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ELECTROCHEMICAL REACTIONS OF POLYPYRIDYL
COMPLEXES OF IRON, COBALT AND NICKEL

by

Ravindra Prasad

This thesis is in submission for the degree of
Doctor of Philosophy at The City University, London

ABSTRACT

The oxidation and reduction of anhydrous metal(II) perchlorate complexes of iron, cobalt and nickel with 2,2'-bipyridyl, 4,4'-dimethylbipyridyl and 2,2',2''-terpyridyl in acetonitrile solutions has been studied by electrochemical methods.

Cyclic voltammetry at a stationary platinum electrode in a medium of 0.1M tetra-n-butylammonium perchlorate indicated that the metal(II) polypyridyl complexes were oxidised and reduced by reversible one electron processes. Confirmation of the one electron transfer processes was obtained using constant potential coulometry in which milligram quantities of the metal(II) complexes were electrolysed in acetonitrile solutions at potentials in the region of the peak potentials of the corresponding cyclic voltammograms.

The preliminary studies in voltammetry and coulometry were followed by preparative scale constant potential electrolyses; gram quantities of metal(II) polypyridyl complexes were oxidised and reduced to the corresponding metal(III) and metal(I) complexes respectively. Solid products were isolated in all the metal(III) preparations carried out; in the case of the preparation of metal(I) complexes, however, it was possible to isolate only the 2,2'-bipyridyl complexes of cobalt(I) and nickel(I). The magnetic susceptibilities of the solid products were determined at room temperature by the Gouy method and the effective magnetic moments of the metal ions calculated. Visible and near i.r. spectra in solution of the complete series of complexes were examined; where possible, band assignments have been made.

(ii)

Values of the standard reduction potentials to the metal(III)/metal(II) and metal(II)/metal(I) couples, obtained from the cyclic voltammetry data, are discussed in terms of crystal field effects.

ACKNOWLEDGEMENTS

Appreciation and grateful thanks are extended to Dr. D. B. Scaife for his invaluable supervision, without which this work could never have come to an end or might not even have started in the first place.

At the same time, opportunity is also taken to thank ■ ■ ■ ■ ■ of Thomas Hill-Jones Ltd., London for permitting me to carry out this research and all my colleagues at the City University for their co-operation.

(iv)

TO MY LATE FATHER PANDIT CHHOTAY LAL

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1. INTRODUCTION

The aim of the present work was to attempt to prepare and study the properties of unusually high and low oxidation state polypyridyl complexes of iron, cobalt, and nickel by electro-oxidation and electro-reduction of the corresponding metal(II) complexes at a platinum electrode. It was hoped that these would include complexes of iron(I), cobalt(I), nickel(I), nickel(III) and possibly some complexes in the +4 oxidation state. As in a previous study of the electro-oxidation of silver(I) polypyridyl complexes,¹ acetonitrile with tetra-n-butylammonium perchlorate as the supporting electrolyte was chosen as the solvent system due to its great potential range (-3.0V to +2.3V versus the Ag/AgNO₃(0.01M) electrode in acetonitrile).

In principle, the use of preparative electrochemical techniques offers a number of advantages over conventional chemical methods. For example, since the potential at a working electrode can be controlled at any selected value within the potential range of the solvent system, the working electrode can be regarded as equivalent to a universal oxidising/reducing agent, the strength of which can be varied according to specific requirements. Another advantage is that separation of the product by an electrochemical reaction is not complicated by the presence of byproducts arising from the use of chemical reagents. The specific nature of the technique is of great importance since it can allow multi-step electron transfer processes to proceed to any selected intermediate stage. A disadvantage, however, of electrochemical methods is that where complexes of unusually high or low oxidation states are to be prepared, the use of a non-aqueous solvent system of

low electrical conductivity is essential; this can lead to low current densities and, consequently, long reaction times.

Before attempting electrochemical preparations of unusual oxidation state complexes of a particular metal, it is necessary, first, to survey the oxidation states which can be generated electrochemically and, if possible, obtain information regarding their stability. This aspect of the study was carried out using cyclic (triangular wave) voltammetry at a stationary platinum disc electrode. Although this technique was first used as early as 1938² its potentialities were not developed until the fifties and sixties, important theoretical contributions being made by Delahay,³ Matsuda,⁴ and Nicholson and Shain.^{5,6} Cyclic voltammetry is an extremely versatile and rapid technique for indicating not only the number of oxidation or reduction steps which occur in electrochemical reactions but also, for a reversible system, the number of electrons transferred in each step. An added advantage is that it can show whether or not the product of each electron transfer step is stable, at least over the time scale of the experiment.

The initial survey of the oxidation states of polypyridyl complexes of iron, cobalt and nickel was followed by the use of constant potential coulometry to confirm the number of electrons transferred in the oxidation and reduction of each metal(II)-polypyridyl complex system studied by cyclic voltammetry. Finally, preparative scale constant potential electrolyses were carried out and, where possible, the products were isolated and their magnetic and spectral properties studied and compared.

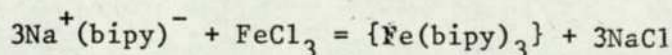
2. LITERATURE SURVEY

Uncommon oxidation state compounds of iron, cobalt and nickel

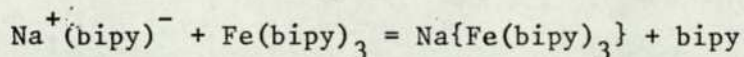
The most common compounds of iron, cobalt and nickel which are stable in the atmosphere are restricted to the +2 and +3 oxidation state compounds of iron and cobalt and to the +2 oxidation state compounds of nickel. Unusual oxidation state compounds of these elements might be regarded, therefore, as those in which the oxidation state of the metal ion is either less than +2 or greater than +3 in the case of iron and cobalt and is other than +2 in the case of nickel. However, in view of the recent developments and advances in the chemistry of low oxidation state metal complexes containing π -bonding ligands such as CO , NO , PR_3 , AsR_3 , SbR_3 , CNR , etc., the zero oxidation state of iron, cobalt and nickel can no longer be considered unusual; a vast range of metal(0) compounds have been prepared and characterised and are well reviewed.⁷⁻¹⁵ It is not proposed, therefore, to include the zero oxidation states in the present literature survey although mention will be made of metal(0) complexes which contain ligands other than those listed above. Further, those compounds prepared from metal carbonyls, nitrosyls, phosphines, etc., and their substituted products in which the metal is present in oxidation states of -2, -1 and +1 will not be covered. Such compounds include the carbonyl halides and hydrides, carbonyl nitrosyls, carbonyl nitrosyl halides and related compounds, the chemistry of which is discussed at length in the reviews cited.

Iron compounds

Low oxidation state complexes of iron with nitrogen donor ligands are very rare and of those reported only a few have been well characterised. Herzog and co-workers¹⁶⁻¹⁸ have prepared tris(2,2'-bipyridyl)iron(0) by reacting lithium(I)2,2'-bipyridyl with iron(III) chloride in anhydrous tetrahydrofuran as solvent containing an excess of 2,2'-bipyridyl. The process, carried out in the absence of air and water, yielded $\text{Fe}(\text{bipy})_3$ as a black precipitate. The compound is very sensitive to air and water; it liberates hydrogen from water to form the red coloured iron(II) complex ion $\{\text{Fe}(\text{bipy})_3\}^{2+}$, and in air turns from black to red, presumably being oxidised to the same iron(II) complex. At 145°C under reduced pressure $\text{Fe}(\text{bipy})_3$ decomposes into metallic iron and 2,2'-bipyridyl. Hall and Reynolds¹⁹ have also reported the preparation of this complex by adding an excess of sodium(I) bipyridyl to anhydrous iron(III) chloride in anhydrous 1,2-dimethoxy ethane, the following reaction being proposed on the basis of the elemental analysis of the product:



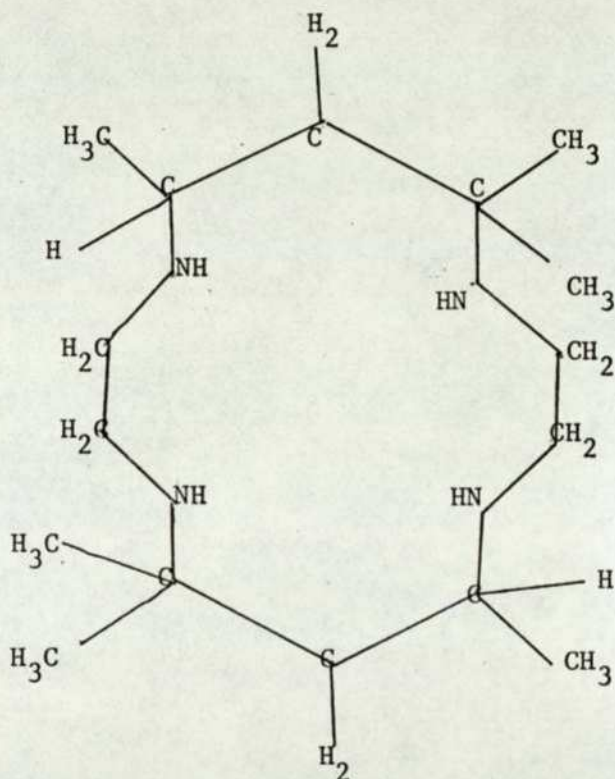
It was suggested that the reduction of the iron might be carried further by the reaction of $\text{Fe}(\text{bipy})_3$ with more $\text{Na}^+(\text{bipy})^-$ according to the equation:



Based on this suggestion, Mahon and Reynolds²⁰ prepared the sodium salt of tris(2,2'-bipyridyl)iron(-1), $\text{Na}\{\text{Fe}(\text{bipy})_3\}$, by the reaction

of sodium(I) bipyridyl with tris(bipy)iron(II) chloride under similar conditions as before.¹⁹

Olson and Vasilveskis²¹ have reported the preparation of an iron(I) complex which is formulated as $\{\text{HFeL}(\text{solvent})\}\text{BF}_4$, where L is the cyclic amine, trans-tetramine, and the solvent is acetonitrile and tetrahydrofuran. Trans-tetramine has the structure:



trans-tetramine

The preparation was based on the reduction of $\{(\text{CH}_3\text{CN})_4\text{FeL}\}(\text{BF}_4)_2$ by sodium amalgam in acetonitrile, the NaBF_4 which formed being separated by extracting the reaction product with tetrahydrofuran and stripping to dryness. The presence of the hydride ion was indicated by an absorption band in the infra-red spectrum at 1769cm^{-1} which disappeared on exposure to air. Chemical evidence also supported

the presence of a hydride ion, carbon tetrachloride reacting to give chloroform; phenol, however, did not yield hydrogen. It was speculated that the hydrogen in the complex might be derived from the amine group of the ligand.

