SYNTHESIS AND CHARACTERIZATION OF COBALT(III) COMPLEXES WITH 4,4′-BIPYRIDINE.

by

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Dedication

To: My mother Anaji Bekere (Aye), my father, my grand father Mama Tahiro, my sisters, my brothers, Yeworkweha Hassen (Workie), and to all my friends of Bale-Goba.

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ABBREVIATIONS

en	ethylenediamine
4 - EtPy	4 - ethyl pyridine
4 - Me Py	4 - methyl pyridine
Py	pyridine
bipy or 4-bipy	4,4′-bipyridine
Pc	phthalocyaninato
Pyz	pyrazine
Vis	visible
UV	ultraviolet
IR	infrared
eqn.	equation
m.pt	melting point
m mol	millimole
kK	kilo Kayser
dc	direct current
br	broad
s	sharp or small
m	medium
sh	shoulder

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ABSTRACT

The synthesis of cobalt (III) complexes using $CoCl_2.6H_2O$, CoS, $CoSO_4.7H_2O$ and 4,4′-bipyridine, in the presence of chlorine gas as an oxidizing agent have been studied.

The elemental analysis, IR spectra and other spectrophotometric analysis revealed the products as $[Co(bipy)Cl_3]$ obtained from $CoCl_2.6H_2O$ as well as CoS, and $[Co(bipy)_2Cl(SO_4)]$ synthesized from $CoSO_4.7H_2O$.

The reaction behaviour of $[Co(bipy)Cl_3]$ with different amines have been studied, and no conclusive results have been attained on the basis of data available at hand.

$[Co(Py)_4Cl_2]Cl$ was treated with 4,4-′bipyridine in an attempt to synthesize mixed ligand complex of Co (III) containing 4,4′-bipyridine and pyridine. In a similar way, $[Co(bipy)Cl_3]$ was treated with pyridine. In both cases, the product was $[Co(bipy)Cl_3]$, which indicated that the formation of mixed ligand complex was not realized under the experimental conditions followed

The dielectric constant of $[Co(bipy)Cl_3]$ was determined and the substance was found to be superconductor, based on ϵ_{dc} (permeability of the sample) value.

1. INTRODUCTION

The chemistry of polymeric transition metal complexes is in its infancy. The coordination chemistry of 2,2′-bipyridine has been extensively studied, yet the ligand properties of the isomeric 4,4′-bipyridine molecule have not been well studied. The first transition metal-4,4′-bipyridine complexes appeared in papers by Peard and Pflaum [1], who reported a complex having the stoichiometric formula $Ag(C_{10}H_8N_2)(NO_3)$ and by Lewis and Mabbs [2], who reported a compound of copper (II) benzoate containing half a 4,4′-bipyridine molecule per formula unit of copper benzoate. As a potential ligand, 4,4′-bipyridine seemed particularly interesting because its structure should preclude chelation and favor coordination of the nitrogen atoms to two different metal ions; i.e., it should coordinate so as to form polymeric complexes.

Coordination compounds of the polynuclear amines are more stable than compounds of the mononuclear ligands.[3] The bidentate polynuclear amines coordinate very strongly with metal in solvents. The increase in stability results from the increased shielding of the metal ion by the large ligand molecules. With metal ion insulated from the solvent, the interaction is no longer an ion dipole interaction between solvent and the metal ion, but rather an interaction between the solvent and the coordinated amine ligands.[3]

1.1. Infrared and Far Infrared Studies of Monomeric and **Polymeric Base Adducts of Phthalocyaninato Transition Metal(II) Complexes.**

Complexes of monodentate base molecules (e.g. pyridine, substituted pyridines and aliphatic amines) with transition metal phthalocyanines have been studied by several groups. The corresponding data for bidentate base molecules have not been extensively reported.[4]

..Investigations on conducting materials containing bidentate molecules were found to act as monodentate (1 and 2) and bidentate (3 and 4) ligands. IR and far IR spectroscopy turned out to be useful tools for distinguishing PcML (1) and $PcML_2$ (2) from Pc-L-MPc (3) and $[PcML]_n$ (4).

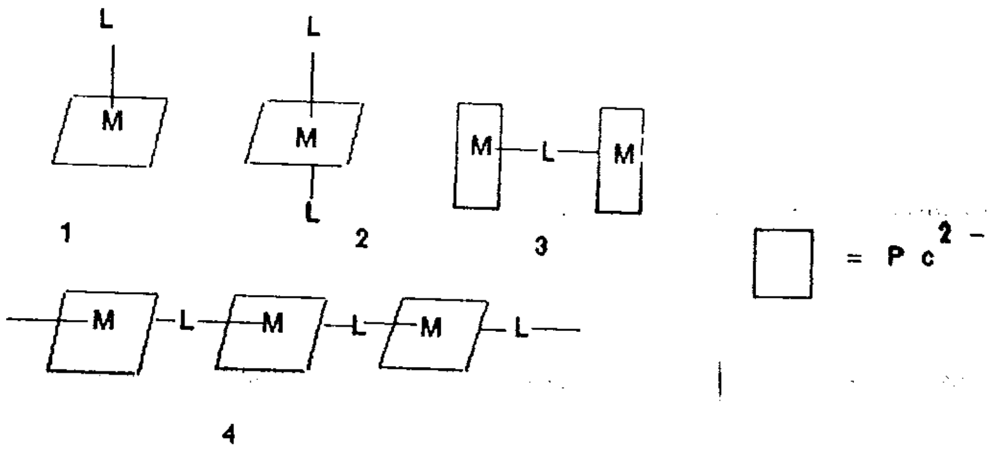


Fig. 1. Monomeric, dimeric and polymeric phthalocyaninato transition metal derivatives (M = Co, Fe; L = pyrazine, 4,4'-bipyridine).[5-7]

In the case of 4,4'-bipyridine, monodentate terminal or bidentate bridging base molecules were distinguished by the sensitivity of in-plane vibrations at 1215 and 1589 cm^{-1} to the coordination state of the ligand. These absorptions [illegible] assigned with the help of the corresponding pyridine and pyridine-d_5 complexes. The intensity of the bands at 1589cm^{-1} for polymeric 4,4′-bipyridine complexes enables a chain length determination by comparison with the spectra of the corresponding monomeric compounds. Infrared absorptions in the range of 1065 - 1130 cm^{-1} are assigned to transition-activated absorptions of the phthalocyaninato moiety, which are caused by complex formation.[4]

The monomeric derivatives PcM(bipy)$_2$ give rise to new bands at 800, 1070, 1215, 1402, 1483 and 1589 cm^{-1}. These absorptions are caused by the ligand and agree with the bands exhibited by the free bipyridine.[8]

The most predominant spectral difference observed for the monomeric compounds containing unidentate terminal 4,4′-bipyridine compound compared with compounds containing the bidentate bridging ligand is the disappearance of the absorption at about 1215, 1402 and 1589 cm^{-1} in PcCo(bipy)$_2$ and PcFe(bipy)$_2$.[8]

The bands around 1215 and 1585 cm^{-1} are also present in the pyridine derivatives PcCo(py)$_2$, PcCo(py) and PcFe(py)$_2$ and are assigned by comparison with the spectra of the corresponding d_5-pyridine complexes to the in-plane C-H bending vibration, and the ring vibration respectively. Considering non-bridging 4,4′-bipyridine as a coordinated pyridine derivative, this suggests a similar assignment for the monomeric 4,4′-bipyridine complexes. The absorption at 1402 cm^{-1} is obviously related to the bis-pyridyl-structure of the ligand, because there is no direct analogy in the spectra of the pyridine compounds.[8]

Bidentate 4,4′-bipyridine is centrosymmetric to its 4,4′-bond-centre. [illegible] pyridyl-units are arranged in one plane ([illegible] nter of symmetry vanishes, when the pyridyl planes are tilted or 4,4'-bipyridine acts as a monodentate ligand. In consequence the above assigned in-plane vibrations of the monomeric complexes lose their infrared activity in dimeric or polymeric compounds, if one assumes a coplanar arrangement of the pyridyl groups.

A characteristic spectral change in the 700 - 800 cm^{-1} region parallels the polymerization. The ligand out - of - plane C-H mode in the spectra of the monomeric compounds decreases in intensity and shifts to higher energy in the polymeric derivative.[8]

The difference in the far IR spectra of PcCo adducts with monodentate and bidentate base molecules may be explained by the different bonding properties of the ligand involved. Since pyrazine and 4,4'-bipyridine are weaker bases than pyridine and its substituted derivatives, π-back bonding from the metal is more likely.[9]

Fig. 2. Symmetry considerations, bidentate 4,4'-bipyridine

1.2 Objectives of the Present Work

1. To synthesize and characterize cobalt (III) complexes by using 4,4'-bipyridine.
2. To study the physical and chemical behaviour of the complex.

In addition to what has been briefly presented in the introductory chapter, chapter 2 deals with a review on cobalt amine complexes, while chapter 3 and 4 are devoted to experimental, and results and discussion respectively.

2. LITERATURE SURVEY

The complex compounds of cobalt (III) are numerous and stable and have played an important role in the development of coordination chemistry.

Virtually all of these have the octahedral structure.[9] They undergo ligand exchange reactions at conveniently measurable rates and have therefore been extensively studied. Thus, a large amount of kinetic data has been given in the literature on simple substitution reactions under various conditions. In addition spectral data for many complexes are available.

2.1. Preparation of Trivalent Cobalt Complexes with 2,2′-bipyridine (bipy).

2.1.1. $[Co(bipy)_2X_2]^+$ (X = Cl^-, Br^-, I^-, NO_2^-) Preparation by Controlled Oxidative Processes

In the series $[Co(bipy)_2X_2]^+$ only substances with X^- = Cl^-, NO_2^-, acetate, and $[Co(bipy)_2CO_3]^+$ as well as $[Co(bipy)_3]^{3+}$ have been described. In most preparations of these complexes the main step consists of the oxidation of divalent cobalt complexes with hydrogen peroxide or oxygen. However, this method is not suitable for preparation of other complexes (e.g., for X^- = I^-), and the reaction with oxygen or hydrogen peroxide as oxidizing agents is not a straight forward operation.[10,11]

A study of complexes of the general type $[Co(bipy)_2X_2$ has shown that these complexes undergo, in most cases, a very easy oxidation and that they can be used as starting material for the preparation [illegible] responding series of trivalent cobalt complexes. Where an oxidizing agent is used, the reduced form of which enters the coordination sphere, and the desired complex is formed in one step without any formation of intermediates.[12]

Bis-Halogeno Complexes - The studies on $[Co(bipy)_2Cl_2]Cl$ have shown that this complex undergoes extremely rapid hydrolysis in aqueous solution. However, the solutions in alcohol are much more stable than the aqueous solutions.[11]

The general method for the preparation of bis-halogeno complexes of the type $[Co(bipy)_2X_2]^+$ makes use of the fact that the solubility of the corresponding divalent complexes in alcohol is rather high and that the divalent complex undergoes an immediate and clean oxidation with the corresponding halogen. The resulting trivalent complex, being much less soluble than the starting material, separates from solution. In this way the previously known $[Co(bipy)_2Cl_2]Cl$, as well as new complexes such as $[Co(bipy)_2I_2]I$ and $[Co(bipy)_2Br_2]Br$, have been prepared.

Bis-Nitro Complex -The original preparation of $[Co(bipy)_2(NO_2)_2]Cl$ was based on the substitution of chloride ions in the $[Co(bipy)_2Cl_2]^+$ by nitrite ions.[37]

The divalent, cobalt complex $[Co(bipy)_2(NO_2)_2]$ undergoes a very easy oxidation. The oxidation by air leads to rather complicated products.[10]

The complex cation $[Co(bipy)_2(NO_2)_2]^+$, unlike the corresponding bis-halogeno cations, is rather stable in aqueous solutions and undergoes only a very slow hydrolysis.

2.2. Complexes of 4,4′-Bipyridine.

2.2.1. Halogen Complexes of 4,4′-Bipyridine and the Infrared Spectra of Pyridine Complexes.

While numerous halogen complexes of simple hetrocyclic amines have been studied in the past, very little attention has been paid to the complexes of polynuclear hetrocycles. A study of the 2,2′-bipyridine-iodine halide complexes gave some indications that the positive iodine may be coordinated to two nitrogen atoms of the bipyridine with the molecule being arranged in the cis configuration.[13] Since such an arrangement is obviously impossible in the case of 4,4′-bipyridine, it was of interest to study the properties of the corresponding halogen complexes.[14]

References to complexes of 4,4′-bipyridine are not plentiful in the literature. The two most pertinent reports describe the formation of complexes with arsenic tribromide and silver nitrate.[20] In both cases evidence is cited indicating that the two addition compounds are polymeric, with a possible structure being

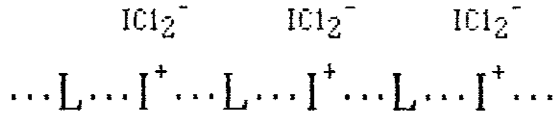
$$\ldots BrHNC_5H_4-C_5H_4NHBr-AsBr_3-BrHNC_5H_4-C_5H_4NHBr-AsBr_3-$$

and,

$$\ldots \overset{NO_3^-}{Ag^+}-NC_5H_4-C_5H_4N-\overset{NO_3^-}{Ag^+}-NC_5H_4-C_5H_4N-\overset{NO_3^-}{Ag^+}$$

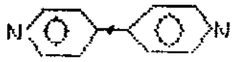
Halogen complexes of 4,4′-bipyridine were found to be insoluble in water and in all common organic solvents, both polar and non - polar. They did dissolve to a slight extent in dimethyl formamide but this dissolution was accompanied by decomposition. Consequently solution spectra of these compounds in the ultraviolet - visible spectral regions could not be obtained, nor could any other convenient physico-chemical studies be made in order to elucidate their structures. In view of the fact that it was impossible to recrystallize the powder obtained in their preparations, suitable crystals could not be obtained for the single crystal X- ray work on the structures of the solids.[13]

It seems that this insolubility can be an indication of the polymeric structure of these complexes. By analogy with the arsenic tribromide-4,4′-bipyridine complex one may write the following structure for the iodine monochloride complex.



$$\cdots L \cdots \overset{ICl_2^-}{I^+} \cdots L \cdots \overset{ICl_2^-}{I^+} \cdots L \cdots \overset{ICl_2^-}{I^+} \cdots$$

L =



(4,4′-bipyridine)

It should be remembered that compounds where positive iodine has a coordination number of two are well known in the literature. Some of the examples are $(C_5H_4N)_2INO_3$, $(C_5H_4N)_2IClO_4$, etc.

If the 4,4′-bipyridine.2ICl complex is polymeric, one would expect it to be somewhat less prone to decomposition than the monomer. In this respect, we have seen that the above complex melts with decomposition starting at 230 °C while the melting point of 2,2′-bipy.2ICl complex is 139 °C which is sharp and reversible. The pyridine.ICl and 2,2′-bipy.2ICl complexes are also decomposed in the KBr pellet press, while the

4,4′-bipy.2ICl gave excellent pellets, indicating a higher stability for the latter compound.[13]

Infrared Spectra

The infrared studies were undertaken in the hope that they might yield some information about the structure of the complexes, particularly that of the 4,4′-bipyridine-ICl complex. Infrared spectra of pyridine, 2,2′-bipyridine and 4,4′-bipyridine were obtained in the region from 300 to 4000 cm^{-1}. These were compared with the spectra of the complexes with iodine monochloride and with silver ion in the same spectral range. The comparisons showed the usual remarkable changes in the appearance of the spectra of pyridines which would be expected from the earlier studies in pyridine complexes.[16-18]

Bipyridine Complexes.

Since the bipyridines are more complicated molecules than pyridine, the spectra are much more complicated and the changes on complexing are even harder to interpret. There are, however, some rather surprising changes in the spectra of the bipyridine which deserve some discussion.

