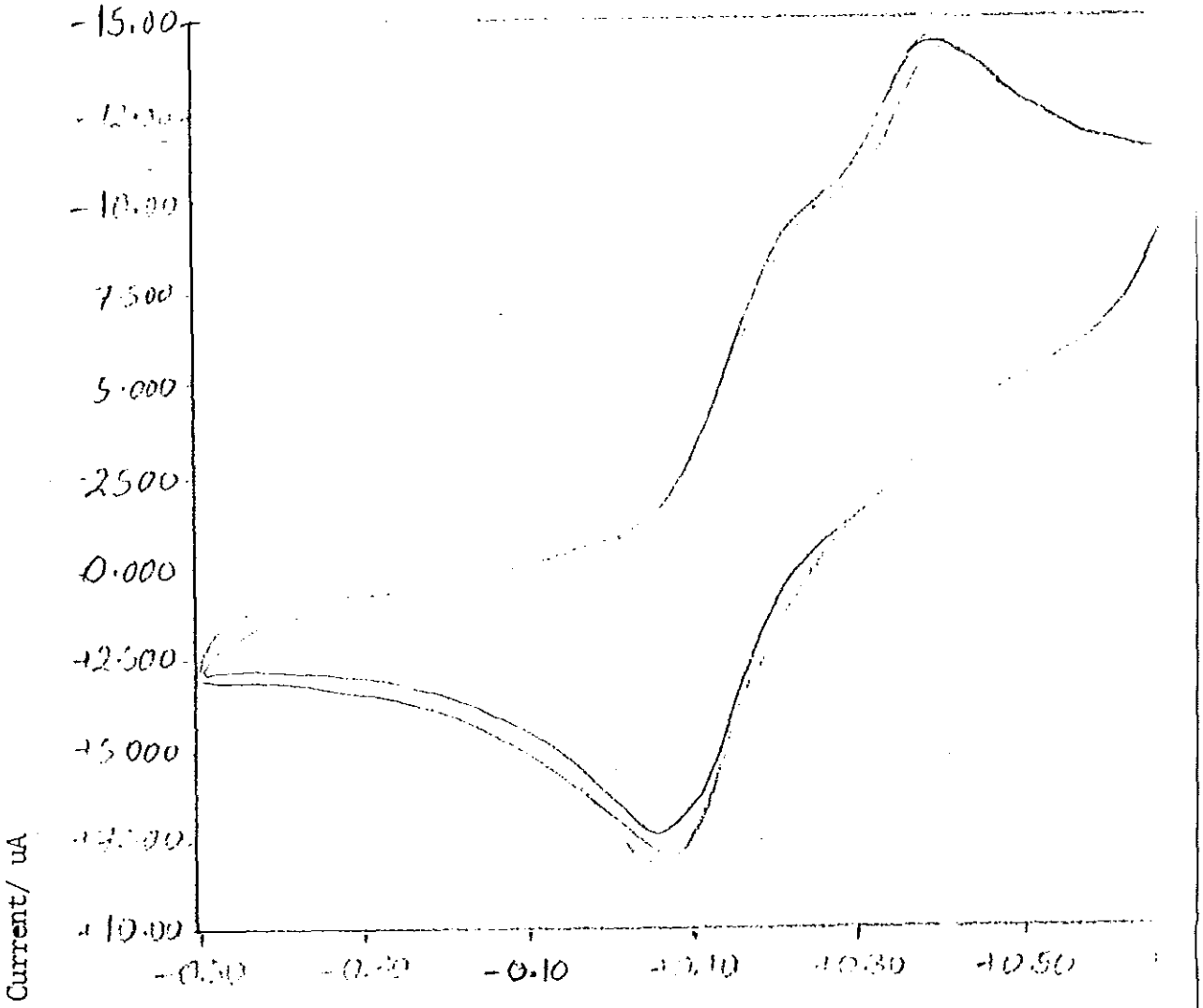


CYCLIC VOTAMMOGRAM OF $[Fe(CN)_5L]^{3-}$

(L = P-nitrophenol)

CONCE: 0.002M

SCAN RATE: 50mV/s



CYCLIC VOLTAMMOGRAM OF $[Fe(CN)_5L]^{3-}$
(L = O-nitrophenol)

CONCE: 0.001M

SCAN RATE: 50mV/s