One of the first iron compounds to be reported having an oxidation state higher than +3 was prepared by Stahl,²² who obtained a deep purple coloured solution when water was added to the fusion product of $\text{Fe}(\text{NO}_3)_3$ and KNO_3 ; this was attributed to the formation of the ferrate(VI) compound K_2FeO_4 , which has more recently been reported by Goralevitch.²⁶

Iron has also been reported to exist in oxidation states of +4, +5, +6 and +8, the last named state, found in FeO_4 ,^{23,24} being theoretically the highest possible oxidation state corresponding to the d^0 configuration. Iron(IV) and the much rarer iron(V) appear to exist only in various alkali and alkaline earth metal ferrate compounds. Iron(IV), however, exists not only in ferrates but also in a few halogen and hydride compounds which have been stabilised by phosphorus and arsenic donor ligands and in a number of dithiolate compounds.

Iron(IV) compounds were first reported in 1909 by Moeser and Borck,²⁵ who claimed to have prepared strontium and barium "orthoferrates" of the type $\text{M}_2^{\text{II}}\text{FeO}_4$ by heating a mixture of $\text{Fe}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$ or a mixture of $\text{Fe}(\text{OH})_3$ and $\text{Ba}(\text{OH})_2$ in an oxygen atmosphere at about 400-600°C. The iron to oxygen ratio in these compounds, however, was non-stoichiometric. Gushee et al.²⁷ following the same method but employing a temperature of 680-720°C obtained a compound of composition $\text{BaFeO}_{2.72}$. It is only quite

recently that the conditions necessary to obtain stoichiometric ferrate(IV) compounds have been achieved. Sr_2FeO_4 can be prepared^{28,29} using high oxygen pressure (not less than 40kbar³⁰), temperatures in the range of 1400°C and reaction times of about 16 hours. Reaction between hexahydroxo ferrate(III) compounds of type $\text{M}_3^{\text{II}}\{\text{Fe}(\text{OH})_6\}_2$ and $\text{M}^{\text{II}}(\text{OH})_2$ at 800-900°C in air yields compounds of the composition $\text{M}^{\text{II}}\text{FeO}_3 \cdot \text{M}^{\text{II}}(\text{OH})_2$ ³¹ where M is Ba or Sr. Scholder et al.³²⁻³⁴ obtained two forms of BaFeO_3 , an amorphous black form (recently prepared³⁵ in a crystalline state) and a dark grey crystalline form. The black ferrate(IV) prepared by decomposing barium ferrate(VI), BaFeO_4 , with aqueous alkali was thought to be a hydrated form whereas the grey form prepared by the thermal decomposition of BaFeO_4 in oxygen was assumed to be anhydrous.

The thermal decomposition of $\text{FeO}(\text{NO}_3)$ is reported by Addison et al.³⁶ to yield iron(IV) oxide, FeO_2 , the magnetic moment of which was found to be 4.91 B.M., close to the spin only moment for a high spin d^4 configuration. This oxide has also been reported as being formed by the reaction of anhydrous FeCl_3 and acidic H_2O_2 .³⁷

If K_2FeO_4 is heated with an excess of lithium hydroxide, Li_2FeO_3 , the only known alkali metal ferrate(IV) is formed and can be extracted with ethanol.³¹ According to Scholder et al.³³ heating AgNO_3 with K_2FeO_4 yields Ag_2FeO_4 and not Ag_2FeO_3 .³⁸

Iron compounds of highly variable composition containing both Fe(III) and Fe(IV) are obtained by thermal decomposition of barium and strontium oxalato ferrate(III) compounds and fusion of Fe_2O_3 with barium or strontium carbonates in the presence of

oxygen.^{28,29,39-46} Compounds of stoichiometry $M^{II}(FeO_{1-2x}^{4+}.Fe_{2x}^{3+})O_{3-x}$, where $0 < x < 0.5$ have been prepared under appropriate conditions,^{29,33,39,43,47} and their properties have been examined, most of the work being centred on the strontium compounds.

The changes in lattice parameters of the mixed ferrate(III)-ferrate(IV) compounds with changing amounts of Fe(IV) have been studied by several workers;^{28,29,39,48-51} structures of the perovskite type are indicated. These compounds are antiferromagnetic^{28,29,40,51} and Mossbauer spectroscopy^{25,28,29,43,44,51,52} confirms the presence of Fe^{4+} ions. Reported values of magnetic moments^{29,49,51} are anomalous and cannot be accounted for quantitatively; it has been suggested that $Fe^{3+}-Fe^{4+}$ interactions are responsible.

It is rather surprising that iron(IV) state occurs when iron is in combination with oxygen but not with fluorine. An exception is the compound K_2FeF_6 which, it has been claimed,⁵³ can be prepared by the fluorination of a mixture of KCl and $FeCl_3$. However, several well characterised Fe(IV) compounds have been prepared in which, unlike the ferrate(IV) compounds, the iron(IV) exists as discrete ions. For example, octahedral complex ions of the type $\{Fe(diars)_2X_2\}^{2+}$ where diars = o-phenylene-bis-dimethylarsine and $X = Cl$ or Br , have been prepared by Nyholm and co-workers.^{54,55} These ions were obtained by oxidation of the corresponding iron(III) complexes with concentrated nitric acid (in nitro-benzene) followed by the addition of the appropriate anion. Black complexes of the type $\{Fe(diars)_2X_2\}Y_2$ where Y is BF_4^- , ClO_4^- or ReO_4^- were isolated. The magnetic properties of complexes of this type containing the diamagnetic anions BF_4^- and ClO_4^- have been studied over the

temperature range 80°K to 300°K. Magnetic moments are consistent with a low spin octahedral configuration t_{2g}^4 with a large tetragonal distortion. The spectra in the far infra-red region are in accordance with halogen atoms being in trans- positions.

The preparation of yellow tetrahydrido phosphine iron(IV) complexes of the type $\{FeH_4(PR_3)_3\}$, (where PR_3 = diphenyl-ethyl phosphine or diphenyl-butyl phosphine) has been reported by Aresta et al.⁵⁶ who reacted sodium borohydride, PR_3 and iron(III) chloride dihydrate in ethanol in the presence of hydrogen gas.

Another group of iron(IV) complexes containing discrete Fe(IV) species are the dithiolates which have been reviewed by McCleverty.⁵⁷ The dark green compounds $(AsPh_4)_2\{Fe(MNT)_3\}$ and $(PPh_4)_2\{Fe(MNT)_3\}$ (where MNT = maleon nitriledithiolate) have been prepared,^{57,58} the observed effective magnetic moments being 3.00 B.M. and 2.89 B.M. respectively, characteristic of low spin octahedral d^4 systems. Mossbauer data⁵⁹ support the d^4 configuration and also indicate that in the reduction of $\{Fe^{IV}(MNT)_3\}^{2-}$ to $\{Fe^{III}(MNT)_3\}^{3-}$ the added electron enters an orbital which is predominantly metallic in character, indicating that the metal rather than the ligand is reduced.

The reaction of tris(dithiocarbamato)iron(III) complexes with BF_3 in benzene solution in the presence of air results in the formation of the corresponding iron(IV) complexes.⁶⁰ In general these are black coloured complexes which have effective magnetic moments in the range 3.15-3.37 B.M. The intramolecular arrangement in tris(N-methyl-N'-benzyl-dithiocarbamato)iron(IV) tetrafluoroborate has been studied by n.m.r. spectroscopy.^{61,62}

The iron(V) oxidation state is very rare and is only

known in alkali metal ferrate(V) compounds. Klemm and Wahl⁶³ first reported K_3FeO_4 in 1953. It was prepared by heating a 3:1 molar ratio mixture of potassium and iron(III) oxides at about 450°C for 2 days in the presence of oxygen.^{64,65} The black product had an effective magnetic moment of 3.67 B.M. at room temperature which is close to the spin only value of 3.87 B.M. for the d^3 configuration. Scholder et al.⁶⁶ obtained a mixture of K_3FeO_4 and Na_3FeO_4 by heating K_2FeO_4 with Na_2O at 450-600°C. A technique has been developed^{64,65,67} for obtaining pure K_3FeO_4 by heating K_2FeO_4 with Na_2O at 750-780°C under oxygen for a very short period; Rb_3FeO_4 has similarly been prepared by replacing Na_2O with $RbOH$.⁶⁸ K_3FeO_4 disproportionates in dilute alkali to give potassium ferrate(VI) and iron(III) oxide.

Iron(VI) exists exclusively in alkali and alkaline earth metal ferrate(VI) compounds of the type $M_2^I FeO_4$ and $M^{II} FeO_4$. The red purple ferrate(VI) anion FeO_4^{2-} can be formed by the oxidation of iron(III) oxide in an alkali melt, by anodic oxidation of metallic iron in a concentrated solution of alkali,⁶⁹⁻⁷³ or by oxidation of Fe_2O_3 with chlorine in concentrated alkali solution.^{29,38,65,73-79} Alkaline earth metal salts are readily precipitated from alkali metal ferrate(VI) solutions in the absence of carbon dioxide.^{65,74,79-82} Pure K_2FeO_4 can best be prepared by the oxidation of Fe_2O_3 , $FeCl_3$ or $Fe(NO_3)_3$ in concentrated potassium hydroxide solution with $KClO$ or $KBrO$,^{64,76,79} a purity greater than 99.5% having been achieved.⁷⁹

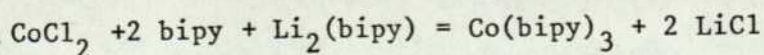
The effective magnetic moment of iron in these compounds varies from 2.88 B.M. to 3.15 B.M., which is consistent with a d^2 configuration. The vibrational,^{69,79,84-86} e.p.r.,^{87,88} and

Mossbauer^{81,89,90} spectra of ferrate(VI) compounds have been studied. The electronic spectra of potassium ferrate(VI) in aqueous solution shows absorbance maxima at 19600cm^{-1} and 12720cm^{-1} having molar extinction co-efficients of $1100\text{cm}^{-1}\text{mol}^{-1}\text{l}$ and $350\text{cm}^{-1}\text{mol}^{-1}\text{l}$ respectively; these transition have been variously assigned.⁹⁰⁻⁹⁶ Ferrate(VI) compounds give rise in solution to the discrete FeO_4^{2-} ion which is an even more powerful oxidising agent than MnO_4^- . Wood⁹⁷ and Latimer⁹⁸ give the standard redox potential of the Fe(VI)/Fe(III) couple as being of the order of +2.0V and +0.8V in acidic and alkaline media respectively.