The stretching at 404 cm^{-1} in free pyridine, which is out-of-plane skeletal bending vibration shows a characteristic shift to higher frequencies in pyridine and in 2,2′-bipyridine complexes. However, in free 4,4′-bipyridine the logical assignment of the band at 374 cm^{-1} presents with a problem in the complexes. This behaviour is quite difficult to

seem to be

[illegible], the intensity of the band at 374 cm^{-1} do[illegible] not very dependent on complex formation in the other compounds.[13]

The upward shift of the band at 605 cm^{-1} in free pyridine on complex formation appears to be similar in pyridine and 4,4′-bipyridine but anomalous in the 2,2′-bipyridine complexes. The possibility of chelate formation in complexes with latter amine results in some differences in its behaviour. The other band which seems to indicate such a difference is the skeletal stretching made at 1420 cm^{-1} , in 2,2′-bipyridine. The analogous frequencies in the other amines seem to remain relatively constant as complexation occurs; in the 2,2′-bipyridine, this band apparently moves upward by some 50 cm^{-1}.

The bipyridines show also quite large changes in the region around 1000 cm^{-1} as complexation occurs. This is to be expected in view of the complexity of this region. There does not appear to be any simple interpretation of these changes, except that they very likely are due to intensity changes resulting from the charge redistribution on complex formation.[13]

It would appear that the changes in spectra, while profoundly affecting the appearance of the spectrum, result mostly from changes in the relative intensities of vibrations. The changes in frequency appear to be of the order of 5% for larger observed changes. Changes of this small magnitude are to be expected only if the formation of the complex does not radically change the chemical bonding in the donor molecule. The spectra of the bipyridines support these general conclusions.[13]

2.2.2. Preparation and Characterization of Divalent Cobalt, Nickel, Zinc, Cadmium and Monovalent Silver Nitrate Complexes with 4,4′-bipyridine.

Molecular conductance, magnetic susceptibility, electronic and IR spectral measurements up to 200 cm^{-1} have been recorded for the complexes isolated in the solid state in order to elucidate the mode of metal-nitrate bonding and the tentative stereochemistry of the complexes.[19]

4,4′-bipyridine formed 2:1 complexes with cobalt and nickel nitrates but 1:1 with zinc, cadmium and silver nitrates. All these complexes (except that of silver) are fairly soluble in dimethyl formamide. Molar conductivities of 10^{-3} M solutions demonstrate that these complexes behave as strong electrolytes in this solvent.[20]

IR spectra of the metal nitrate complexes studied here indicate that both the nitrogens of 4,4′-bipyridine are bonded to metal ions and that the bipyridine is bridged between two metal ions. The steric position of nitrogen atoms in 4,4′-bipyridine precludes chelation, but favors coordination to different metal ions, thus leading to polymer chain formation.

Electronic spectrum of the brown 1:2 cobalt-nitrate 4,4′-bipyridine complex shows absorption bands at 8890, 19230, 20830 cm^{-1} and a shoulder which are due to $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ ν_1; $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ ν_3; respectively. These features are characteristic of divalent cobalt ion in weak octahedral field and ruled out a tetrahedral environment which would show a much stronger absorption in the 14000 - 16000 cm^{-1} region. The shoulder at 22220 cm^{-1} is probably a consequence of spin - orbit coupling in the $^4T_{1g}(P)$ [illegible] assignments and the quartet levels it is calculated that the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ transition should occur at a slightly lower energy than the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ band. However, since the $^4A_{2g}$ state is derived from a $t^3_{2g}\,e_g^4$ configuration while $^4T_{1g}(F)$ from $t^5_{2g}\,e_g^2$ configuration, the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ transition is essentially a two electron process and hence should be weaker than the other transitions. This weakness combined with the proximity of the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(p)$ transition results in the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ transition unobserved. From the Tanabe - Sugano diagrams for a d^7 case one would predict three peaks in octahedral divalent cobalt compounds where $^4A_{2g}$ and $^4T_{1g}(P)$ energy levels cross each other giving rise to only two peaks.

The electronic spectral and magnetic susceptibility measurements of 1:2 cobalt and nickel nitrate-4,4′-bipyridine complexes are consistent with pseudo-octahedral environments around the metal atoms.

In addition to the ligand absorption bands (modified slightly on account of coordination) IR spectra of both these complexes show absorption bands at about 1410, 1310, 1010, 790, 735 and 710 cm^{-1} due to coordinated nitrato groups.[21,22] Consideration of magnetic moments, electronic spectral and the IR bands due to coordinated nitrato groups suggests that the 1:2 cobalt and nickel nitrate - 4,4′ - bipyridine complexes are polymeric pseudo - octahedral structures with the metal atoms surrounded by four nitrogen atoms (from bridging 4,4′-bipyridine molecules) and two oxygens (from two terminally bonded nitrato groups) in the solid state (structure I).

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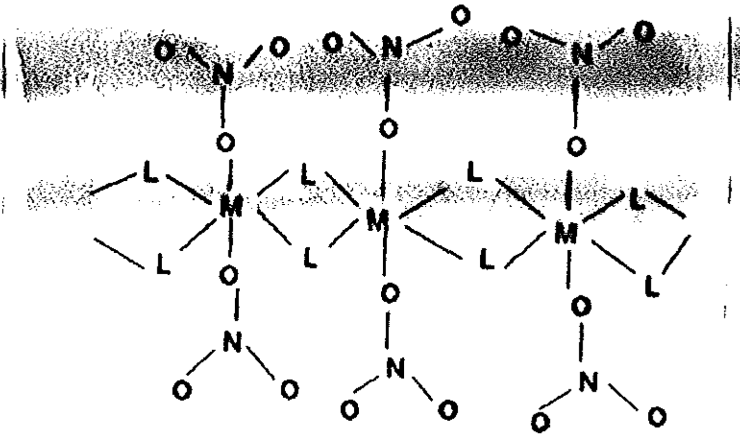
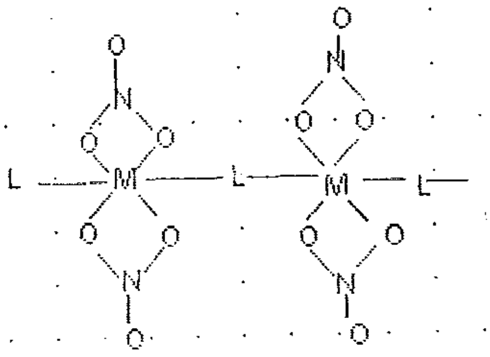


Structure I: M = Co or Ni

$CoL_2(NO_3)_2$, $NiL_2(NO_3)_2$, L = 4,4′-bipyridine

IR spectrum of the 1:1 silver nitrate - 4,4′-bipyridine complex shows a strong absorption band at 1365 cm^{-1} and medium intensity bands at 832 and 710 cm^{-1} , characteristic of ionic nitrate in the complex. Furthermore, IR spectrum of this complex exhibits only one band of very weak intensity at 1763 cm^{-1} in the combination tone region indicating the exclusive presence of ionic nitrate with bidentate bridging 4,4′-bipyridine and ionic nitrate. The 1:1 silver nitrate - 4,4′-bipyridine complex was suggested to have a two - coordinate linear polymeric chain structure similar to the 1:1 silver nitrate - pyrazine complex which has been shown by X - ray structural studies to consist of (-Ag-ligand-Ag- $)_x$ chains with nitrate ions linking the polymer chain.[20,23]

In addition to the ligand modes IR spectra of the 1:1 zinc and cadmium nitrate - 4,4′-bipyridine complexes show absorption bands at about 1480, [illegible]30, 1035, 810, 740 and [illegible]05 cm^{-1} w[illegible] [illegible]inated nitrato [illegible] groups. With bidentate bridging 4,4′-bipyridine molecules and bidentate chelating nitrato groups the 1:1 zinc and cadimum nitrate - 4,4′-bipyridine complexes are assigned to have six-coordinated polymeric octahedral environments of two nitrogen atoms (of bridging bipyridine) and four oxygen atoms (from two bidentate chelating nitrato groups) around the metal atoms.[21,22] (structure II)



Structure II: M = Zn or Cd

$ZnL(NO_3)_2$, $CdL(NO_3)_2$,

2.2.3. 4,4′-bipyridyl Complexe with Co(II) acetates

$CoL_2(OAc)_2$ (L = 4,4′-bipyridyl), was prepared in the solid state and characterized on the basis of their magnetic susceptibilities, electronic and IR spectral measurements.[24]

No absorption bands were observed which could be attributed to water or ethanol in any of the spectra thus establishing that these compounds are free from coordinated [illegible] ethanol.

IR spectra of the complexes studied indicate that both the nitrogens of the ligand are bonded to different metal ions. The steric position of the two nitrogen atoms in 4,4′-bipyridine precludes chelation but favors coordination to two different metal ions thus leading to polymer chain formation.[25]

Cobalt(II) Complexes - Cobalt(II)acetate forms 1:1 complex with 4,4′-bipyridine only. It showed magnetic moment value of 4.70 B.M indicative of octahedral coordination. Its electronic spectrum shows two main bands at 10260 and 21050 cm^{-1} with shoulders on either side. These bands are assigned to the transitions $^4T_{1g}(F) \dashrightarrow {}^4T_{2g}$ (F) (ν_1) and $^4T_{1g}(F) \dashrightarrow {}^4T_{1g}$ (p) (ν_3), respectively, characteristic of a weak octahedral field around cobalt(II). Electronic and IR spectral data of the 1:1 Co(II) acetate - 4,4′-bipyridine complex is consistent with a six-coordinated, polymeric octahedral structure where four oxygen ,atoms from the two acetate groups (trans to each other) and two nitrogen atoms from the bridging 4,4′-bipyridine molecules around the Co(II) ions in the solid state.[26]

2.2.4. Complexes of 4,4′-bipyridyl with Transition Halides.

All the complexes which were formed between 4,4′-bipyridine and the halides of the heavier 1st row transition elements were isolated as 1:1 adducts and they were all insoluble in common polar and non-polar solvents.[27]

The spectra indicate that the IR of (4,4′-bipy) is some what modified

[illegible]

Table I.

Reflectance spectra (kK)* of the isolated complexes.[27]

(a) Pseudo-tetrahedral complexes of Co(II).

Complex	Charge transfer	$^4A_2 \longrightarrow {}^4T_1(p)$	$^4A_2 \longrightarrow {}^4T_1(F)$
$CoCl_2$(4-bipy)	38.6 br; 32.8 br	18.4 s; 17.6; 15.2;	8.4 s; 5.7 s
$CoBr_2$(4-bipy)	36.5 br; 32.5 br	18.1 s; 15.2;	8.4 s; 5.8 s
CoI_2(4-bipy)	36.4 br; 30.2 br, 25.6 sh	14.8 s; 14.2 sh;	7.8 s; 5.6s;

(b) Octahedral complexes of Ni(II).

Complex	Charge transfer	$^3A_{2g} \longrightarrow T_{1g}(p)(\nu_3)$	$^3A_{2g} \longrightarrow T_{1g}(\nu_2)$	$^3A_{2g} \longrightarrow {}^3T_{2g}(\nu_3)$
$NiCl_2$(4-bipy)	27.7	23.2 br	13.3 s	8.5
$NiBr_2$(4-bipy)	35.8; 32.4 br.	22.5 sh	13.3 s	7.9 s; 5.2 s
NiI_2(4-bipy)	36.4 br; 28.3	23.2	11.1 m	7.3 m

(c) Octahedral complexes of Cu(II).

Complex	Charge transfer	$^2E_g \longrightarrow {}^2T_{2g}$
$CuCl_2$(4-bipy)	37.5 br; 31.9 sh	12.6 vs
$CuBr_2$(4-bipy)	36.8 br; 28.4 br; 24.2 m	13.2 vs.

* kK=kiloKayser, 1 kK=1000 cm^{-1}

Table II.

Diffuse Reflectance Spectra (in κK units) of Some 4,4′-bipyridine Complexes.[28]

(i) Pseudo-octahedral Co(II) Complexes:

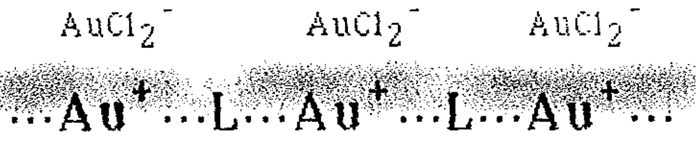
	charge transfer	$^4T_{1g} \longrightarrow {}^4T_{1g}(p)$	$^4T_{1g} \longrightarrow {}^4A_{2g}$	$^4T_{1g} \longrightarrow {}^4T_{2g}$
$[Co(4\text{-bipy})(H_2O)_4][SO_4]$	45.4, 35.5 br	20.5 sh, 18.7	16.3 sh	8.8
$[Co(NCS)_2(4\text{-bipy})_2](H_2O)_4$	45.1, 35.8 br, 28.9	18.5, 17.5 sh		8.8

(ii) Pseudo-octahedral Cu(II) Complexes:

	charge transfer	$^4E_g \longrightarrow {}^2T_{2g}$
$[Cu(4\text{-bipy})(H_2O)_4][SO_4](H_2O)$	45.3 br, 37.5, 35.8, 27.0 sh	13.9, 9.8 sh

(iii) Pseudo-octahedral Ni(II) Complexes:

	charge transfer	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}$	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}$
$[Ni(4\text{-bipy})(H_2O)_4][SO_4]$	46.0 br, 37.4 br	26.1	15.4	9.2
$[Ni(NCS)_2(4\text{-bipy})_2](H_2O)_2$	44.5, 37.6 br	29.2 sh	16.4	10.0 br
	34.6 br, 29.2 sh			



$$\begin{array}{ccc} AuCl_2^- & AuCl_2^- & AuCl_2^- \\ \cdots Au^+\cdots L\cdots & Au^+\cdots L\cdots & Au^+\cdots \end{array}$$

L = 4,4'-bipyridine

Fig. 3. Structure of the Polycationic Complex $[Au(bipy)]^+$.

This compound is colourless and not conducting. This indicates that besides strong bonds in the chain, also the square planar, equatorial ligand system seems to be essential for the conductivity.

The structure of a one - dimensional organic conductor is stabilized by the tetradentat planar phthalocyanine molecule complexing each octahedrally coordinated central atom in its equatorial plane.[31,32]

2.4 Coordination Compounds of Lanthanide Nitrates and Chlorides with 4,4'-bipyridine.

The complexes are of the general form $M(NO_3)_3(4\text{-bipy}).XH_2O$, where M is for elements from lanthanide series, and X = 2,3,4 or 5. The preparation of $M(NO_3)_3(4\text{-bipy})_2.(H_2O)_2$ and $MCl_3(4\text{-bipy}).XH_2O$ were reported.[33]

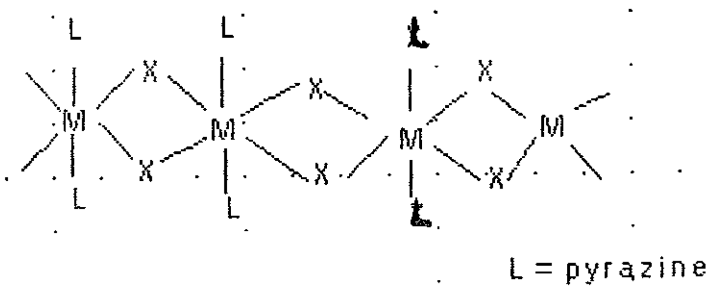
Two molecules of 4,4'-bipyridyl are associated with each metal atom in the case of nitrates, and one in the case of the chlorides.[33]

The room temperature magnetic moments are found to be near the theoretical values for the tripositive lanthanide ions, indicating that there is no anti-ferromagnetic interaction. The reflectance spectra are typical of f ---> f electronic transition.[33]

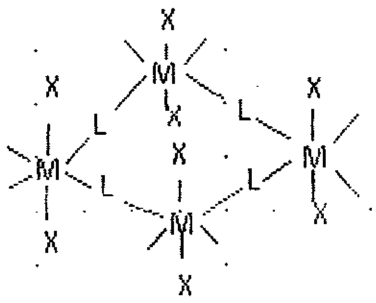
The complexes are stable in air and the IR spectra show the presence of water. The spectra of the chlorides are similar to those of the 1st transition elements with the same ligand in which a polymeric structure has been suggested. On the other hand in the case of the nitrates the spectra are similar to those of the transition elements with 2,2′-bipyridyl. Bands for coordinated nitrate groups are present, but no bands around 1380 and 830 cm^{-1} for ionic nitrat.[34,35] An X - ray analysis [36] of the complex $La(NO_3)_3(2,2'\text{-bipy})_2$ has shown that the coordination number of the metal is ten with each of the three nitrate groups being bidentate. The other four positions in the complex were occupied by the two bidentate 2,2′-bipyridyl molecules. 4,4′-bipyridyl in its complexes can not act as a bidentate chelating ligand for geometrical reasons. Thus, the two molecules of water are required to be coordinated to the metal to complete the coordination sphere. The vacuum thermogram of $Nd(NO_3)_3(4\text{-bipy}).(H_2O)_2$ showed that the compound did not start to lose weight until 170 °C. The loss of the coordination water in $Nd(NO_3)_3(4\text{-bipy}).(H_2O)_2$ was accompanied by general decomposition of the complex. In the case of chlorides, it seems likely that the compounds have a polymeric structure, containing bridging chloride and 4,4′-bipyridyl.[37]

2.5. Miscellaneous Cobalt Complexes with Bidentate Bridging Groups.

The electronic spectra and room temperature magnetic moments of complexes $MX_2(Pyz)_2$, (M = Co or Ni; X = Cl, Br, or I; Pyz = pyrazine) have shown that in these compounds the metal atoms are octahedrally coordinated. This coordina [illegible] either by bridging of halogen atoms, leaving the pyrazine groups unidentate, structure (III a), **or bridging of pyrazine ligands with terminal halogens, structure (III b).**



Structure III a



Structure III b

On the basis of a mid-IR spectral criterion for the unidenticity of pyrazine, structure (III a), analogous to that found for α- $CoCl_2(Py)_2$, was preferred.

In view of the octahedral coordination of the metal atoms, the halogen atoms must be in terminal positions. A number of geometrical **arrangements may be suggested, on the basis, of which the regular sheet** structure (III b) is the most symmetrical. It is clear that the spectra of these complexes are very different to those known to have halogen bridged octahedral structures as in structure (III a).[38]

The comparison made on electronic spectra of $MX_2(Pyz)_2$ compounds, with the spectra of corresponding X- bridged $MX_2(Py)_2$ series, led to the **conclusion that the crystal field splitting energy of pyrazine was greater** than that of pyridine, and was explained in terms of greater π - bonding of **th[illegible] ligand.**[38]

$CoCl_2(Pyz)_2$ has octahedral polymeric sheet structure based on single crystal X-ray diffraction studies. The structure is made up of parallel sheets each consisting of an infinity square array of cobalt atoms bridged by bidentate pyrazine groups. The sheets alternate so that the cobalt atoms in one sheet lie vertically above and below the centers of the squares formed by the cobalt atoms of the adjacent sheets. Two chlorine atoms complete the octahedral configuration of each cobalt atom. The pyrazine rings are tilted about the N-N axes at angle of 44.4° to the plane of the cobalt atoms, so that there are two orientations possible for each pyrazine ring depending on the direction of tilt. Pyrazine's are arranged with identical orientation round all the cobalt atoms of one sheet.[38,39]

[illegible] ination of nitroge

3. EXPERIMENTAL

3.1. Equipments

UV-VIS spectra were recorded on a Beckman DU-65 Spectrometer in the region 750-238 nm, and a Milton Roy Spectronic 1001 PLUS. IR-spectra in the region of 400-200 cm^{-1} were recorded on a Pye Unicam SP 3-300 IR-Spectrometer as KBr disc and Nujol mull. For Atomic Absorption Varian Techtron 1100 Spectrometer was used. Decomposition temperature were measured on a Bocknonscope<M> type electrically heated microscope. Conductivity was measured by TeraOhmmeter GUARD instrument.

Reagents:

Absolute ethanol was used as supplied for synthesis. Solvents for other work were used after purification.

The amines used were p-anisidine (BDH, Analar), p-toluidine (BDH, Analar), O-anisidine (BDH, reagent grade), benzyl amine (BDH, reagent grade), n-butyl amine (BDH, reagent grade), pyridine (Riedel-dehen, reagent grade), diethyl amine(30% alcoholic solution), and 4,4'-bipyridine (BDH, Analar).

The $COCl_2.6H_2O$, CoS and $CoSO_4.7H_2O$ used were BDH reagent grade. For qualitative tests H_2SO_4 , HNO_3, HCl, $FeCl_3$, $K_2Cr_2O_7$, KI and HgI_2 have been used and all are laboratory grade.

For elemental analysis $AgNO_3$, HNO_3, HCl and KSCN were used to determine chlorine. For the determination of sulphate ion $BaCl_2$ and HCl were used. For the [illegible] gen $HClO_4$, CH_3COOH, and crystal max violet were used. For the detection of sulfur, Na_2S and acetone were used.[69] For the generation of chlorine gas MnO_2 and HCl were used.

Cobalt was determined by Atomic Absorption Spectroscopy using air-acetylene flame at 2407 Å resonance line. Chlorine was determined by Volhard's method.[41] Sulphate ion was determined by gravimetric analysis as barium sulphate.[41] Nitrogen was estimated by titration with perchloric acid in acetic acid using 1 % crystal violet in acetic acid as indicator.[42]

3.2. Preparation of Cobalt(III) Complex Using 4,4′-bipyridine and $CoCl_2.6H_2O$.

$$CoCl_2.6H_2O \quad + \quad bipy \quad + 1/2Cl_2 \xrightarrow{-6H_2O} Co(bipy)Cl_3 \qquad (1)$$

A solution of 4,4′-bipyidine (1.6 g, 10.2 m mole) in ethanol (20 ml) was added with constant stirring to a hot solution $CoCl_2.6H_2O$ (1 g, 4.2 m mole) in ethanol (30 ml), while gaseous chlorine was slowly introduced in to the solution under cooling for 15 minutes. The precipitate that was formed was collected by suction filtration, washed with absolute ethanol followed by diethyl ether and finally dried at about 70 °C, to give analytically pure violet crystals.

Yield: 0.86 g (64%) m. pt above 300 °C,

Elemental analysis for $[Co(bipy)Cl_3]$: found (calculated) Co= 18.00%(18.34%)

N = 8.25% (8.71%), Cl = 32.74% (33.12%)

Vis (DMF) $\lambda_{max(1)}$ = 660 nm

300 nm [illegible] chlorides)

Uv (ethanol) λ_{max} = 238 nm

IR (KBr disc) **ν (Co-Cl), 350 cm^{-1}, (for terminal chlorides)**

ν (Co-Cl), 565 cm^{-1} (for bridging chlorides)

ν (Co-N), 400 cm^{-1}.

3.3. Preparation of Cobalt(III) Complex Using 4,4′-bipyridine and CoS.

$$CoS + bipy + 3/2Cl_2 \text{ -------->} [Co(bipy)Cl_3] + S \qquad (2)$$

CoS (0.4 g, 4.4 m mole) was mixed with ethanol (50 ml) and refluxed by stirring with magnetic stirrer for 12 hrs., so that about 85% of the salt was dissolved in the alcohol. The dissolved portion of the mixture was taken and to the hot solution of this a solution of 4,4′-bipyridine (1.6 g, 10.2 m mole) in ethanol (20 ml) was added with constant stirring. Mean while, gaseous chlorine was slowly introduced in to the solution under cooling for 15 minutes. The precipitate which precipitated out was suction filtered washed with ethanol, followed by dry ether and finally dried at about 70 ^{0}C, to get analytically pure violet crystals.

Yield: 0.16 g (11.3%) : m. pt above 300 ^{0}C,

Elemental analysis for [Co(bipy)Cl$_3$]: found (calculated) Co= 18.00%(18.34%)

N = 8.41% (8.71%), Cl = 32.76% (33.12%)

Vis (DMF) $\lambda_{max(1)}$ = 655 nm,

$\lambda_{max(2)}$ = 602 nm

Uv (ethanol) λ_{max} = 238 nm

r disc) (Co-Cl), 50 cm^{-1}, (fo [illegible]

Co = 12.03%(11.71%)

N = 11.02% (11.14%), Cl = 6.82% (7.06%), SO_4 = 18.43%(19.09%)

Vis (DMF) $\lambda_{max(1)}$ = 660 nm

$\lambda_{max(2)}$: 600 nm

Uv (ethanol) λ_{max} = 238 nm

IR (KBr disc) ν (Co-Cl), 350 cm^{-1},

ν (Co-N), 400 cm^{-1},

covalent sulphate 1150 cm^{-1}

3.5 Reaction of Amine with the Complex.

The reaction between [Co(bipy)Cl_3] and the different amines were carried out following the same procedure as described below.

The complex [Co(bipy)Cl_3] (0.05 g, 0.15 m mole) was dissolved in absolute ethanol (30 ml) and cooled in ice (since the complex dissolves to a small extent in ethanol, it was the dissolved portion that was taken for the reaction). To the dissolved portion nearly a 1:1 amount of amine in absolute ethanol (10-15 ml) was added drop wise with stirring and continued cooling for 8 hrs. (for aliphatic amines it was allowed to react over night) and then allowed to stand at room temperature for 1 hr. The solid obtained was then filtered off and washed with absolute ethanol several times and dried in a disccator over potassium hydroxide.

(See Table 4, for the experimental data).

3.6. Reaction of Excess Amine (p-Toluidine, p-Anisidine, Benzyl amine and O-Anisidine) with Co(bipy)Cl_3.

The reaction with p-toluidine , p-anisidine, o-anisidine and benzyl amine were repeated following the same procedure as described in section 3.5, using two fold amount of the amine.

In another experiment the reaction was repeated by steadily increasing the amount of p-toluidine and o-anisidine. However, in all cases the same crystals were obtained by using approximately 1:1 molar ratio of the amine and the complex. This conclusion was based on the basis of their UV and IR spectra, conductivity measurement and decomposition temperature.

3.7. Qualitative Test for Amine in the Reaction Product.

An aqueous solution of the product obtained from reaction of p-toluidine and [Co(bipy)Cl_3] was treated successively with concentrated sulphuric acid, $K_2Cr_2O_7$ solution and HNO_3. (The product was partially soluble in water). The characteristic colour change from yellow to blue then to brown which could be observed in the presence of p-toluidine was not observed. This observation probably indicates the absence of the p-toluidine in the complex.[43]

Similarly an aqueous solution of a dark violet product from the reaction of p-anisidine and [Co(bipy)Cl_3] was treated with HCl solution of $FeCl_3$. The violet colour that could have been observed in the presence of p-anisidine was not seen in this case indicating probably its absence in the product of the reaction.[43]

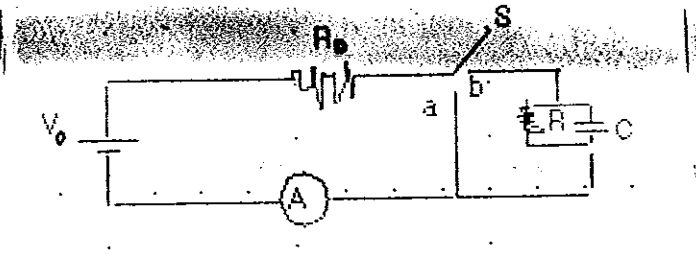


Fig.5. The equivalent circuit of Fig. 4., R is the resistance of the sample.

When "S" was connected to "b" the current amplitude was found out to decrease than when "S" was connected to "a" , because of the capacitor of the pellet. The current value decreases in the ratio of $I_0/I_t = \kappa^2$, where I_0 is the current measured when "S" is connected to "a", I_0 = 0.085 ampere, I_t is the current measured when "S" is connected to point "b", I_t = 0.0025 ampere, and κ is dielectric constant.

i.e. $\kappa^2 = I_0/I_t = 0.085/0.0025 = \kappa^2 \Longrightarrow \kappa = 5.8$

The dielectric constant was determined in the above case by dispersion method.[47] The dielectric constant (κ) is used to get d-c permeability of the sample (ϵ_{dc}).

i.e. $\epsilon_{dc} = \kappa\epsilon_0$, ϵ_0 is the permeability of free space = 8.85×10^{-12} (C^2/Nm^2)

∴ $\epsilon_{dc} = 5.13 \times 10^{-11}$ (C^2/Nm^2), this value is in the region of super conducting material, hence $Co(bipy)Cl_3$ is in super conducting region, when compared with ϵ_{dc} of other material.[47]

4. RESULTS AND DISCUSSION

All the complexes formed from $CoCl_2.6H_2O$, CoS, and $CoSO_4.7H_2O$ using 4,4′-bipyridine are coloured, and their analytical data are given in Table 3. The complexes are found to be insoluble in most common organic solvents, both polar and non-polar, which probably reflects the polymeric nature of the complexes. They did dissolve to a slight extent in dimethyl formamide (DMF) and partially in ethanol forming turbid solution. Mostly, this dissolution is accompanied by decomposition. This has hindered the possibility to study the spectroscopic and electronic properties of the complexes. The melting point of all these compounds are greater than 300 °C, which indicate the contribution of the bipyridine nitrogen to coordination.

The complexes formed by using $CoCl_2.6H_2O$ and "CoS" with 4,4′-bipyridine are found to be same, this is true from the elemental analysis, UV-VIS, IR-spectra and other data.