On heating, K_2FeO_4 decomposes⁶⁵ into K_3FeO_4 , K_2FeO_2 and oxygen, while BaFeO_4 gives BaFeO_3 and oxygen. Becarud⁶⁹ has carried out a thermogravimetric analytical study of the decomposition of barium and strontium ferrates(VI) in air.

Cobalt compounds

Lower oxidation state complexes of cobalt with nitrogen donor ligands are rare and of these only few have been well characterised. Tris(2,2'-bipyridyl)cobalt(0) was first prepared by Herzog et al.⁹⁹ by dissolving dilithium bipyridyl in anhydrous tetrahydrofuran and adding a solution of cobalt(II) chloride and 2,2'-bipyridyl in T.H.F. The reaction was carried out in the absence of oxygen and water. Recrystallisation from ether yielded pure black crystals of $\text{Co}(\text{bipy})_3$. The suggested reaction was as follows:



The air sensitive complex was found to be paramagnetic

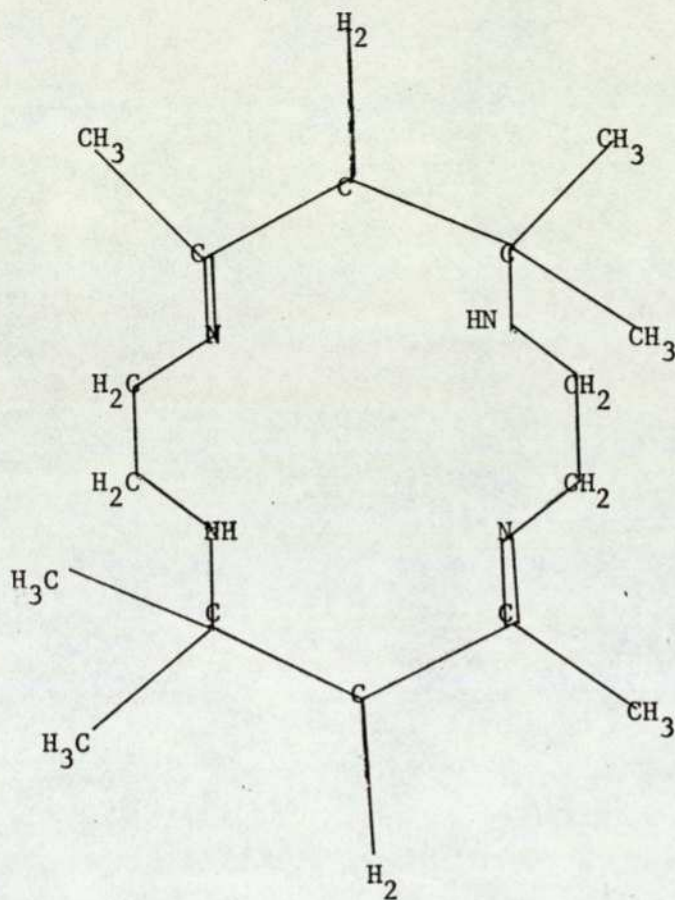
and the magnetic moment of 2.23 B.M. at 20°C indicated the presence of one unpaired electron.

The reduction of potassium hexacyano cobaltate(II) with excess of alkali metal (Na or K) in liquid anhydrous ammonia results in the formation of a brown-violet compound of composition $K_4\{Co(CN)_4\}$ and it has been suggested that the diamagnetism of this compound is due to a binuclear structure $K_8\{Co_2(CN)_8\}$.¹⁰⁸ However, if the amount of potassium added is only 2.3 mole per mole of $K_3\{Co(CN)_6\}$, the reaction leads to the formation of the yellow cobalt(I) complex $K_3\{Co(CN)_4\}$.¹⁰⁹ This compound readily oxidises in air and gives a red-brown product if warmed above room temperature.

The cobalt(I) state in complexes containing 2,2'-bipyridyl, 4,4'-dimethyl-2,2'-bipyridyl and 1.10-phenanthroline have recently been reported. Waind and Martin¹⁰⁰ prepared $\{Co(bipy)_3\}(ClO_4)$ by electrochemical reduction of $\{Co(bipy)_3\}(ClO_4)_2$. Sodium amalgam was also used as a reducing agent in an aqueous solution in the absence of oxygen and in the presence of an excess of ligand. The complex was diamagnetic, consistent with a spin paired d^8 configuration. Vlcek¹⁰¹ also has prepared $\{Co(bipy)_2\}(ClO_4)$ as black crystals, sparingly soluble in water, by the reduction of $\{Co(bipy)_3\}(ClO_4)_2$ with sodium borohydride in a mixed ethanol water solvent. The magnetic moment of this complex was reported to be 3.2-3.4 B.M., and was independent of temperature between 70-340°K. Martin et al.¹⁰² agree with the results reported by Vlcek¹⁰¹ but Maki et al.¹⁰³ who also prepared $\{Co(phen)_3\}(ClO_4)$ by a method very similar to that described above have disputed that Vlcek¹⁰¹ was able to prepare $Co(bipy)_2^+$ and claim that the product was more likely to be $Co(bipy)_3^+$.

Fitzgerald et al.¹⁰⁴ have carried out circular dichroism and optical rotatory dispersion studies on $\text{Co}(\text{bipy})_3^+$ and $\text{Co}(\text{dimbipy})_3^+$ complexes. The characterisation of complexes of cobalt(I) of the type $\{\text{Co}(\text{bipy})_x\}^+$ where $x = 2$ or 3 is difficult due to their instability which makes elemental analysis unreliable. It is normally assumed that a complex containing three chelate ligands will be formed when the preparation is carried out in the presence of an excess of ligand.¹⁰⁰⁻¹⁰⁴ Other evidence, however, has been obtained in support of the cobalt(I) state. For example, transitions in the u.v. and visible are claimed to be consistent with a d^8 octahedral configuration.¹⁰⁵ Saito¹⁰⁶ has studied the infra-red spectra of 2,2'-bipyridyl and 1,10-phenanthroline complexes of cobalt(I). The sharp absorbance at 390cm^{-1} was attributed to a metal-nitrogen stretching mode; absorption in the range $400-150\text{cm}^{-1}$ for $\text{Co}(\text{phen})_3^+$ was found to be similar to that of $\text{Zn}(\text{phen})_3^{2+}$ and the peaks at 200 and 175cm^{-1} were assigned to metal-nitrogen stretching modes.

Cyclic amine complexes of cobalt(I) of the type $\{\text{CoL}\}\text{ClO}_4$ $\{\text{CoL}\}\text{BF}_4$, where $L = \text{trans-tetramine}$ or trans-diene , have been reported by Vasilveskis and Olson¹⁰⁷ by reduction of the corresponding cobalt(II) complexes with sodium amalgam in acetonitrile and tetrahydrofuran respectively. (The structure of trans-tetramine is given on page 7. trans-diene has the structure given on page 16.) It was found that the technique of controlled potential electrolysis could not be used to prepare these compounds on account of their instability.



trans-diene

Compounds of cobalt in the +4 oxidation state are rare and often poorly characterised. They occur only in compounds in which cobalt is bonded to fluorine or oxygen. However, of the binary compounds, cobalt tetrafluoride CoF_4 is unknown and cobalt dioxide CoO_2 has not been firmly characterised. The preparation of CoO_2 as a brown-black solid and an olive-green hydrate has been claimed ^{110-112,118} by oxidising cobalt(II) salts using hypochlorite, hypobromite, or hydrogen peroxide in strong sodium hydroxide solution. A method of preparing cobalt(IV) oxide by electrolytic oxidation has also been reported. ¹¹³⁻¹¹⁵ Values of the standard

electrode potentials of -0.28V and $+0.56\text{V}$ (versus standard Hg/HgO electrode) have been reported for the $\text{Co(IV)}/\text{Co(0)}$ and $\text{Co(IV)}/\text{Co(III)}$ couples respectively in alkaline solution.¹¹³ Corresponding values in acid solution have been determined¹¹⁴ as $+0.64\text{V}$ and $+1.5\text{V}$ (versus N.H.E.). However, the cobalt(IV) state in CoO_2 is still not considered to be fully established.¹¹³⁻¹¹⁵ A well characterised red-brown micro-crystalline compound, BaCoO_4 , has been prepared by heating barium and cobalt(II) hydroxides or $\text{Ba}_2\{\text{Co(OH)}_6\}$ in an atmosphere of oxygen at 1050°C . It is found to contain discrete CoO_4^{4-} ions and has an orthorhombic $\beta\text{-K}_2\text{SO}_4$ structure ($a = 7.65\text{\AA}$, $b = 5.85\text{\AA}$ and $c = 10.34\text{\AA}$); the distance between Co^{4+} and O^{2-} being $1.76\text{\AA}$.¹¹⁶ Scholder³⁴ has also reported the preparation of Sr_2CoO_4 and Na_4CoO_4 , but these are poorly characterised. Ba_3CoO_5 ³⁴ and $\text{SrBa}_2\text{CoO}_5$ ¹¹⁷ can also be prepared and their structures have been examined; ruby-red hexagonal crystals of composition Li_8CoO_6 have also been reported.¹¹⁹ Complex oxides containing both Co(III) and Co(IV) in varying amounts have been prepared^{27,120}; for example, by heating a finely ground mixture of BaNO_3 and either Co(II) nitrate or carbonate at 680°C for 24 hours, a compound of composition $\text{BaCoO}_{2.85}$ was obtained. The mixed valency cobalt compounds $\text{SrCoO}_{2.78}$ and $\text{Li}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.55}$ containing 59.3% and 60.0% cobalt respectively have also been prepared and show unusual magnetic properties.^{48,49,121,122} These compounds contain Co^{4+} and Co^{3+} ions and exhibit spontaneous magnetisation below room temperature. The magnetic moments of the two compounds at room temperature are 3.32 B.M. and 3.65 B.M. respectively which are far below the spin only values of 5.50 B.M. and 5.52 B.M. estimated

on the basis of the known Co(IV) and Co(III) contents.¹²² Goodenough¹²² suggests that the anomalous magnetic behaviour can be explained by a model in which cobalt(IV) is present in a 2T_2 ground state, cobalt(III) having 1A_1 and 5T_2 ground states of comparable energies, the two magnetic sub-lattices forming parallel (1,1,1) planes. Zanne¹²³ has reported six different phases of barium cobaltate(IV) at 900°C and demonstrated that cobalt(IV) has the t_{2g}^5 configuration in this compound.