When "CoS" was made to react with 4,4′-bipyridine by passing chlorine gas to the mixture, the sulfide was oxidized to elemental sulfur by chlorine gas. The amount of sulfur produced and isolated was also equal to the amount of sulfur in CoS that was used. As a result "CoS" forms identical complex as that one formed by $CoCl_2.6H_2O$ with 4,4′-bipyridine. Note that chlorine gas oxidizes also the cobalt from +2 to +3.[10]

By taking in to account the results of the chemical analysis, the electronic spectra, the geometry of the central ion based on its oxidation number and the bonding nature of [illegible] following formula and

Table III

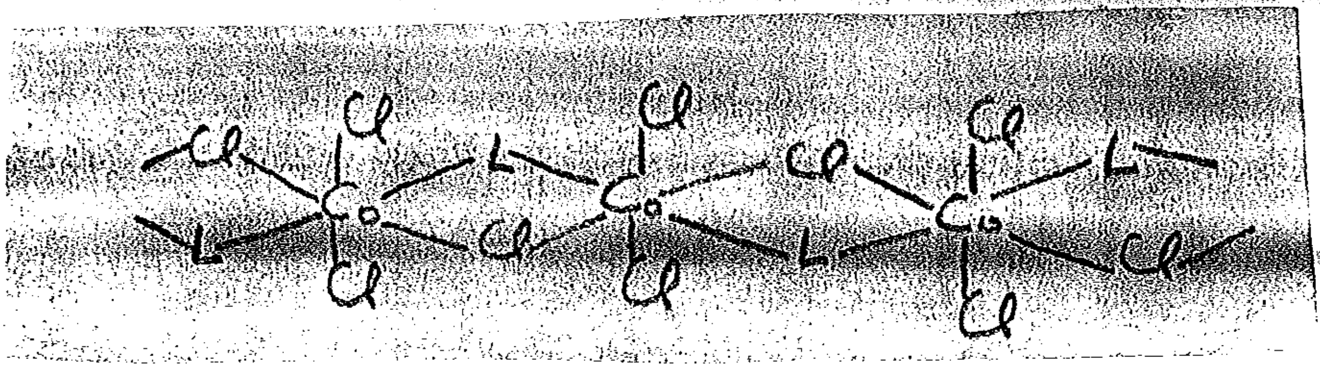
Analytical Data

	Complex	Yield %	Colour	Found (calculated) %**			
				Cobalt	N	Cl^-	$SO_4^=$
1.	$CoCl_2$ / bipy	64	violet	18.00	8.25	32.74	
				(18.34)	(8.71)	(33.12)	
2.	CoS / bipy	11.3	violet	18.00	8.41	32.76	
				(18.34)	(8.71)	(33.12)	
3.	$CoSO_4$ / bipy	30	bright violet	12.03	11.02	6.82	18.43
				(11.71)	(11.14)	(7.06)	(19.09)

** The % compositions are based on formula $[Co(bipy)Cl_3]$ for complex 1 and 2, whereas complex 3 it is based on $[Co(bipy)Cl(SO_4)]$

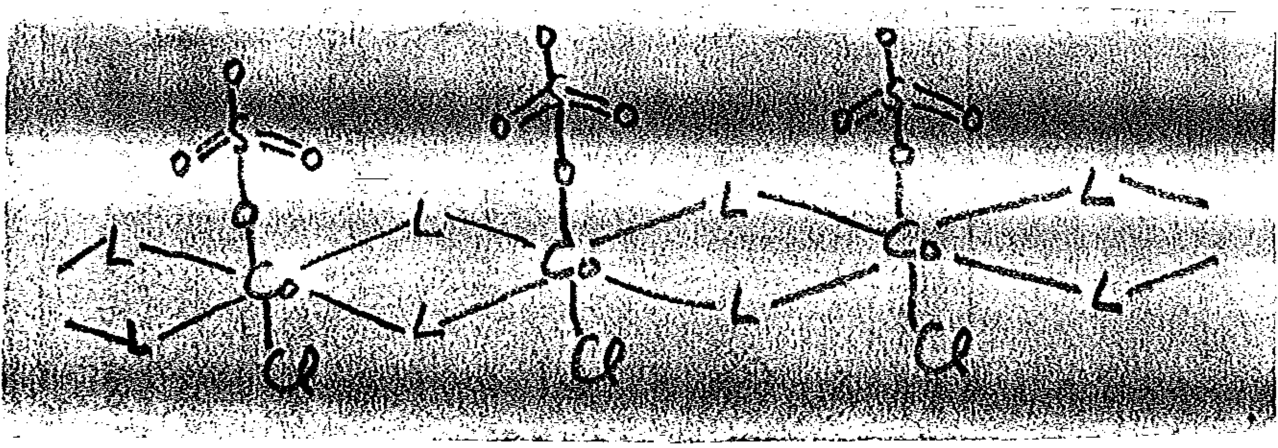
structures are proposed:-

(i) for the complex formed between $CoCl_2.6H_2O$ or CoS and 4,4-'bipyridine the formula of the complex is $[Co(bipy)Cl_3]$ and its structure is:-



i.e. an octahedral plymeric structure with trans configuration in which there is a halogen and 4,4-'bipyridine bridging molecules. This structure is similar to the ones reported before for related compounds.[33,37]

(ii) for the complex formed between $CoSO_4.7H_2O$ and 4,4'-bipyridine the formula of the compound is $[Co(bipy)_2Cl(SO_4)]$ and its structure is :-



This is also a polymeric structure, in which 4,4′-bipyridine only acts as a bridge between two metal ions.

The proposed formula and structure are in line with the experimental results.

4.1. Spectral Analysis

4.1.1. UV-VIS

The complexes synthesized as well as the reaction products of the amines are not soluble in most common solvents, it was difficult to get spectra in visible region. However, the complexes give a turbid solution in dimethyl formamide (DMF) and ethanol. When the turbid solution with DMF was heated to about 70 °C for 15 minutes a clear blue solution was obtained, which has two absorption bands around 600 nm, and 660 nm in the visible region probably corresponding to the spin allowed transitions from $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ states. (i.e. $^1A_{1g} \text{------>} {}^1T_{1g}$ around 600 nm, and $^1A_{1g} \text{------>} {}^1T_{2g}$ around 660 nm). These transitions are usually observed in the case of low spin complexes. 4,4-′bipyridine is highly strong field ligand in spectrochemical series, which forms low spin complexes and in these cases it stabilizes Co^{+3} complexes. Very dilute solution of the complex as well as the reaction product of the amines in ethanol were taken for UV, which gave rise to a band around 238 nm that can be assigned to charge transfer.

The UV spectra of the reaction product except for n-butyl amine was different from that obtained from $Co(bipy)Cl_3$. This probably indicates that a reaction might have taken place between the amines and the complex. The residue of the reaction show similar spectra with that of the starting material, except for diethyl amine.

The filterate of the reaction product of benzyl amine and the residue of the reaction of diethyl amine have more or less similar band around 250 nm with shoulders on both sides. Diethyl amine is highly volatile, hence the UV of the filterate can not be obtained.

The filterate of the reaction product of p-toluidine, p-anisidine and O-anisidine have similar bands around 236 nm and 290 nm. The spectra of the complex that was prepared without using chlorine gas as an oxidizing agent has two bands around 236 nm and 280 nm, which is more or less similar with the spectra of the filterate of the reaction product of the above amines. The bands can be assigned to transitions $^4T_{1g}(F) \text{------>} {}^4T_{2g}(F)$ and $^4T_{1g}(F) \text{------->} {}^4T_{1g}(P)$, which is a charactersitic of a weak octahedral field around cobalt (II). Therefore, in this case it seems that p-toluidine, p-anisidine and o-anisidine may have reduced cobalt from +3 to +2.

4.1.2. IR-Spectra.

All the three complexes have similar spectra, except that the complex of $CoSO_4$ / bipy has a broad band around 1150 cm^{-1} , which is characteristic for covalent sulfate.[45] The strong bands around 1600 cm^{-1} is due to pyridine ring vibrations of C=C and C=N stretching modes.[46] Monomeric compounds containing unidentate terminal 4,4'-bipyridine have no bands

[illegible] stretching vibrations [illegible]

Table IV.

Some Properties of the Product Obtained by Reacting with [Co(bipy)Cl_3] Different Amines

Product obtained from Reaction with	Yield %	m. pt (°C)	Colour	Conductivity 0.05 g/100 ml water	λ_{max} nm in absolute ethanol
P-anisidine	83	> 300	dark violet	1.2×10^{-5} ohm^{-1}	295,236
P-toluidine	54	> 300	violet	3.0×10^{-5} ohm^{-1}	290,236
O-anisidine	90	> 300	violet	1.8×10^{-6} ohm^{-1}	285,236
Benzyl amine	89	~ 40	reddish brown	2.0×10^{-4} ohm^{-1}	246
n-butyl amine	41	> 300	dark brown	3.6×10^{-5} ohm^{-1}	234
Diethyl amine	67	> 300	dark brown	7.5×10^{-5} ohm^{-1}	250

4.1.3. Conductivity Measurement

The measurment of conductivity was not precise, because of difficulty of solubility as the substances were found to be slightly soluble in water. The pure $Co(bipy)Cl_3$ complex has a conductivity value of 2×10^{-5} ohm^{-1}, and that of distilled water is 1.55×10^{-5} ohm^{-1}.

The conductivity of $[Co(bipy)Cl_3]$ was also determined in the solid form using a pellet of the complex, at normal temperature.

i.e. $R = \rho l / A$, but $\rho = 1/\sigma$, from which $\sigma = l / RA$

Where R = resistance; ρ = density ; l = thickness, A = cross sectional area ($A = \pi r^2$), σ = conductivity,

R = 2.181 k ohm , l = 0.25 cm, r = 0.625 cm,

$\therefore \quad \sigma = l/RA = l/R(\pi r^2) = 0.25/[(2.181 \times 10^3)1.23] = 9.32 \times 10^{-5}\ cm^{-1}$

Thus, the conductivity of the complex in solid form is 9.32×10^{-5} cm^{-1} and in aqueous solution 2×10^{-5} ohm^{-1}. The difference can be due to partial solubility of the complex, (due to the effect of solution) and due to undetected experimental errors.

During the measurment of the current a square signal of different frequency and amplitude have been switched and the current was found to be amplified than the axial direction. Although the measurment was made for high frequency signal effect, low frequency has also been observed and the sample is highly transparent in the frequency range of the order of 0.1 - 1 Hz. The sample has been observed to generate pulses and signals of different shape and frequency, because of the capacitive action of the pellet

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Declaration

I, the udersigned, declare that this thesis is my work and all sources of materials used for the thesis have been duly acknowledged.

Name Elias Abadula

Signature

Place and date of submission January, 1993

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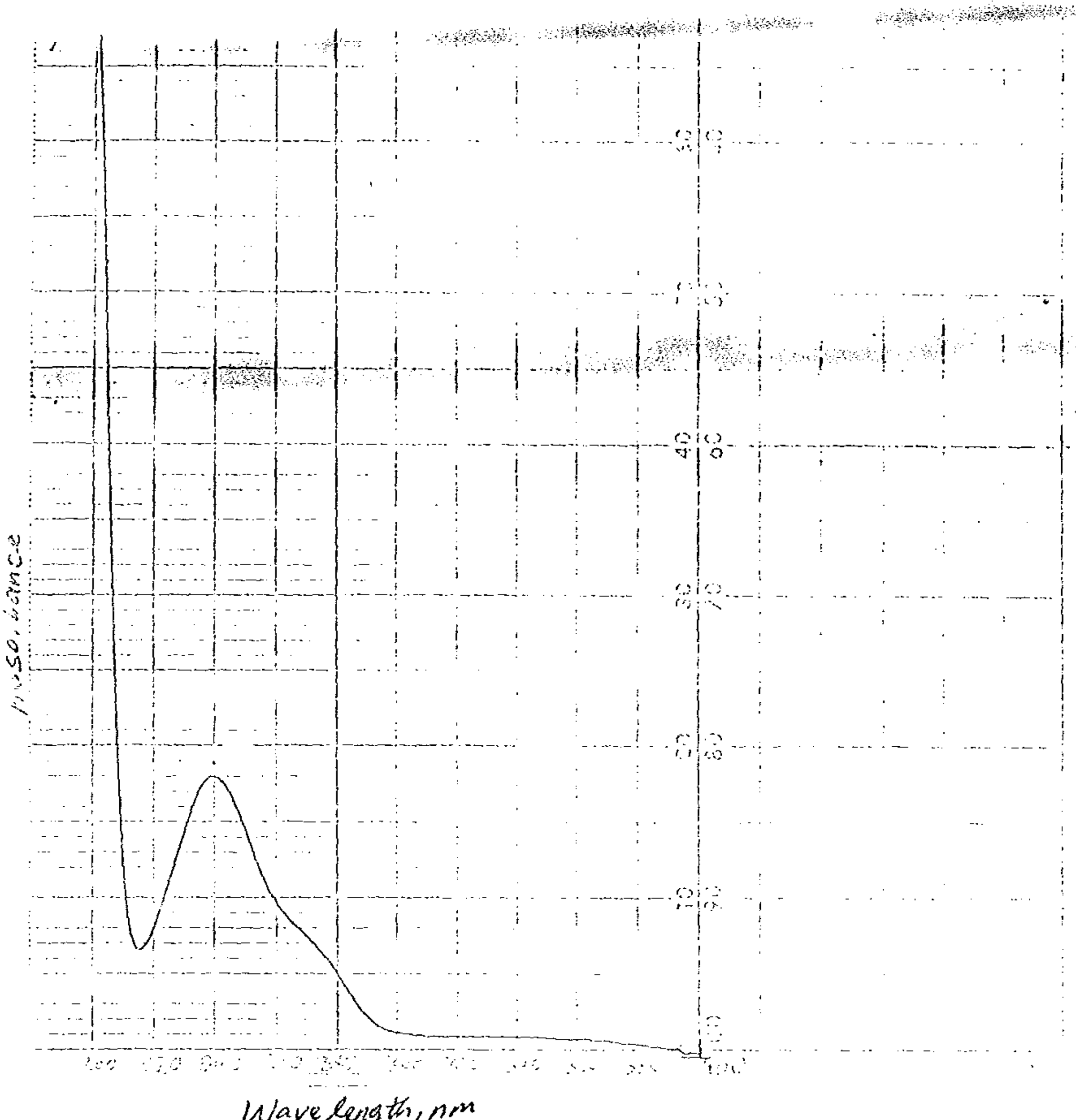