Yakel⁴⁸ has estimated the ionic radius of Co^{4+} ion as 0.48Å by X-ray diffraction by substituting Co^{4+} and Sr^{2+} for Co^{3+} and La^{3+} in $LaCoO_3$. The electron spin resonance spectrum of Co^{4+} , present as an impurity in a Al_2O_3/MgO single crystal, displays an eight line hyperfine pattern which is consistent with a 2T_2 ground state for the Co^{4+} ion.¹²⁴

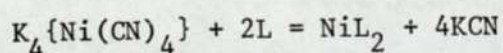
The complex cobalt(IV) fluoride Cs_2CoF_6 can be prepared by direct fluorination of either $CsCoCl_4$ or $CsCo(SO_4)_2$.¹²⁵⁻¹²⁷ Rb_2CoF_6 has been recently reported.⁴⁸ Klemm and Huss⁵³ have reported the preparation of K_3CoF_7 , although the method used has been found by Myer and Cotton¹²⁸ to give a product containing K_3CoF_6 as an impurity. Brown-gold crystals of K_2CoF_6 are isomorphous with K_2PtCl_6 structure.¹²⁷ The electronic spectrum of $CsCoF_6$ has been determined both in solution¹²² and in the solid state.^{122,129} Magnetic moments for Cs_2CoF_6 and Rb_2CoF_6 are found to be consistent with a 2T_2 ground state; these compounds exhibit ferromagnetic behaviour.¹²⁵⁻¹²⁷ When added to anhydrous hydrofluoric acid above 0°C Cs_2CoF_6 dissolves with the liberation of fluorine.¹³⁰

Wahl et al.⁶⁴ observed that fusion of KO_2 or CsO_2 with Co_3O_4 in oxygen in a 1:1 alkali metal to cobalt ratio produced compounds of approximate composition $\text{M}^{\text{I}}\text{CoO}_3$. These compounds are believed to be mixtures of $\text{M}^{\text{I}}\text{O}_2$ and $\text{M}^{\text{I}}\text{Co(III)Co(IV)O}_4$ rather than cobaltate(V) species. Compounds of the type $\text{M}_3^{\text{I}}\text{CoO}_4$ (where $\text{M} = \text{K}, \text{Na}, \text{Rb}$ or Cs) have recently been prepared^{68,131,132} and are thought to contain Co^{5+} . K_3CoO_4 was obtained as a blue-black hygroscopic product by heating a mixture of potassium and cobalt oxides in a molar ratio of 3:1 for a period of 23 hours at $460\text{--}550^\circ\text{C}$ under an oxygen atmosphere.^{25,131} Evidence for the +5 oxidation state in this compound was obtained from elemental analysis and from the quantitative assessment of its oxidising power to liberate iodine from iodide in acid solution. The ease of isomorphic doping into the colourless K_3PO_4 host to form intense blue crystals was further evidence for the presence of Co(V) . K_3CoO_4 exhibits unusual magnetic properties.¹³¹ In the pure compound, the cobalt has an effective magnetic moment corresponding to the presence of only 2 unpaired electrons. However, when mixed crystals containing K_3CoO_4 and K_3PO_4 are formed the effective magnetic moment increases with dilution of the cobalt until it corresponds to 4 unpaired electrons consistent with a d^4 (Co(V)) configuration when the percentage of cobalt present has been reduced to about 3.2%. Brendel and Klemm¹³¹ have observed two different X-ray powder patterns corresponding to different forms of K_3CoO_4 ; one form has a pattern analogous to that of K_3MO_4 (where $\text{M} = \text{P}, \text{V}, \text{Mn}$ or Fe) and is unstable, transforming into the other stable form over a period of about 48 hours. Scholder⁶⁸ has prepared Na_3CoO_4

as red-violet crystals by heating Co_2O_3 and Na_2O in a ratio of 1:3 at 400°C under an oxygen pressure of 100atm. Kingsley et al.¹³³ have reported the preparation of KCoO_3 by heating $\text{KO}_{0.7}$ with CoO for 24 hours at $300\text{--}400^\circ\text{C}$ under an oxygen atmosphere of 50atm.

Nickel compounds

Low oxidation state compounds of nickel containing the cyanide group have been known for a long time. Tetracyano nickelate(0), $\text{K}_4\{\text{Ni}(\text{CN})_4\}$, was first prepared by Easters and Burgess¹³⁴ by reducing potassium tetracyano nickelate(II) with potassium metal in anhydrous liquid ammonia. The first stage of the reduction led to the formation of the red coloured nickel(I) complex, $\text{K}_3\{\text{Ni}(\text{CN})_4\}$ which was further reduced to give the yellow $\text{K}_4\{\text{Ni}(\text{CN})_4\}$. The intermediate nickel(I) complex in this reaction had previously been reported by Bellucci and Corelli.¹³⁶ In liquid ammonia, tetracyano nickelate(0) reacts with 2,2'-bipyridyl, or 1,10-phenanthroline at -33°C resulting in the complete substitution of the CN^- groups¹⁴³ viz:



where L is either 2,2'-bipyridyl or 1,10-phenanthroline. Similar substitution reactions using phosphines and arsines have also been carried out.¹³⁵

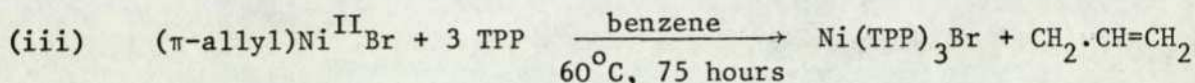
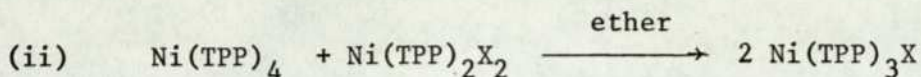
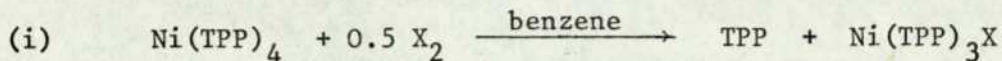
Nickel(I) complexes are rare and only few are known. The nickel(I) complex $\text{K}_3\{\text{Ni}(\text{CN})_4\}$ described above is stable in ammonia vapour up to 160°C but is oxidised in air and is a powerful reducing agent. It evolves hydrogen from aqueous solution and

reduces solutions of silver and gold salts to the metals. The magnetic properties of potassium tetracyano nickelate(I) have been studied by Bast and Pfab¹³⁷ both in the solid state and in solution. The observed diamagnetism of the nickel(I) complex (d^9 configuration) was explained in the terms of the existence of the dimeric nickel(I) species, $Ni_2(CN)_6^{4-}$ containing a Ni-Ni bond. Cryoscopic data¹³⁷ support this hypothesis. The structure of the dimer has not yet been established. Preliminary X-ray studies of the complex¹³⁸ indicated the presence of bridging cyanide groups and the Ni-Ni distance was estimated at $2.6\text{\AA}$. However, the infra-red spectrum of the complex reported by Griffith and Wilkinson,¹³⁹ suggests that the anion is planar with no bridging cyanide groups, i.e. $\{(CN)_3-Ni-Ni-(CN)_3\}^{4-}$. Recently, the monomeric paramagnetic potassium tetracyano nickelate(I) complex has been prepared by Nast and Krakkay¹⁴⁰ by the reduction of nickel(II) cyanide with hydrazine in an alkaline solution. The complex was found to have a magnetic moment of 1.7 B.M. indicating the presence of one unpaired electron consistent with the d^9 configuration.

Although low oxidation state complexes containing phosphorus donor ligands have been specifically excluded from present survey, an exception will be made in the case of nickel(I) since this state is particularly uncommon. Complexes of nickel(I) with triphenyl phosphine have been reported by Porri et al.¹⁴¹ Reaction of π -allyl nickel(I) halides with triphenyl phosphine in the presence of norbornene at room temperature in a benzene-diethyl ether mixed solvent (containing 80% ether) yields

$\{(PPh_3)_3Ni\}X$. For $X = Cl$, the reaction proceeds at room temperature, the bromide and iodide being prepared at the boiling point of the solvent system. If the complexes are recrystallised from a benzene-ether mixture containing more than 50% benzene, the recrystallised products are found to contain up to 3 moles benzene per mole complex depending on the concentration of benzene in the solvent. The complexes slowly decompose in air but are stable in a nitrogen atmosphere, exhibiting paramagnetic moments of 1.9 B.M. (chloride) and 1.98 B.M. (bromide and iodide). X-ray data indicate a tetrahedral structure for the complex cation. In benzene, dissociation occurs giving a low value for the molecular weight. Corain et al.¹⁴² have prepared complexes of nickel(I) cyanide with ditertiary phosphines by reducing the corresponding nickel(II) complexes with sodium borohydride in ethanol. Yellow products of composition $Ni(diph)_{1.5}(CN)$, unstable in air were isolated, the ditertiary phosphines used being either 1,4-bis(diphenyl phosphino)propane or 1,4-bis(diphenyl phosphino)butane. The magnetic moments of these complexes are in the range 2.0 to 2.3 B.M. as expected for a d^9 configuration with a small orbital contribution. Electronic reflectance spectra indicate a square planar nickel atom environment and it is suggested that the complexes should be formulated as binuclear species $(CN)(diph)Ni(diph)Ni(diph)(CN)$ where the central diph group bridges the two nickel atoms, each with a square planar arrangement of one cyanide group and three phosphorus atoms. Heimbach¹⁴³ has reported the preparation of nickel(I) with triphenyl phosphines

by three methods viz:



(TPP = triphenyl phosphine and X = chlorine)

The highest yields were obtained by the second reaction. The magnetic moment of $\text{Ni(TPP)}_3\text{Cl}$ was found to be 2.2 B.M., which is somewhat higher than the spin only value (1.73 B.M.) for one unpaired electron required by the d^9 configuration.

Recently Bradley et al.¹⁴⁴ have described a number of three co-ordinated complexes of nickel(I) of the type $\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}(\text{L}_1)_2$ and $\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}\text{L}_2$, where, $\text{L}_1 = \text{PPh}_3$, $\text{P}(\text{Me}_2)\text{Ph}$, PMePh_2 , PEtPh_2 , PEt_2Ph , or PEt_3 , and $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. The air sensitive yellow complexes were prepared by the reaction of $\text{NiCl}_2(\text{L}_1)_2$ and $\text{NiCl}_2(\text{L}_2)$ with lithium bis-trimethylsilylamide, $\text{LiN}(\text{SiMe}_3)_2$, in benzene. Magnetic moment determinations indicated the presence of one unpaired electron, consistent with the d^9 configuration. The unusual three co-ordination of the nickel atom was confirmed by X-ray crystal structure analysis.

Cyclic amine complexes of nickel(I) perchlorate have been reported by Olson and Vasilveskis.¹⁴⁵ Complexes of the type $\{\text{Ni}(\text{L})\}(\text{ClO}_4)$ where L is trans- or cis-tetramine or trans- or cis-diene were prepared by reducing the corresponding nickel(II)

complexes with sodium amalgam in oxygen-free acetonitrile for 6 hours. The products were precipitated from solution by the addition of oxygen-free water. Magnetic susceptibility determinations gave moments in the range 1.70-1.89 B.M. indicating the presence of one unpaired electron as expected for the d^9 configuration.

Partial oxidation of nickel(II) salts in alkaline solution results in a black or dark brown oxidised product which contains some nickel in an oxidation state higher than +2. It is claimed that anhydrous higher nickel oxides of composition Ni_2O_3 , NiO_2 or Ni_3O_4 can be prepared by the thermal decomposition of hydrated and anhydrous nickel(II) salts in the presence of oxygen.¹⁴⁶⁻¹⁴⁸ However, the proper characterisation of these higher oxides has been questioned and requires further investigation.¹⁴⁹⁻¹⁵⁵

A number of methods for preparing hydrated higher oxides of nickel have been described by Glemser and Einerhand¹⁵⁵ and Besson.¹¹² $NiO(OH)$ was prepared by anodic oxidation and by chemical oxidation using persulphate and halites in alkaline solution. Poor crystallinity and their ability to incorporate varying amounts of water and alkali metal ions made characterisation and structure determination difficult. Electrochemical oxidation of $\beta-Ni(OH)_2$, which has the brucite structure, yields $\beta-NiO(OH)$.¹⁵⁶⁻¹⁵⁹ Another form, $\gamma-NiO(OH)$, can be similarly prepared but its structure is complicated being based on a $CdCl_2$ type structure with an elongated cell.^{156,158} The amount of alkali metal in this compound depends upon the method of preparation.^{159,160} Oxidation of $K_2Ni(CN)_4$, $Ni(OH)_2 \cdot 2NiO(OH)$ and $4Ni(OH)_2 \cdot NiO(OH)$ by persulphate gives $\alpha-NiO(OH)$.^{159,160} Several other forms of

nickel(III) oxide are mentioned in Gmelin's handbook.¹⁶¹

Compounds of Ni(III) of the type $M^I\text{NiO}_2$ (where M is sodium or lithium) can be prepared by bubbling oxygen through the appropriate molten alkali hydroxide in a nickel tube at a temperature of about 800°C.¹⁶² Both Li^+ and Ni^{3+} ions in LiNiO_2 have been shown to be octahedrally co-ordinated to oxygen,¹⁶² the observed Ni-O and Li-O distance being close to those expected from the sums of ionic radii. However, Bade et al.^{163,164} report that LiNiO_2 has a structure similar to that of $\alpha\text{-NaFeO}_2$ and may therefore be a mixed valence compound containing Ni^{2+} and Ni^{4+} .

LaNiO_3 , prepared by heating a stoichiometric mixture of the oxides or carbonates at 900°C^{165,166} or the oxalates¹⁶⁷ at 800°C is rhombohedral with low spin Ni^{3+} ions at the centre of a regular octahedron of oxygen ions; the compound exhibits metallic conductivity at temperatures between 200°C and 300°C. AgNiO_2 has been reported to be prepared by the reaction of AgNO_3 with potassium nickelate(III).¹⁶⁸ The formation of $\text{BaNiO}_{2.5}$ results if nickel(II) carbonate or nickel(II) nitrate is heated with barium hydroxide.^{27,169,170}

The dark brown deposits appearing on a nickel anode during the electrolysis of various solutes in liquid hydrogen fluoride¹⁷¹⁻¹⁷³ may be due to formation of a higher fluoride of nickel. Similar substances have been observed by Stein et al.¹⁷⁴ on dissolving K_3NiF_6 or K_2NiF_6 in anhydrous hydrogen fluoride. X-ray powder patterns indicate the presence of NiF_2 and KHF_2 only; however, the substance liberates HF and traces of fluorine gas on heating in vacuum which indicates considerable oxidising

power. The only binary nickel(III) halide to have been reported is NiF_3 which has been recently prepared as a black solid by Court and Dove¹³⁰ by the reaction of K_2NiF_6 with AsF_5 in anhydrous liquid hydrogen fluoride. The magnetic moment of the product was found to be 2.41 B.M., which is higher than the expected value for a d^7 spin paired configuration; this was thought to indicate contamination of the product with nickel(II) fluoride.

Unlike the yellow complex fluorides of nickel(II) and nickel(IV), nickel(III) fluorides of the type $\text{M}_3^{\text{I}}\text{NiF}_6$ (where M is potassium or sodium) are a violet-rose colour, the complex fluoride BaNiF_5 being violet-grey. K_3NiF_6 can be prepared by the fluorination of mixtures of nickel(II) sulphate or nickel(II) chloride and potassium chloride at 300-400°C;^{126,132} isolation of the pure product, however, is difficult due to contamination by nickel(II) and nickel(IV) fluoride complexes.¹⁷⁴ Attempts to prepare pure Na_3NiF_6 have also resulted in the formation of an impure product.¹⁷⁵ Potassium and sodium nickel(IV) fluorides are not high spin, as are the isoelectronic cobalt(II) fluoro complexes; neither are they fully spin paired, however, having anomalous temperature dependent intermediate moments.^{126,175,176} The magnetic behaviour of the mixed crystals $\text{K}_3\text{NiF}_6/\text{K}_{2.8}\text{AlF}_{5.8}$ indicates O^{2-} may replace F^- and cause an oxidation of nickel(III) to nickel(IV) in the system.¹⁷⁶ The electronic spectra of nickel(III) complex fluorides have been studied by several workers,^{129,177} but are found to be difficult to interpret due to their complexity. K_3NiF_6 is stable up to 450°C under reduced pressure and dissolves in anhydrous liquid hydrogen fluoride, disproportionating into

nickel(II) and nickel(IV). The barium salt, BaNiF_5 , is claimed to have been prepared by the fluorination of barium tetracyano nickelate(II), $\text{Ba}\{\text{Ni}(\text{CN})_4\}$, at about 300°C .¹²⁵ A brown modification of the same composition evidently develops upon further heating at 500°C .

Complexes of nickel(III) in which the nickel is bonded to atoms other than fluorine or oxygen are also known. The presence of unstable $\{\text{Ni}(\text{NH}_3)_x\}^{3+}$ ions by oxidising $\{\text{Ni}(\text{NH}_3)_6\}^{2+}$ with the NH_2 radical using a radiolytic technique¹⁷⁸ has been reported. Diene complexes of nickel(III) containing ligands such as glycine, ethylenediamine and propylenediamine are obtained by oxidising the corresponding nickel(II) complexes with chlorine or bromine in methanol.¹⁷⁹⁻¹⁸¹ The anions of the nickel(III)-diene complexes can easily be replaced by the perchlorate ion by treatment with perchloric acid. The magnetic susceptibilities of these complexes fall into two categories, one with one unpaired electron and the other with a small paramagnetic moment of the order of 0.5-0.8 B.M.^{182,183} Treatment of nickel(II)-diene complexes with potassium iodide and iodine results in the formation of polyiodide complexes of nickel(II) instead of the expected corresponding nickel(III) complexes.¹⁸⁴ Bush and co-workers^{185,186} have prepared nickel(III) complexes of tetradentate macrocyclic amine ligands such as macrocyclic 2,3-dimethyl-1,4,8,11-tetra-aza-cyclo-tetra-decane and derivatives obtained by hydrogenation or oxidative dehydrogenation of 2,12-dimethyl-1,7,11,17-tetra-aza-bicyclo-11,31-hepta-deca-1 (17)2,11,13,15-pentane. Oxidation of the corresponding nickel(II) complex with nitrosyl tetra-fluoroborate, concentrated nitric acid or ammonium persulphate yields complexes of the type $\{\text{Ni}(\text{L})\text{X}_2\}\text{ClO}_4$

where X is Br, Cl, NCO, NO₃, $\frac{1}{2}$ SO₄ or ClO₄ and L is the cyclic amine. Olson and Vasilveskis¹⁴⁵ prepared similar complexes of nickel(III) electrolytically in acetonitrile. The ligands used were trans- and cis-diene and trans- and cis-tetramine cyclic amines. The magnetic moments of these complexes indicate one unpaired electron consistent with a low spin d⁷ configuration. Gore and Bush¹⁸⁶ used e.p.r. spectroscopy to confirm the +3 oxidation state of nickel in these complexes.