Fig.1. UV spectrum of $(Co(bipy)Cl_3)$

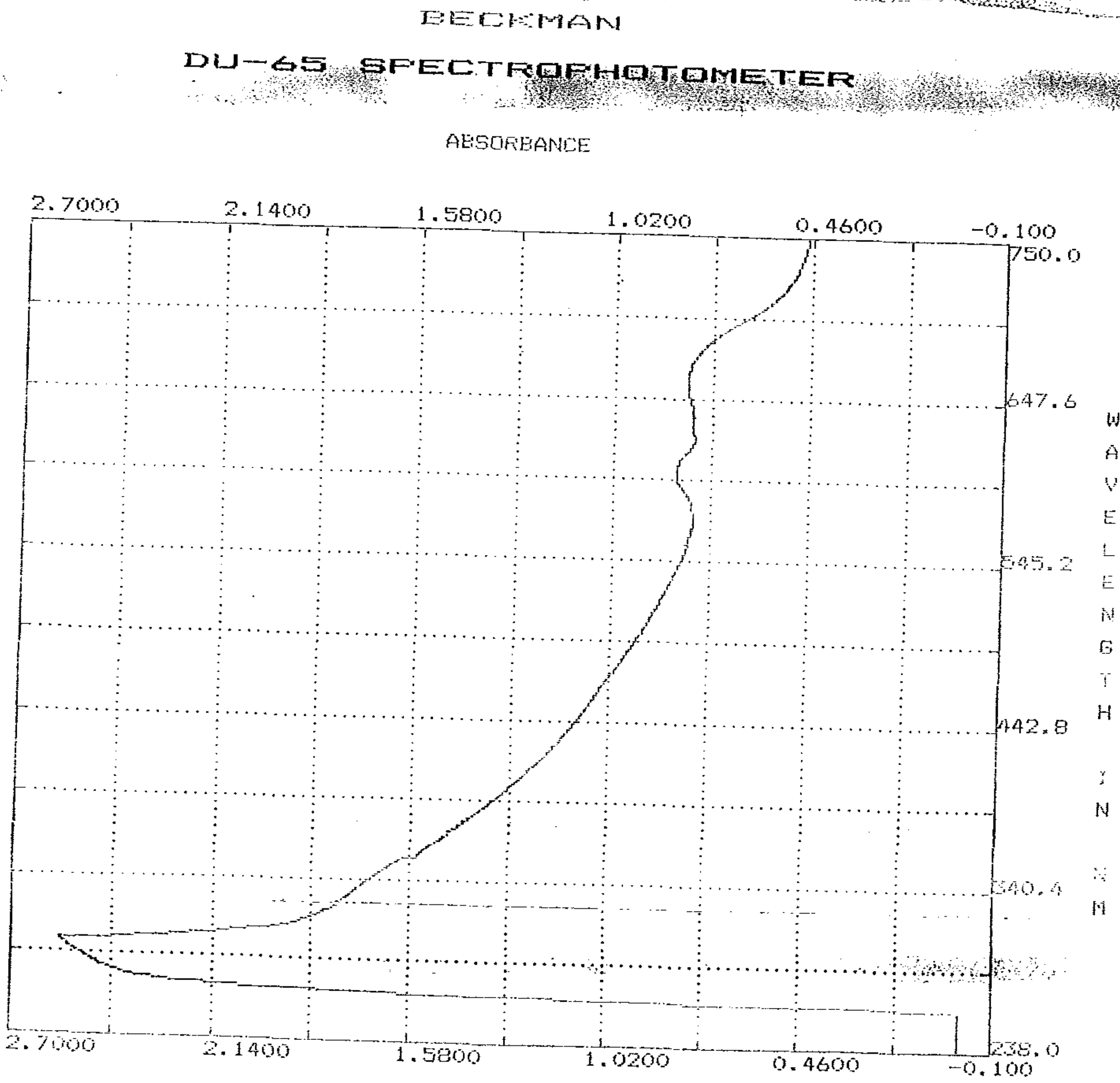
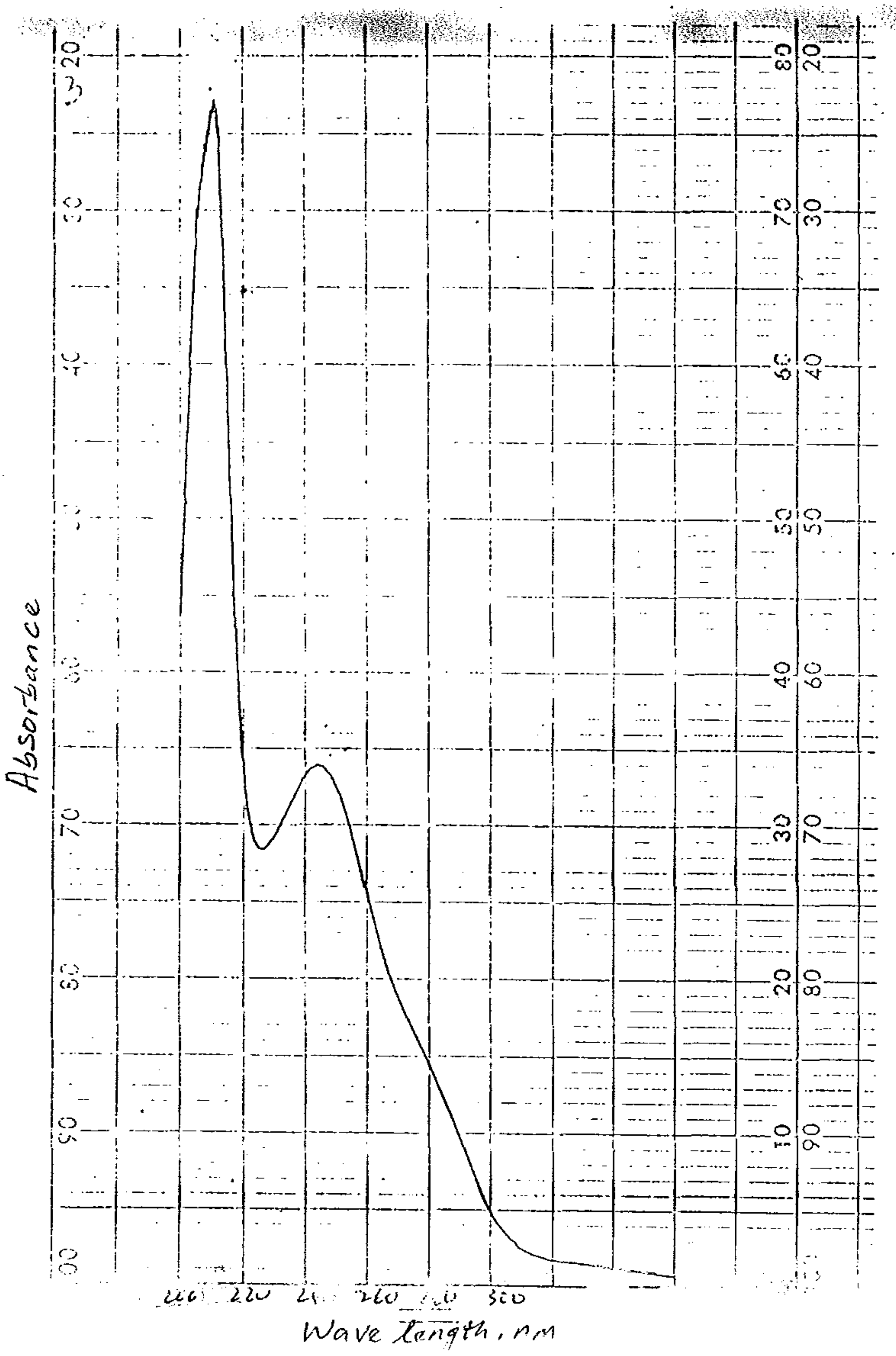


Fig.2 UV Spectrum of (Co(bipy)Cl_3)

Fig.3. UV-spectrumof the reaction product of n-butylamine.



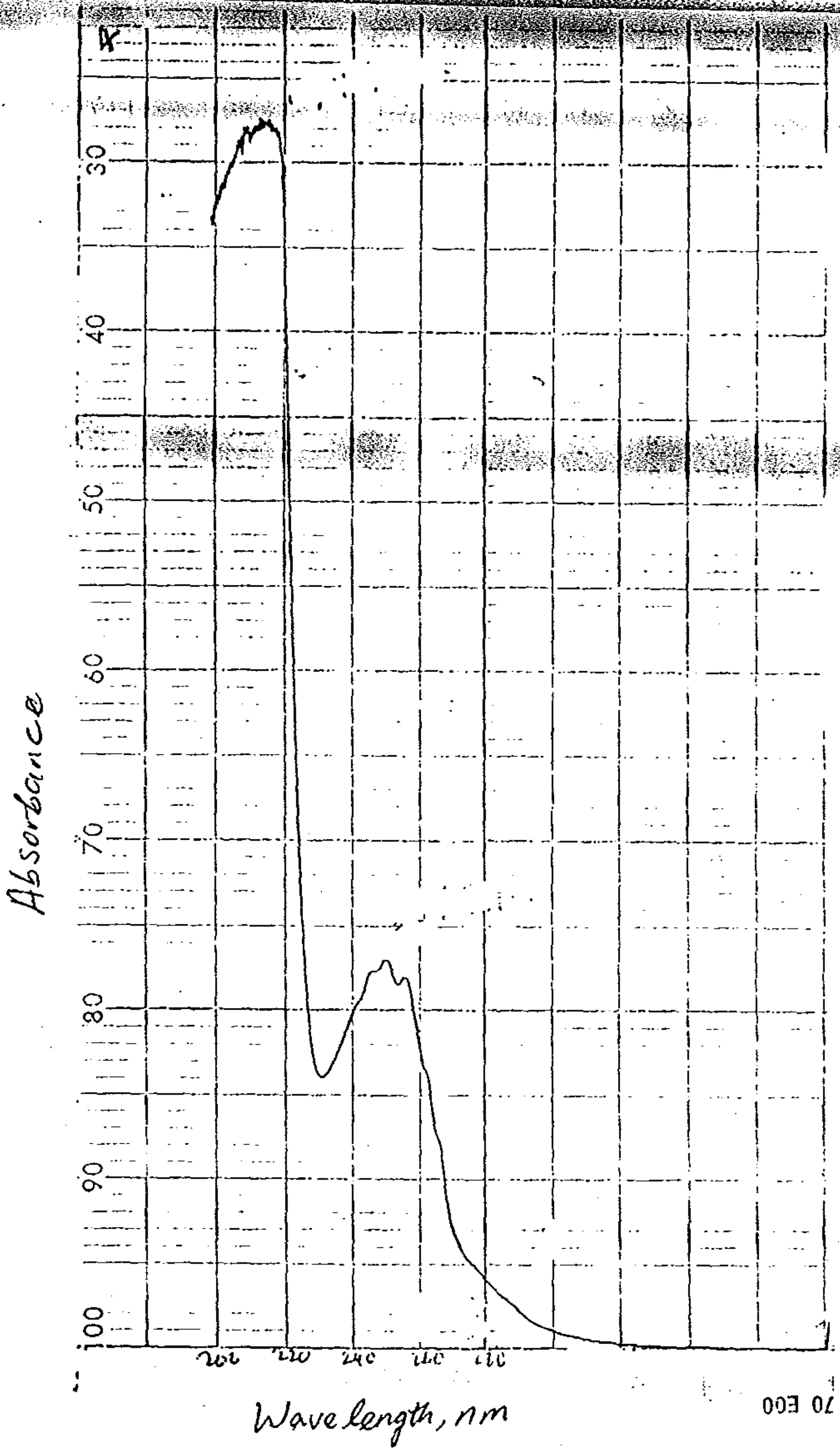


Fig.4. UV-spectrum of the reaction product of benzylamine.

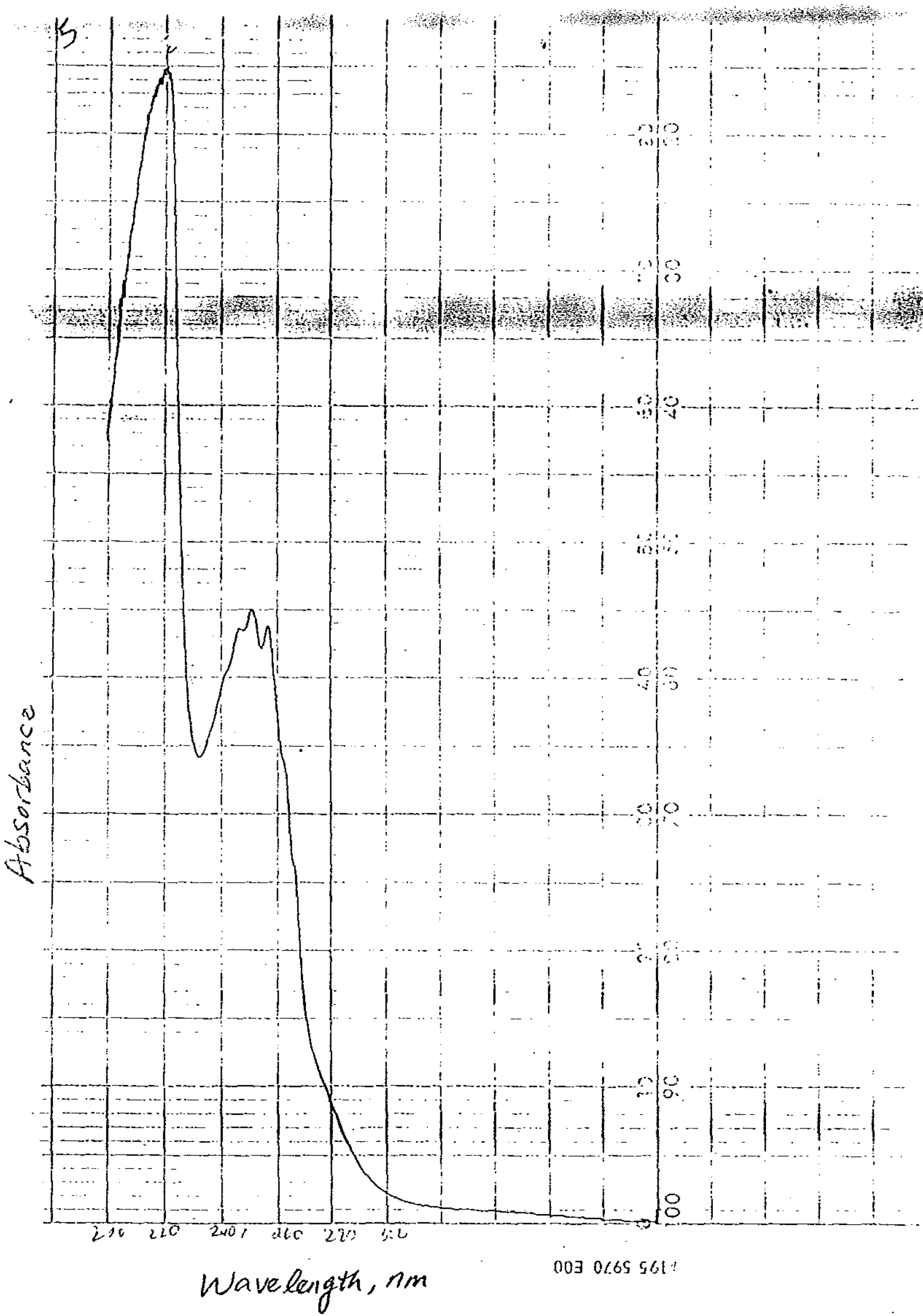
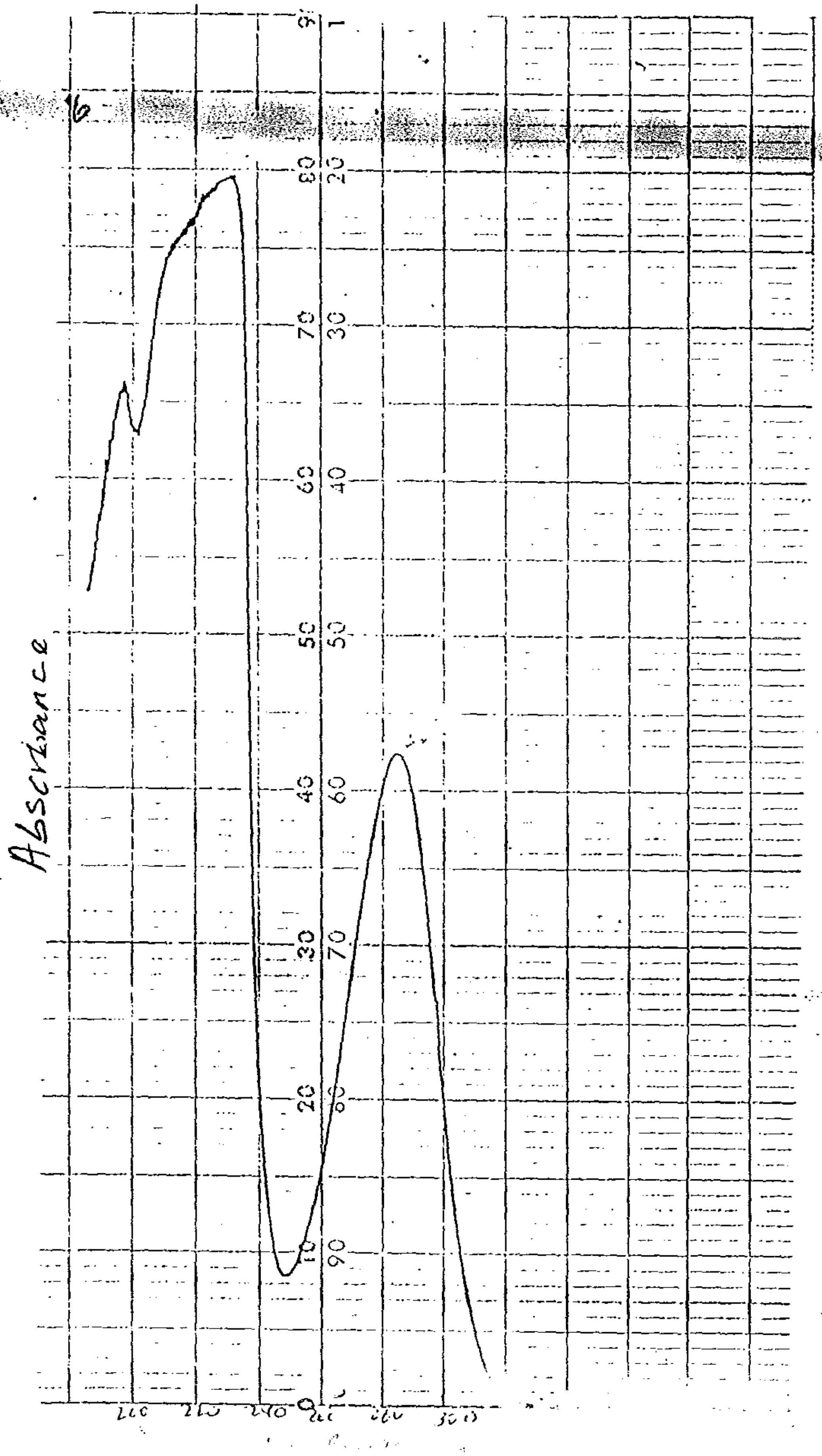


Fig.3. UV-spectrum of the reaction product of [illegible]
diethylamine.