Blue black biuret complexes of nickel(III) have been prepared by Bour et al.^{187,188} by oxidising a solution formed by dissolving hydrated nickel(II) sulphate in an aqueous solution of potassium hydroxide containing biuret (HNCONRCONH where R = H or alkyl). Both chemical and electrochemical oxidation techniques were employed which yielded K{Ni(bi)₂}. Another tetradentate cyclic ligand used to stabilise nickel(III) is tetraphenyl-porphyrin; the Ni(III) complex, which can be prepared by electrochemical oxidation of the corresponding nickel(II) complex,^{189,190} is unstable and is slowly reduced back to the nickel(II) complex.

Several nickel(III) complexes containing oxime ligands have been reported. The black complex {Ni(dmgh)₂}Br (where dmgh₂ is dimethylglyoxime) and {Ni(dmgh)₂}(Br)₃ are produced by the oxidation of bis(dimethylglyoxime)nickel(II) by bromine in an organic solvent.^{191,192} However, the claim by Simek¹⁹³ to have prepared nickel(III) complexes of the type {Ni(dpgH₂)X}, where dpgH₂ is diphenylglyoxime and X is Cl or Br, is refuted by Foust and Sanderberg.¹⁹⁴ Persulphate oxidation of nickel(II)

complexes of syn-2-benzoypyridineoxime and syn-2-phenylacetylpyridine-oxime in an aqueous ammonia solution has been reported by Drago and Baucom¹⁹⁵ to give the corresponding nickel(III) complexes.

Nitrosyl chloride, nitrosyl bromide or bromine can oxidise $\{\text{Ni}(\text{PEt}_3)_2\}\text{X}$ (where X is Cl or Br) to $\{\text{Ni}(\text{PEt}_3)_2\}\text{X}_3$,¹⁹⁶⁻¹⁹⁸ the nearly zero dipole moment observed in these compounds favouring a trigonal bipyramidal structure with equatorial halide groups. Confirmation of the structure of the complexes by X-ray techniques has not been possible because of their instability.¹⁹⁹ Similar complexes containing the ligands PMe_3 , $\text{P}(\text{Pr}^n)_3$ and $\text{P}(\text{Bu}^n)_3$ have also been prepared although in a less pure state than triethyl phosphine complexes.¹⁹⁶ The complex $\text{Ni}(\text{PMe}_2\text{Ph})_3\text{Br}_3$ has been prepared by oxidation of $\text{Ni}(\text{PMe}_2\text{Ph})_3\text{Br}_2$ by bromine;²⁰⁰ the structure of this complex has been determined as trigonal bipyramidal.^{201,202} Arsenic donor ligands have also been used to stabilise nickel(III) complexes. Diarsine complexes of nickel(III) in alcoholic solution are oxidised by air in the presence of hydrochloric acid,²⁰³ yielding $\{\text{Ni}(\text{diars})_2\text{Cl}_2\}\text{Cl}$ (diars = o-phenylene-bis(dimethylarsine). Metathesis with the appropriate alkali metal salt yields the corresponding bromide and thiocyanate complexes while the chloride group is removed by perchloric acid.²⁰³ On the basis of their far infra-red spectra Lewis et al.²⁰⁴ have proposed an octahedral structure with chloride groups in trans positions; this has been confirmed by X-ray analysis.^{205,206} Tridentate arsine complexes of nickel(III) bromide have been reported by several workers.²⁰⁷⁻²⁰⁹ Cunningham

et al.²⁰⁷ prepared bis(o-dimethylarsinophenyl)-methylarsine nickel(III) bromide by dissolving the corresponding nickel(II) complex in chloroform and oxidising with bromine in carbon tetrachloride and extracting with petroleum ether. The deep blue colour of the nickel(II) complex turns red as the reaction proceeds. A complex of the type $\{Ni(L_3)\}Br_3$ where L_3 is the tritertiary arsine ligand $MeAs(CH_2CH_2CH_2AsMe_2)_2$ has been synthesised and characterised by Barclay and co-workers.^{208,209} Barclay and Bernard²¹⁰ have also reported the preparation of several nickel(III) complexes containing the tetratertiary arsine ligand $As(CH_2CH_2CH_2AsMe_2)_3$ (TTA) and having the composition $\{Ni(TTA)_2\}Y$ where Y is halide or perchlorate. The magnetic susceptibility of these compounds corresponded to effective magnetic moments in the range 1.94-1.98 B.M. consistent with low spin d^7 configurations. Results of structure determinations of these complexes by e.s.r. spectroscopy have been inconclusive.^{70,201-206,211}

Nickel(III) complexes having oxygen donor ligands are very rare, only two examples having been cited. Addison and Ward²¹² obtained $Ni(NO_3)_3 \cdot N_2O_5$ by reacting hydrated nickel(II) chloride or nitrate with dinitrogen pentoxide. Heating under vacuum expelled N_2O_5 and below room temperature the composition of the product approached that of $Ni(NO_3)_3$. The effective magnetic moment of this compound was found to be 4.54 ± 0.02 B.M. at $21^\circ C$ which is of the same order as high spin cobalt(II) complexes. Nickel(III) oxyfluorosulphate $Ni(SO_3F)^{213}$ has been prepared by treating nickel(II) carbonate or oxide with

peroxydisulphuryldifluoride in a closed vessel, the volatile products being removed at -40°C under reduced pressure. Evidence for the presence of nickel(III) in $\text{Ni}(\text{NO}_3)_3$ and $\text{NiO}(\text{SO}_3\text{F})$ is that they will oxidise an equimolar amount of potassium iodide yielding iodine.

Electrolytic oxidation of nickel(II) compounds in alkaline solution is reported as a method of preparing NiO_2 which is obtained as a black solid.^{112,155,214} Such preparations, however, give products containing less than stoichiometric amounts of oxygen; they are, therefore, thought to contain impure, possibly hydrated NiO_2 . The amorphous nature of these compounds and their very strong oxidising power makes characterisation extremely difficult.

Lander and co-workers^{169,170} have prepared the black nickel(IV) compound, BaNiO_3 , by heating nickel(II) oxide with BaO_2 or $\text{Ba}(\text{OH})_2$ in the presence of excess oxygen at a temperature of about 700°C . Heating the compound further to temperatures higher than 750°C resulted in the formation of $\text{Ba}_3\text{Ni}_3\text{O}_8$ and $\text{Ba}_2\text{Ni}_2\text{O}_5$ with the loss of oxygen. BaNiO_3 is insoluble in alkali but soluble in acids and is a powerful oxidising agent, liberating chlorine from dilute hydrochloric acid. The variation of magnetic moment (1.24 B.M. at room temperature) with temperature follows the Curie-Weiss equation over the range $50-300^{\circ}\text{C}$. Viltage²¹⁵ has reported the formation of a very unstable intermediate sodium nickelate(IV) compound in the preparation of sodium nickelate(III) produced by heating Na_2O_2 and NiO between $200-400^{\circ}\text{C}$. Klemm and co-workers^{64,164} have reported the preparation of $\text{M}_2^{\text{I}}\text{NiO}_3$ (where

M is sodium, potassium or rubidium) along with other nickelate(IV) ions having variable composition by fusing nickel(II) oxide with alkaline peroxides. Magnetic studies indicate that these compounds may contain peroxide and/or superoxide groups.

The fluorination of $M_2^I\{Ni(CN)_4\}$ or $M_2^I\{NiCl_4\}$ where M is potassium, rubidium or caesium produces red crystalline compounds of the type $M_2^I\{NiF_6\}$.^{53,126,216-221} These compounds have cubic structures like $K_2\{PtCl_6\}$ and do not exhibit polymorphism,²¹⁶ unlike most of other 3d hexafluoro-metallates. $Na\{NiF_6\}$ ^{217,218} has been prepared by fluorinating Na_2NiO_3 at $280^\circ C$ under a pressure of 120atm. and by heating a mixture of sodium fluoride and nickel(II) fluoride in the molar ratio of 2:1 to $350^\circ C$ under a pressure of 350atm. The product was found to be contaminated with both Na_3NiF_3 and Na_3NiF_6 . Pure Na_2NiF_6 is cubic like the structure of K_2PtCl_6 ²¹⁹ but is very sensitive to moisture and loses part of its fluorine under an argon atmosphere; the presence of decomposition products might explain why Guinier photographs²¹⁹ indicate a hexagonal structure form together with a cubic form. Several electronic spectral studies of hexafluoro nickelate(IV) compounds have been reported.^{129,219,220} Bougon²¹⁷ and Reisfeld²²¹ have studied the far infra-red spectra of these compounds, bands being observed at $650cm^{-1}$, $560cm^{-1}$, $520cm^{-1}$, $350cm^{-1}$ and $310cm^{-1}$ which were assigned to vibration modes of the NiF_6^{2-} ion.

Hydrated periodato complexes of nickel(IV), $Na(K)NiO_6 \cdot nH_2O$, have been prepared by periodate, persulphate or hypochlorite oxidation of nickel(II) salts in the presence of the appropriate ions.²²²⁻²²⁵ Although diamagnetic behaviour is expected for a

spin paired d^6 configuration, these complexes are weakly paramagnetic having effective magnetic moments of about 1.0 B.M. which is possibly due to the presence of a nickel(III) impurity. The structure of the sodium and potassium complexes have been studied by X-ray techniques. Brown²²⁸ and Vannerberg^{226,227} determined the Ni - O distance as 2.1 $\text{\AA}$. Nyholm²²⁹ has reported the preparation of $\{\text{Ni}(\text{diars})_2\text{X}_2\}^{2+}$ (where X is chloride or bromide) by oxidising $\{\text{Ni}(\text{diars})_2\text{X}_2\}\text{X}$ with concentrated nitric acid. The compound was found to be diamagnetic, consistent with a low spin d^6 configuration (t_{2g}^6).

Formaldoxime complexes of nickel(IV) have been reported by several workers,²³⁰⁻²³³ one of the best known of which is $\text{Na}\{\text{Ni}(\text{CH}_2\text{NO})_6\}$. A well characterised nickel(IV) complex is the stable, violet coloured bis(2,6-diacetyl pyridine dioximato) nickel(IV) which has been reported by Baucom and Drago.²⁴³ This complex was prepared by dissolving hydrated nickel(II) chloride in an ammoniacal aqueous-acetone mixed solvent system containing 2,6-diacetyl pyridine dioxime and oxidising with ammonium persulphate. Again, this nickel(IV) compound is diamagnetic as expected for a d^6 low spin configuration.

3. SOME THEORETICAL ASPECTS OF VOLTAMMETRY

The relationship between the applied potential and cell current for a diffusion controlled cathodic polarographic wave associated with the reduction of a metal ion or complex to a lower oxidation state is given by the expression:²³⁵

$$E = E_{\frac{1}{2}} + \frac{R T}{n F} \ln \frac{i_L - i}{i} \quad (1)$$

where

$$E_{\frac{1}{2}} = E^0 - \frac{R T}{n F} \ln \frac{D_O^{\frac{1}{2}}}{D_R^{\frac{1}{2}}} \quad (2)$$

where E^0 is the standard potential of the reaction $Ox + ne = Red$; E is the applied potential; $E_{\frac{1}{2}}$ is the half wave potential at which the current, $i = i_L/2$, i_L being the limiting current or wave height; D_O and D_R are respectively the diffusion co-efficients of the oxidised form (Ox) and the reduced form (Red) of the electroactive species; R , T , and F are respectively the gas constant, temperature and the Faraday. A similar expression is obtained for an oxidation wave.

The assumptions made in the derivation of equations

(1) and (2) are:

- (i) the electron transfer process is reversible i.e. the potential at the electrode is given by the Nernst equation applied to the concentration of species at the electrode surface.
- (ii) a linear concentration gradient exists at the electrode surface; the diffusion is therefore assumed to take place across a layer

of constant thickness.

(iii) the applied potential is invariant during the time interval of the current measurement; this, of course, is not strictly adhered to in classical polarography where the applied potential is varied slowly with time.

The limiting current for a diffusion controlled wave at a dropping mercury electrode is given by the Ilkovič equation:

$$i_L = k n C D^{1/2} m^{2/3} t^{1/6}$$

where k is a constant, C , D are respectively the concentration of the species (diffusion coefficient D) diffusing to the electrode, m is the weight of mercury dropping per unit time and t is the drop time. Similar equations can be produced for reduction waves at different types of solid electrodes.

When the applied potential at a stationary planar electrode is not constant but is varied at a rate which is fast compared to the rates used in classical polarography, the wave obtained exhibits a peak current which is given by the equation:

$$i_p = k' n^{2/3} A D^{1/2} C_b V^{1/2} \quad (3)$$

where i_p is the peak current, A is the area of the electrode, V is the rate of change of applied potential and C_b is the bulk concentration of the electroactive species (diffusion co-efficient D) diffusing to the electrode. The constant k' in equation (3) is called the Randles-Sevcik constant and is named after the two

workers who, independently, first solved the diffusion problem in sweep voltammetry.^{236,237} Again, a rapid charge transfer process (reversible process) is assumed.

The shape of the single sweep peak voltammogram can be visualised as the superimposition of a current-time decay curve on a steady state polarogram. With a constant applied potential at a stationary electrode one obtains a decay of current ($i \propto t^{\frac{1}{2}}$), the current falling as the diffusion layer thickness increases, this depletion process accounting for the appearance of the current peak. The voltammogram is characterised by the peak potential E_p or the half-peak potential $E_{p/2}$, i.e. the potential at which $i = i_{p/2}$. For the reversible case, it can be shown using a numerical calculation method,⁵ that for a cathodic wave at a stationary planar electrode the peak potential ($E_{p,c}$) at 25°C is given by the expression:

$$E_{p,c} = E_{\frac{1}{2}} - \frac{0.0285}{n} \quad (4)$$

where $E_{\frac{1}{2}}$ is the half-wave potential for an infinitely slow sweep rate at the same electrode. It can also be calculated that

$$E_{p/2,c} - E_{p,c} = \frac{0.057}{n} \quad (5)$$

where $E_{p/2,c}$ is the half-peak potential of the wave. For an anodic wave equation (4) becomes

$$E_{p,a} = E_{\frac{1}{2}} + \frac{0.0285}{n} \quad (6)$$

where $E_{p,a}$ is the anodic peak potential. The theory of peak voltammetry for irreversible systems is much more complicated than for the reversible case; a definitive treatment has been given by Nicholson and Shain.⁵ The effect of a slow electrode transfer process is to give a more spread out voltammogram with less well defined peaks for which equation (4), (5) and (6) no longer hold.

In cyclic voltammetry, a triangular voltage-time scan is employed. The cycle is composed of a forward sweep over a selected voltage range (normally up to about 3.0V) followed by a reverse sweep over the same scan range and at the same rate of scan (usually of the order $10-100V\ min^{-1}$). In this case, the forward part of the voltammogram is identical to that described above. However, if the forward sweep is, say, in the cathodic direction the reduced form of the electroactive species will be present at the electrode surface when the sweep direction is reversed. The reduced form will then be re-oxidised on the reverse scan and an anodic peak will be obtained to give a cyclic voltammogram of the type shown in figure 1, page 39. If the applied potential at the end of the forward sweep is sufficiently in excess of $E_{p,c}$ so that the concentration of the oxidised form at the scan surface of the electrode is zero (i.e. all converted to the reduced form) and if the reduced form is chemically stable then the peak current of the forward (cathodic) sweep $i_{p,c}$ will be equal to that of the peak current of the reverse (anodic) wave $i_{p,a}$. Further, from equations (4) and (6) it can be seen that

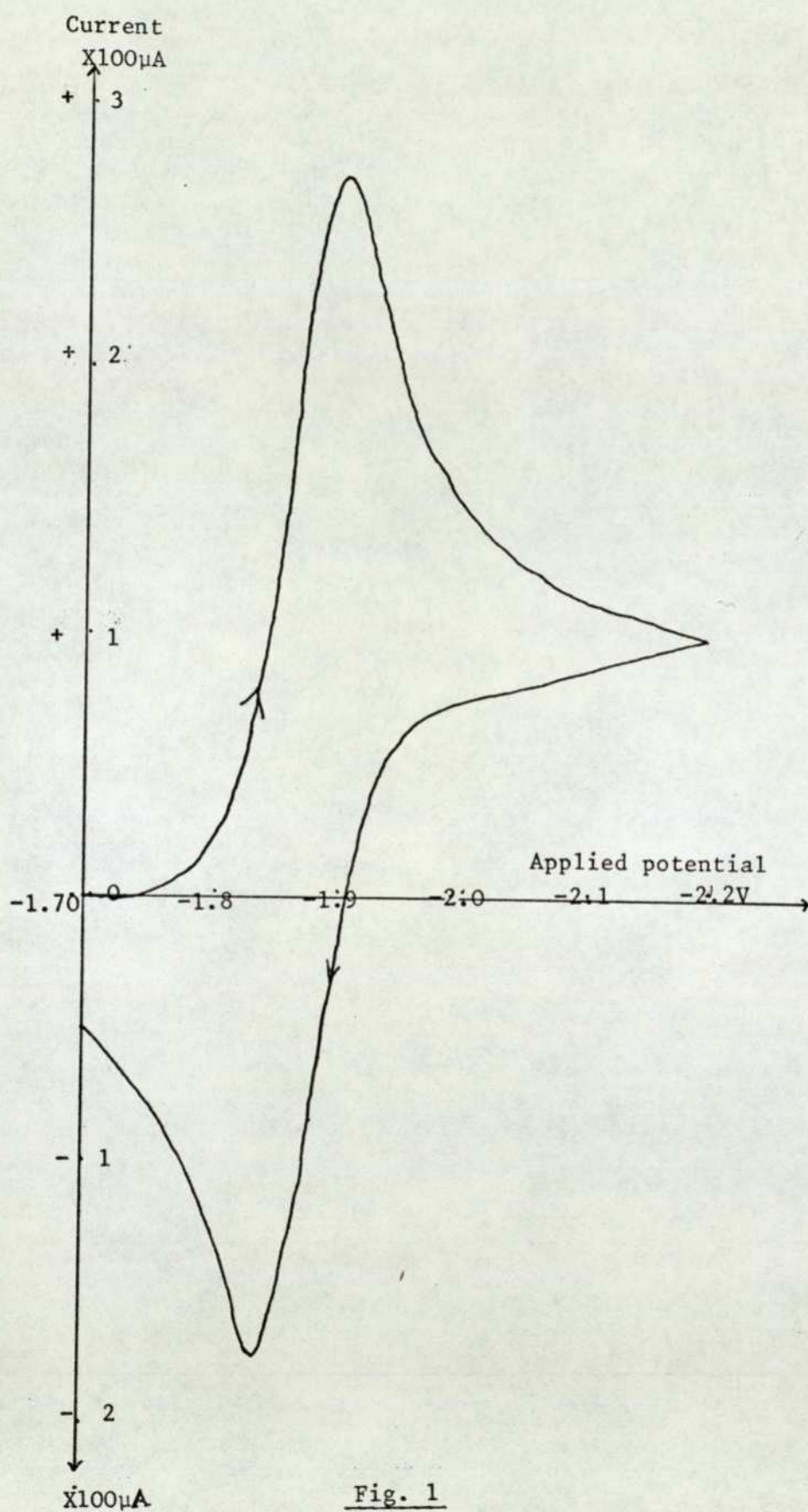


Fig. 1

Cyclic voltammogram (2nd peak of cathodic sweep) of $\{\text{Co}(\text{bipy})_3\}(\text{ClO}_4)_2$

$$E_{p,a} - E_{p,c} = \frac{0.057}{n} \quad (7)$$

and that

$$\frac{E_{p,a} + E_{p,c}}{2} = E_{\frac{1}{2}} \quad (8)$$

The criteria for a reversible electron transfer process are:

- (i) The peak potentials are independent of the sweep rate.
- (ii) The peak currents are proportional to C_b and to $V^{\frac{1}{2}}$.
- (iii) The ratio of the peak currents for forward and reverse sweeps is unity.
- (iv) The peak separation is given by $\frac{0.057}{n}$ V.