Fig.6. UV-spectrum of the reaction product of o-anisidine.



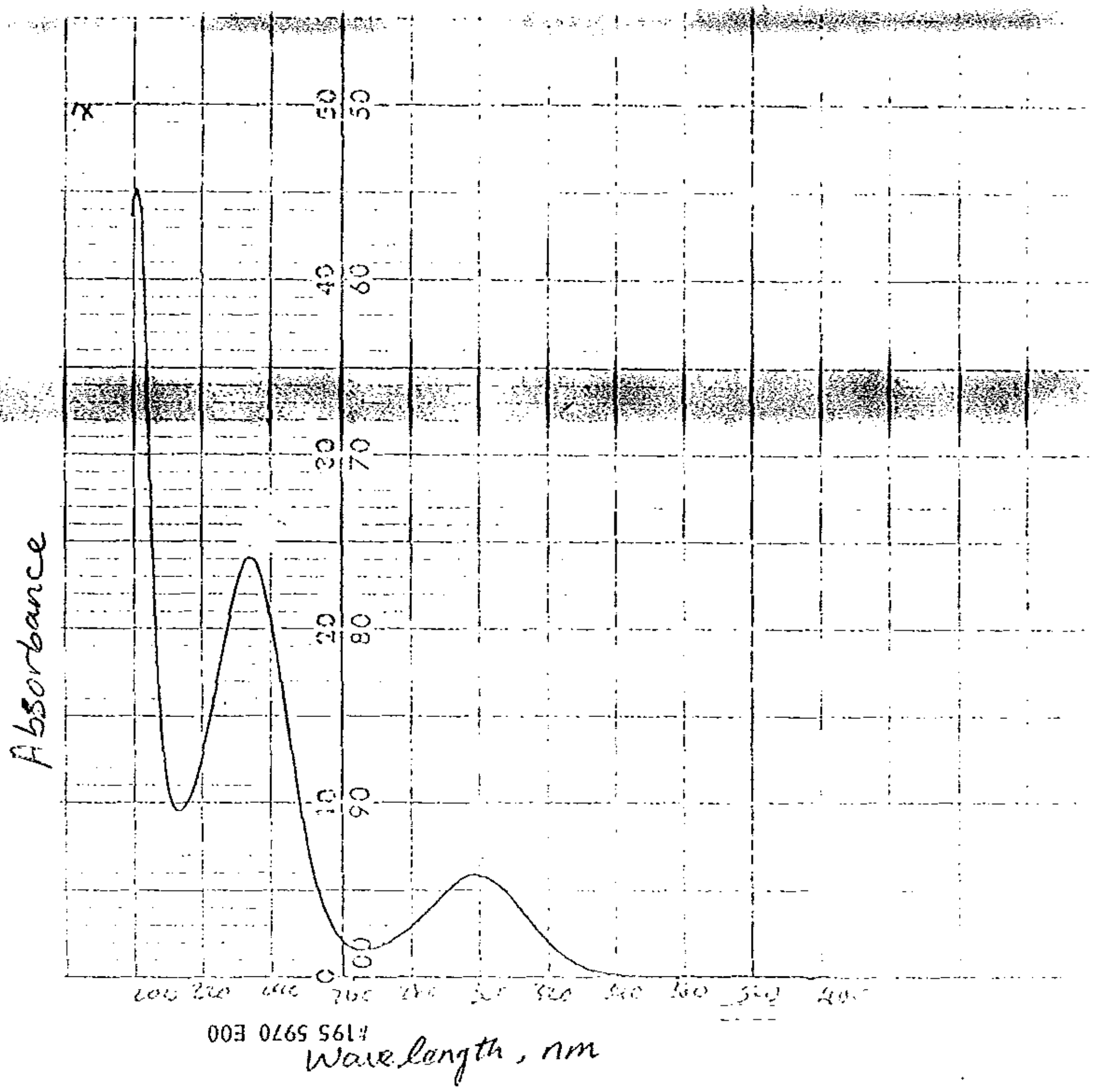


Fig.7. UV-spectrum of the reaction product of P-anisidine.

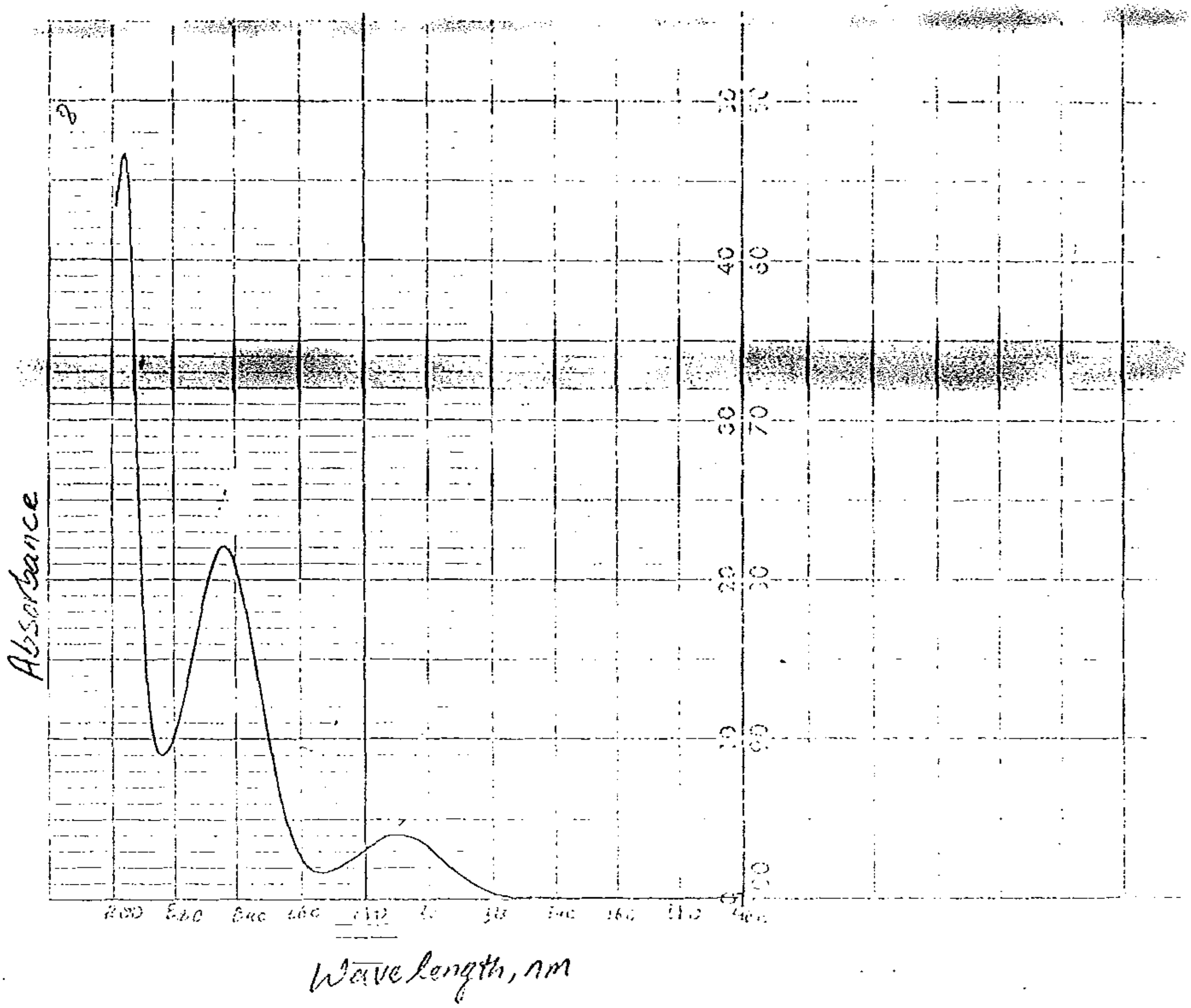


Fig. [illegible] UV-spectrum of the reaction product of P-toluidine.

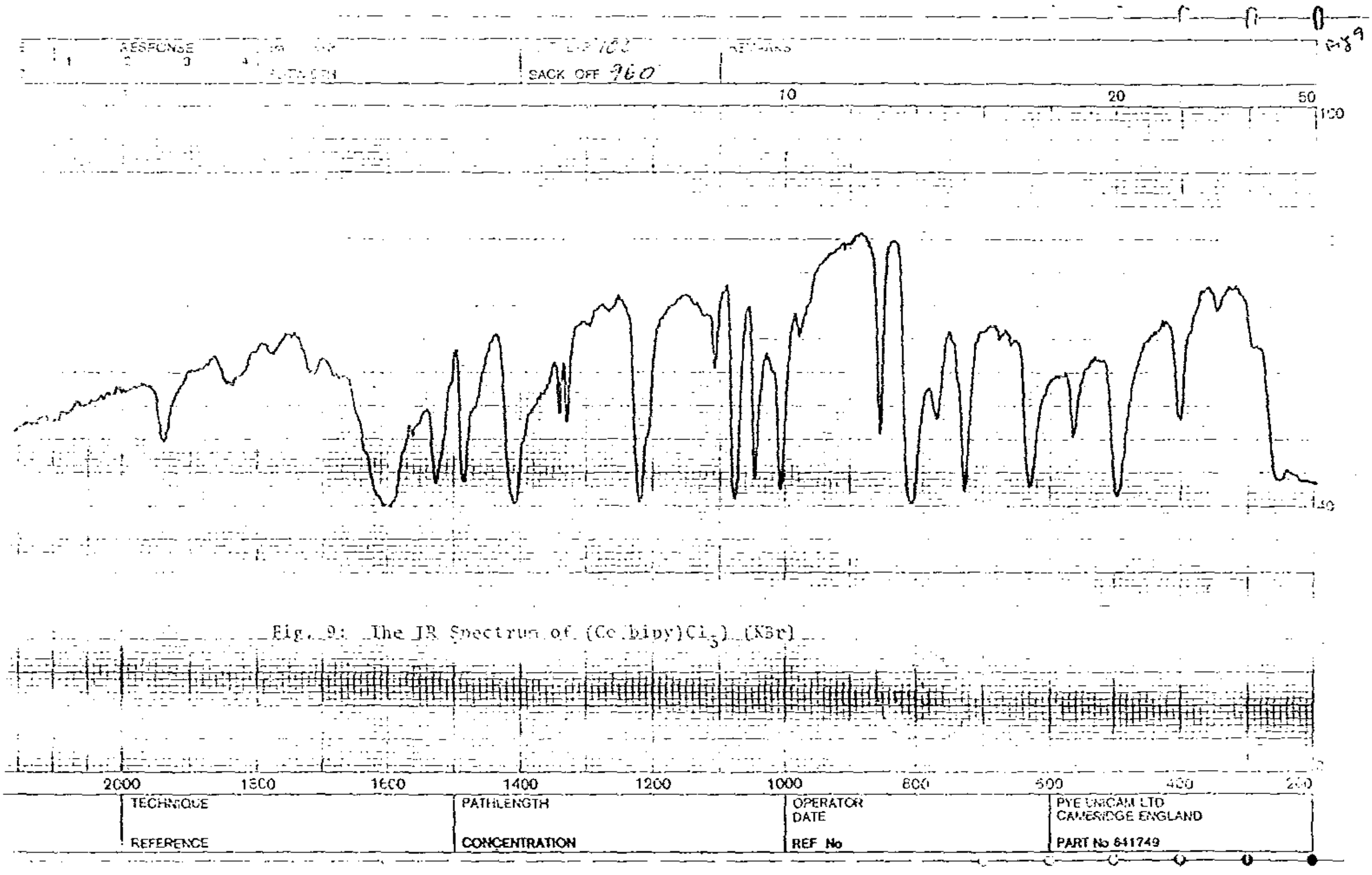


Fig. 9: The IR Spectrum of (Co bipy)Cl_3) (KBr)

10

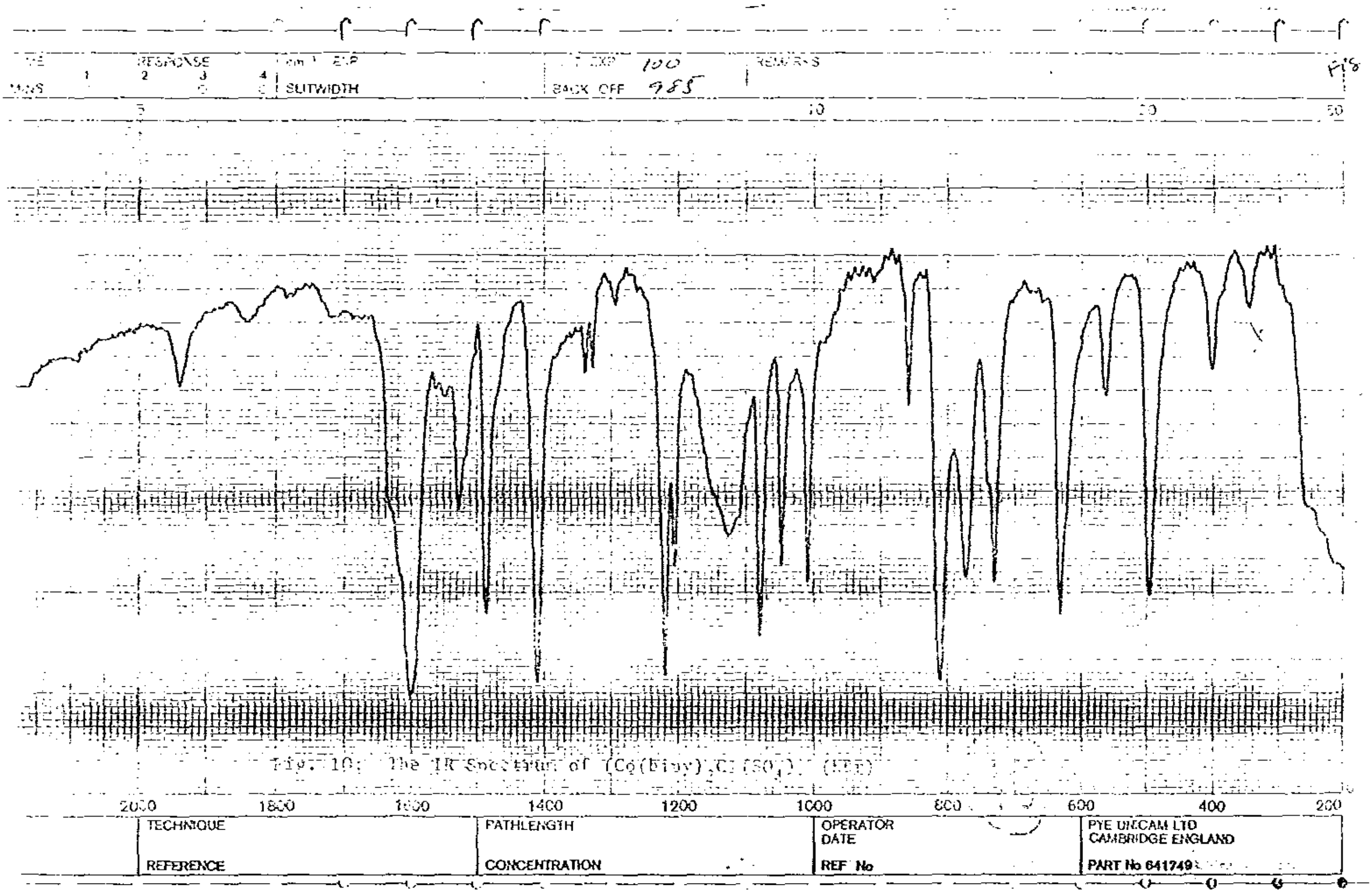


Fig. 10: The IR Spectrum of [Co(Bipy)$_2$Cl](SO$_4$) (KBr)

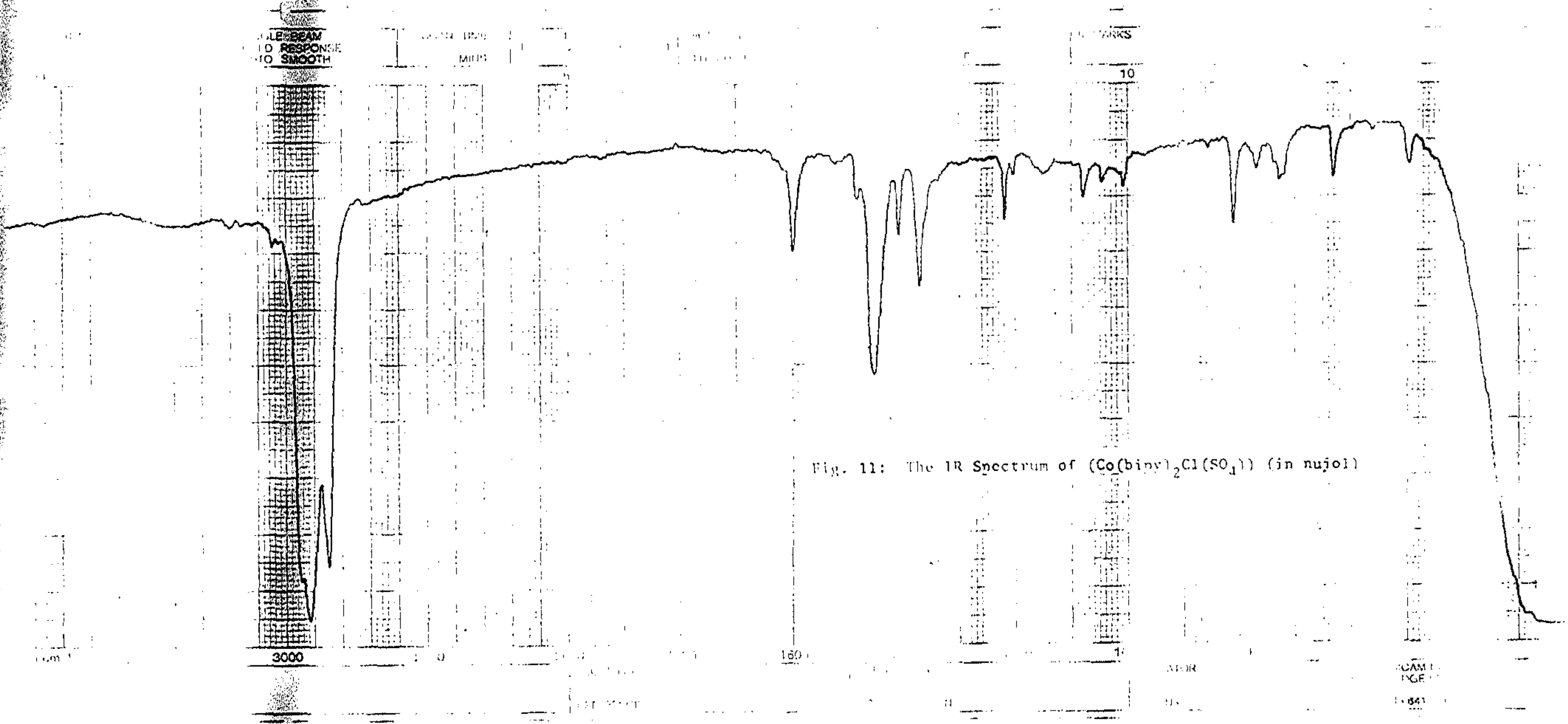


Fig. 11: The IR Spectrum of $(Co(bipy)_2Cl(SO_4))$ (in nujol)

Fig

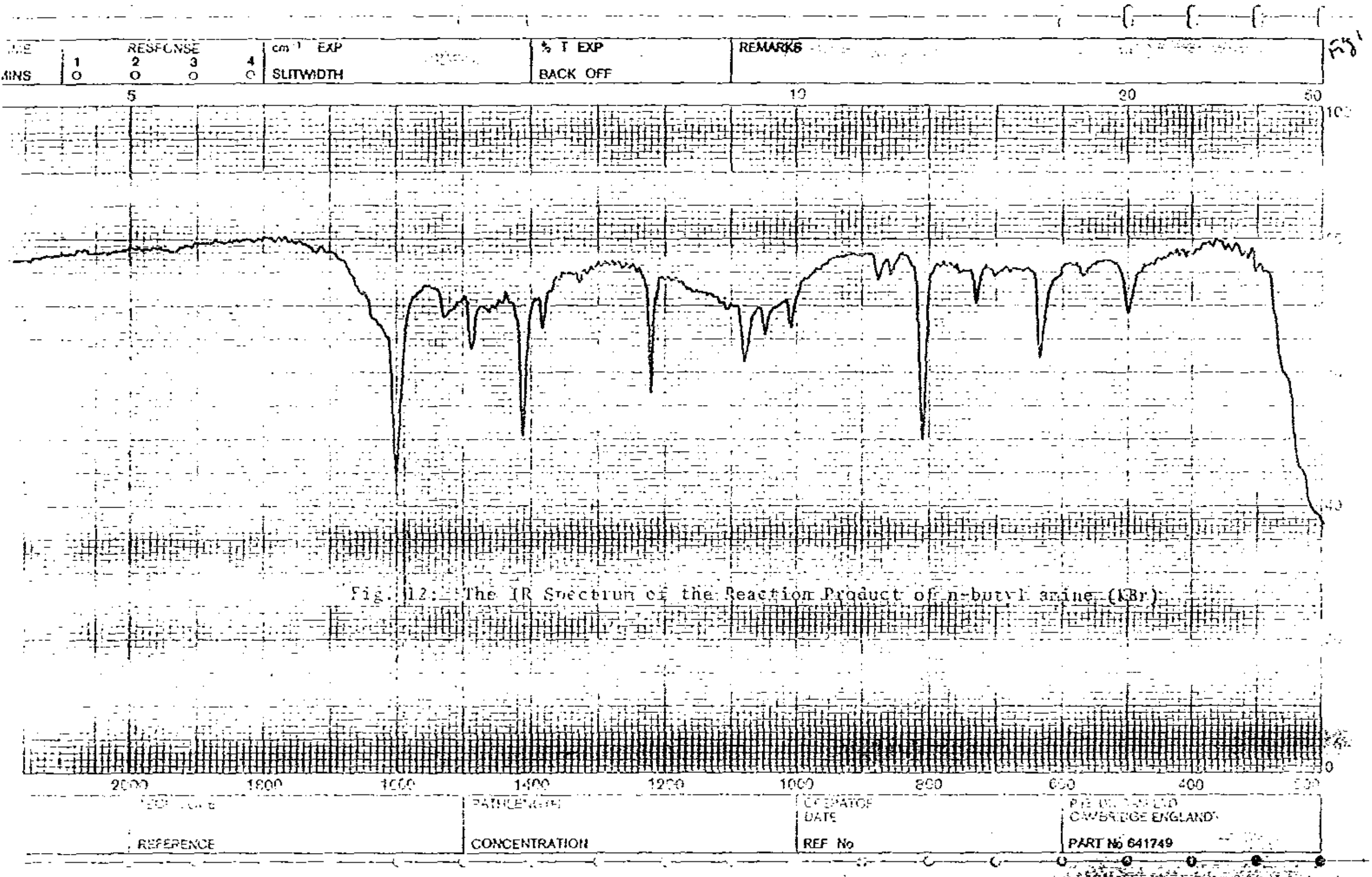


Fig. 12: The IR Spectrum of the Reaction Product of n-butyl amine (KBr)

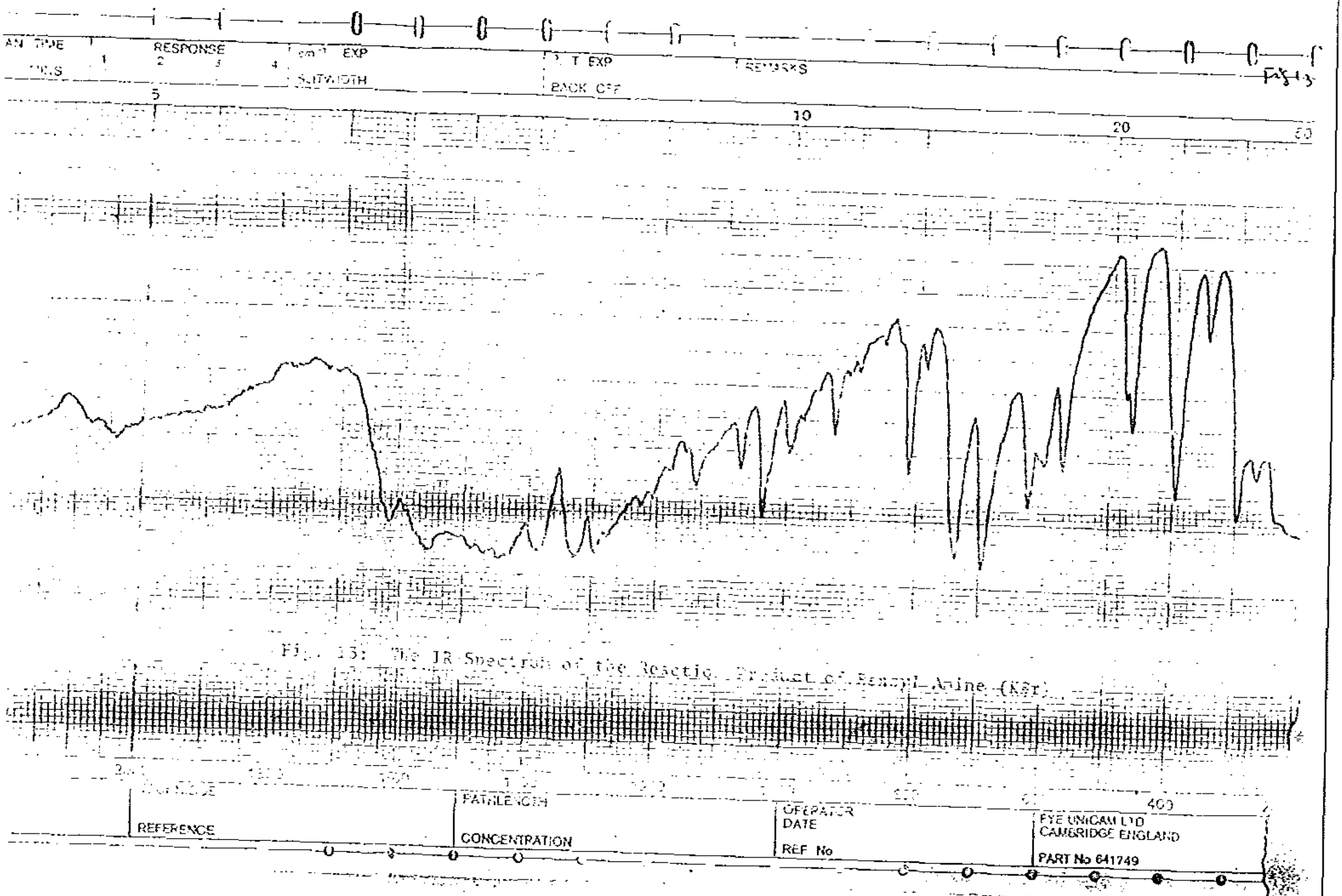


Fig. 13: The IR Spectrum of the Reaction Product of Benzyl Amine (KBr)

Fig 14.

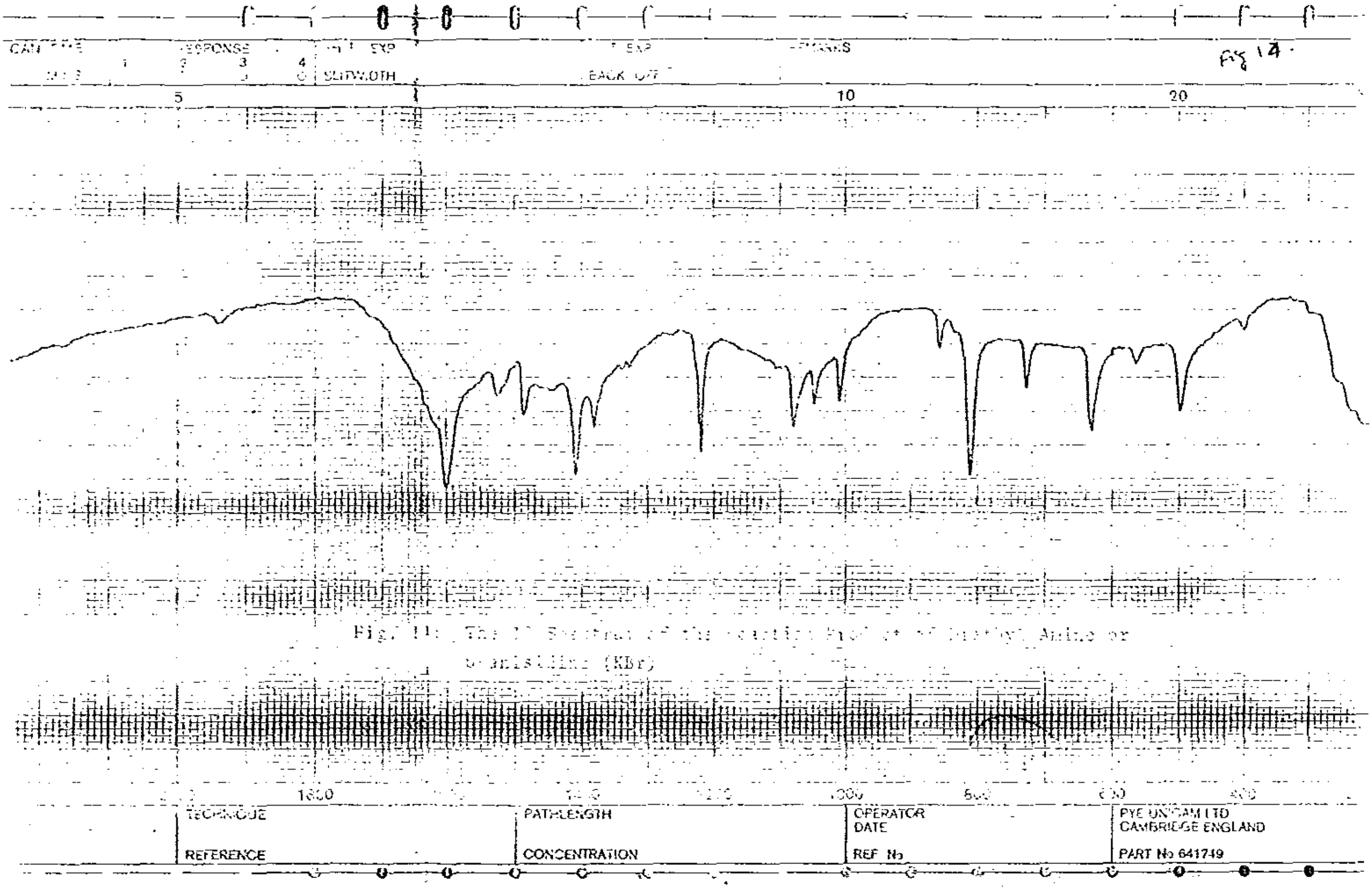


Fig. 14: The IR Spectrum of the Reaction Product of Diethyl Amine on o-anisidine (KBr)

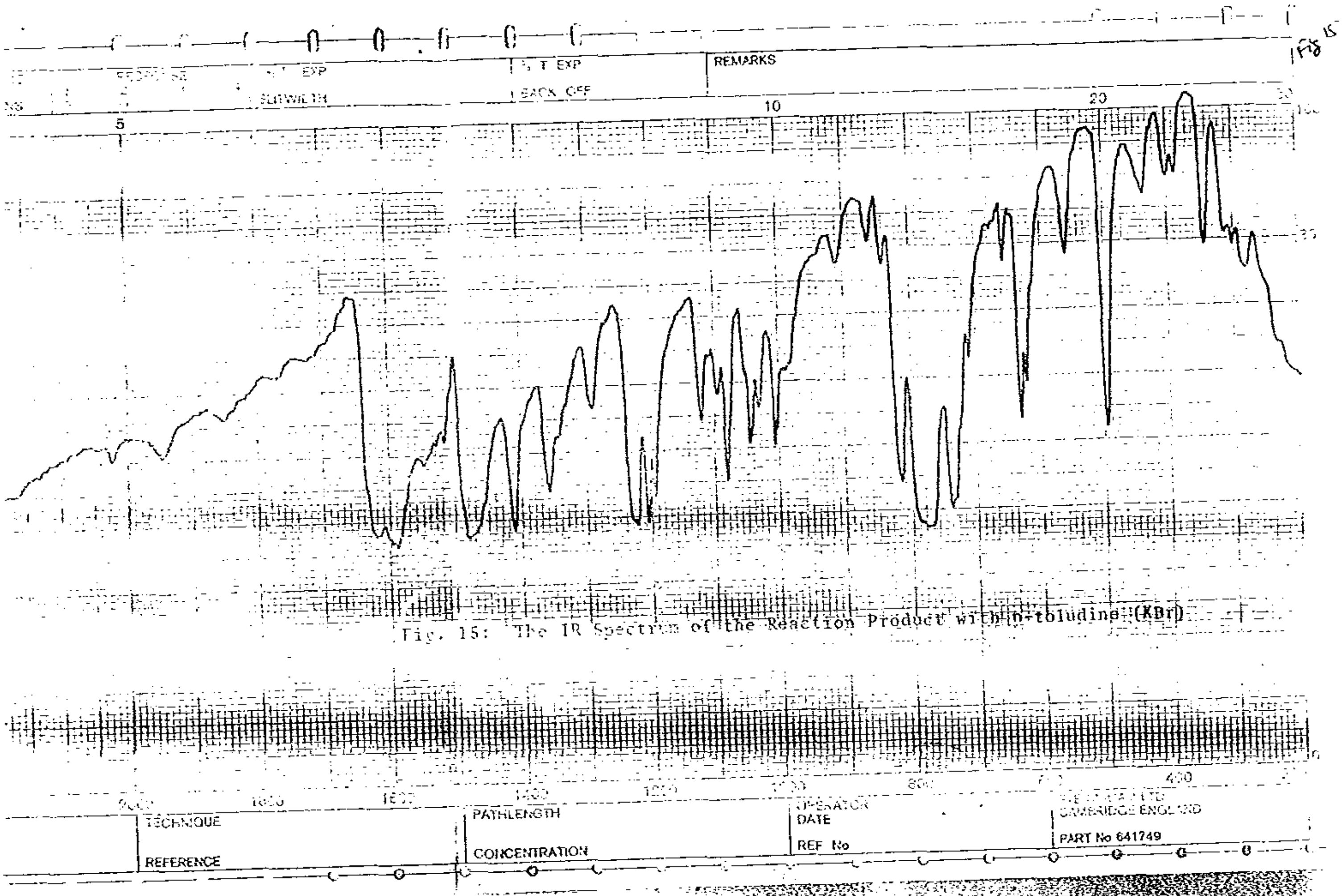


Fig. 15: The IR Spectrum of the Reaction Product with p-toluidine (KBr)

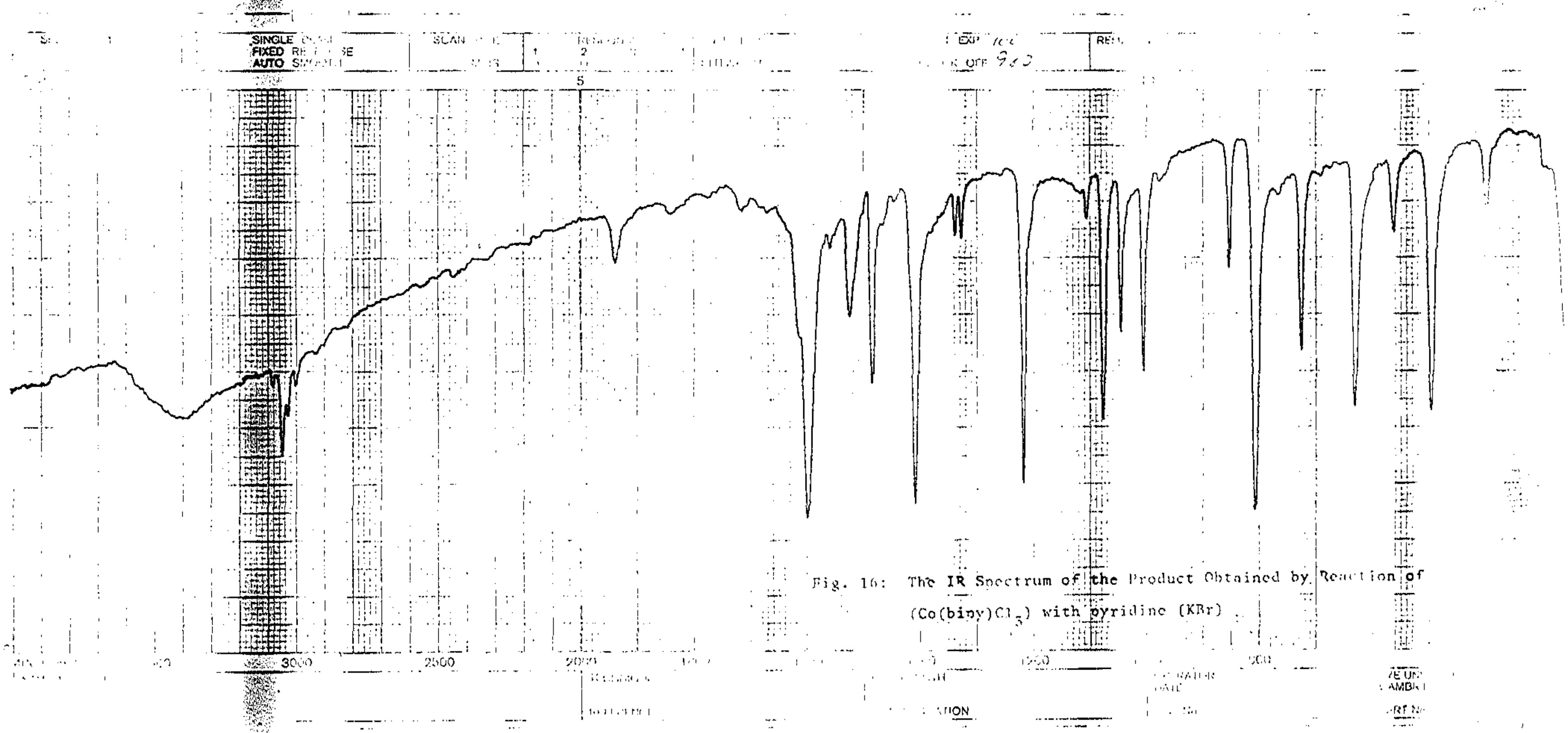


Fig. 16: The IR Spectrum of the Product Obtained by Reaction of (Co(bipy)Cl$_3$) with pyridine (KBr)

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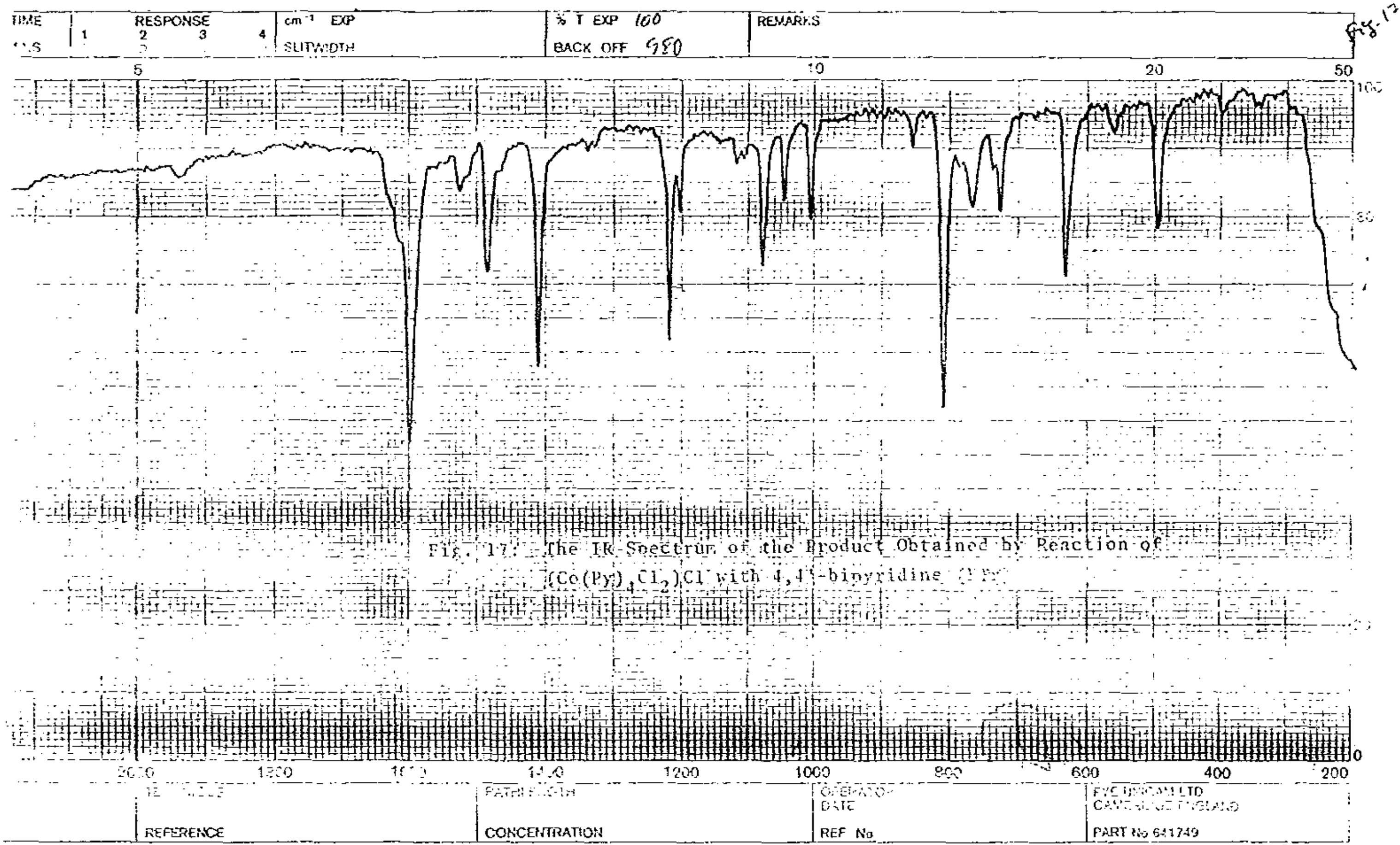

Fig. 17: The IR Spectrum of the Product Obtained by Reaction of $(Co(Py)_4Cl_2)Cl$ with 4,4'-bipyridine [illegible]

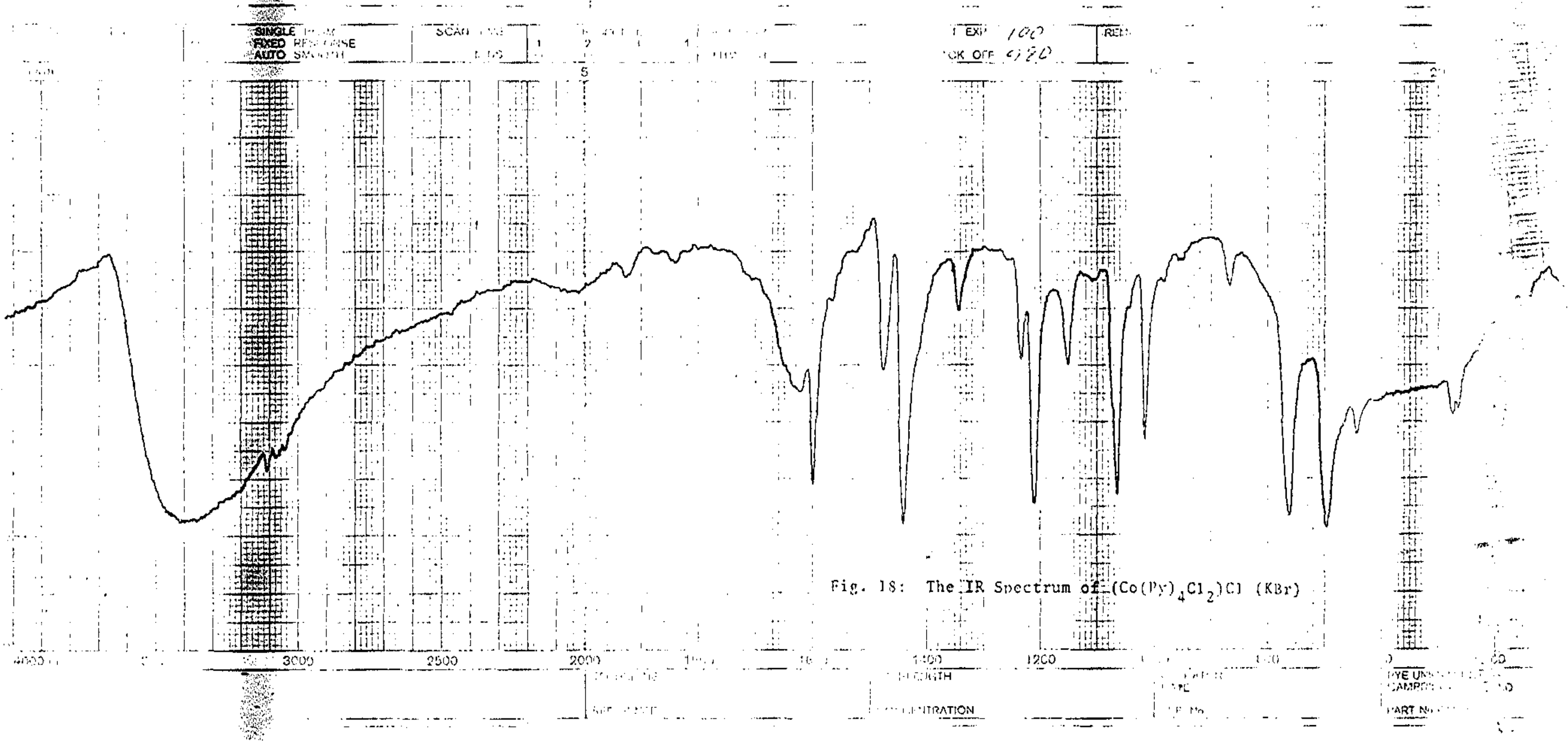

Fig. 18: The IR Spectrum of $(Co(Py)_4Cl_2)Cl$ (KBr)

Fig.20 UV-VIS Spectrum of $(Co(bipy)Cl_3)$ in Ethanol