Cyclic voltammetry is an extremely useful tool for detecting and studying follow-up chemical reactions. For example, if an electron transfer process is followed by some chemical reaction involving the product to give an electro-inactive species then the reverse current peak will be less than the forward peak. In the limiting case, for an extremely fast chemical reaction, the reverse wave would be completely absent. Variation of the sweep rate will give voltammograms from which kinetic data can be derived. A more complicated state of affairs would exist if the product of the chemical reaction were itself electro-active giving the possibility of two reverse wave peaks. Nicholson and Shain⁵ have produced a theoretical treatment for the various possible situations which

might arise in cyclic voltammetry and have included cases where the electron transfer process is taken to be irreversible.

4. EXPERIMENTAL

4.1. Chemicals

4.1.1. Acetonitrile

Commercial grade acetonitrile supplied by Eastman Kodak, New York, contains water, unsaturated nitriles e.g. acrylonitrile, aromatic hydrocarbons such as benzene and various hydrolysis products such as acetamide, ammonia and acetic acid. The same products are also formed in the electrochemical oxidation of pure acetonitrile contaminated with water.²³⁸

Over the last decade a number of methods²³⁹⁻²⁴⁷ have been reported for purifying acetonitrile for use as a solvent in electrochemical studies because of its great stability with respect to oxidation and reduction.

Classical methods for the purification of acetonitrile involving repeated distillation from phosphorus pentoxide after treatment with bases e.g. potassium hydroxide, potassium carbonate or alumina, are considered unacceptable since it has been found that the solvent polymerises under these conditions.²⁴⁰

During the last decade several different methods, each having some particular advantage have been developed for the purification of acetonitrile.²⁴⁰⁻²⁴⁷ A careful survey of these methods, however, suggests that none of them can be successfully applied to acetonitrile when the solvent is manufactured as a by-product of the polymer industry in which the concentration of impurities varies greatly from batch to batch.

The method used in the present study for purifying acetonitrile was a modification of the methods of Osa and Kuwana²⁴⁶

and Walter and Ramaley.²⁴⁷

The distillation apparatus is presented in figure 2, page 45. It consisted basically of a 3 litre flask, a 1 metre heated fractionating column packed with glass helices and a 3 litre collecting flask protected by a calcium chloride guard tube.

2.5 litre of acetonitrile was refluxed with about 40g anhydrous aluminium(III) chloride for about an hour to remove any unsaturated nitriles present. It was then fractionally distilled at a rate of $15\text{-}20\text{cm}^3 \text{ min}^{-1}$. The distillate, mixed with about 20g anhydrous lithium carbonate and 20g potassium permanganate, was refluxed for an hour and then distilled rapidly, the distillate being acidified by adding 30g anhydrous sodium hydrogen sulphate. The column and glassware were washed thoroughly first with 0.25M sulphuric acid to remove any amide formed and then with distilled water. After drying the glassware in an oven at about 140°C overnight, the column was reassembled and the acidic distillate was refluxed for about 2 hours. This was followed by rapid distillation. About 5g of powdered calcium hydride was added to the distillate which was then refluxed for about 5 hours before distilling at a rate of about $10\text{cm}^3 \text{ hour}^{-1}$. The distillation procedure with calcium hydride was repeated and the final distillate in the boiling range $81.0 \pm 0.5^\circ\text{C}$ was collected over 4A molecular sieve (supplied by B.D.H.) transferred to a dark coloured bottle and stored in the dry-box. In each distillation stage the first and last 100cm^3 of the distillate were rejected; in the case of the

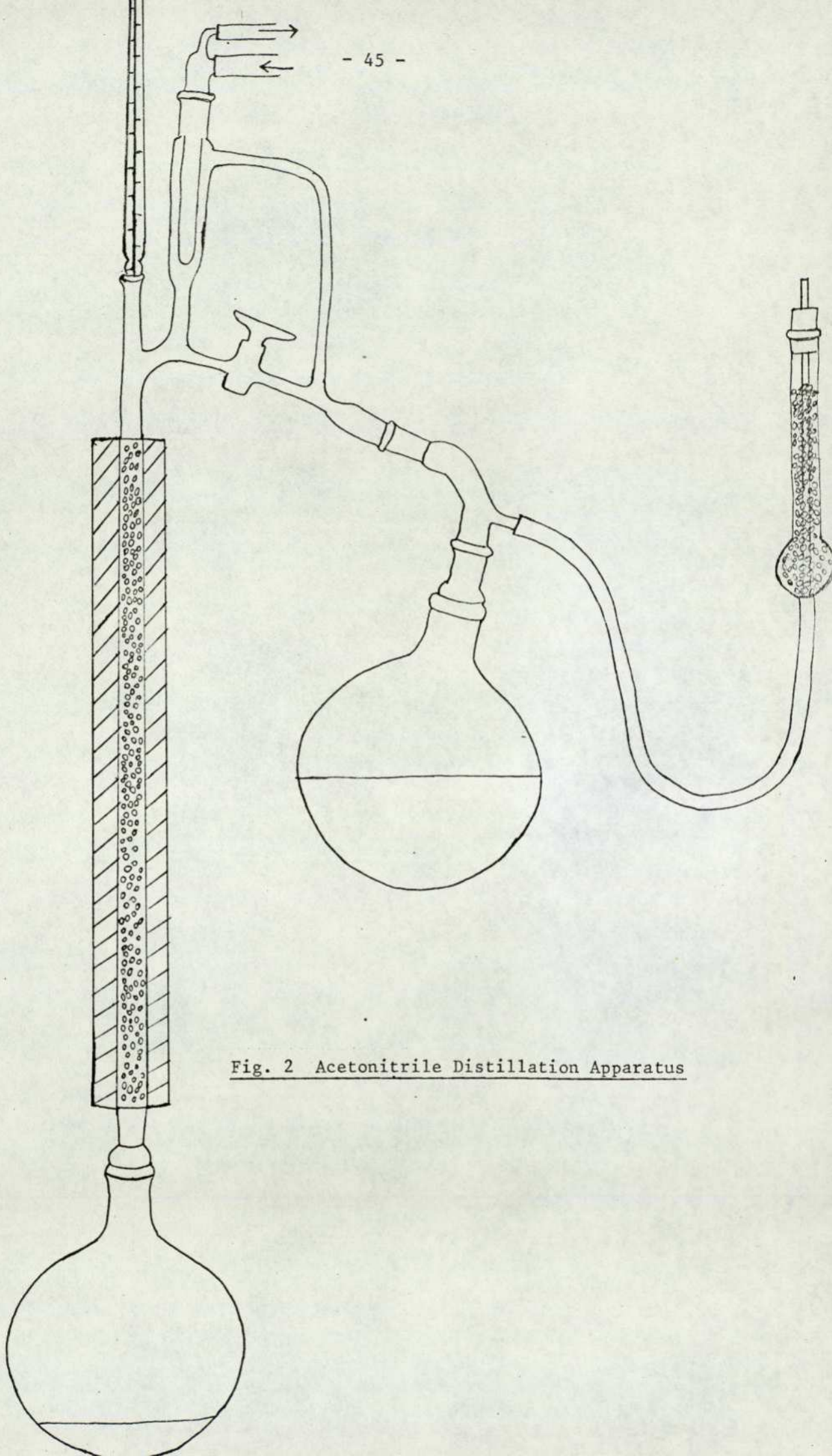


Fig. 2 Acetonitrile Distillation Apparatus

final distillation the first and last 200cm³ of the distillate were rejected to ensure the quality of the purified product.

4.1.2. Tetra-n-butylammonium perchlorate

The basic method of preparing tetra-n-butylammonium perchlorate is to neutralise tetra-n-butylammonium hydroxide with perchloric acid; the salt is only sparingly soluble in cold water and precipitates from solution. Two methods of recrystallising quaternary ammonium salts have been reported. Luder et al.²⁴⁸ used chloroform, ether and ethyl acetate while Kolthoff and Coetzee²⁴⁹ recrystallised the salts from water. Although the use of organic solvents for recrystallisation is the easier technique, the complete removal of the solvent from the product, even after prolonged drying under reduced pressure, is extremely difficult. Recrystallisation from water, while tedious due to the large volumes required, was used in the present work since a solvent-free product could more readily be obtained.

100g of a 40% w/w solution of tetra-n-butylammonium hydroxide (G.P.R. grade supplied by B.D.H.) was diluted to about 300cm³ with distilled water in a litre beaker, and neutralised by adding dropwise from a burette a 35% w/w solution of perchloric acid (prepared from G.P.R. grade perchloric acid supplied by B.D.H.). Checks on the acidity of the solution during neutralisation were made using pH paper. When the pH value was about 6, a further 2cm³ of the acid was added. The resulting mixture, from which the salt had separated as white crystals, was cooled in ice. When the solution had cooled to about 6-7°C, it was filtered through a Whatman No. 30

filter paper in a Buckner funnel. The mass of white crystals was washed with three portions of 100cm³ ice cold distilled water. The product was dissolved in about 100cm³ of warm 95% ethanol and this solution was gradually added to 4 litre of boiling distilled water in a 5 litre beaker. The water was boiled until the salt just started to crystallise. The beaker was then cooled in ice and the recrystallised product filtered off. A second crop of the salt was obtained by reducing the volume of the filtrate from the first recrystallisation until the solution was again saturated and then cooling in ice as before. The two crops of the crystals were combined and the recrystallisation process repeated twice. The final product was dried for 24 hours under reduced pressure in a vacuum oven at about 80°C.

Yield = 44.8g

% theoretical yield = 83.4%

Melting point 212 ± 1.0°C

Values of 207°C and 213°C have been reported by Luder et al.²⁴⁸ and Schroer et al.²⁵⁰ respectively for the melting point of tetra-n-butylammonium perchlorate.

4.1.3. Ligands

2,2'-Bipyridyl

2,2'-Bipyridyl (puriss) supplied by Koch-Light Lab. Ltd., Colnbrook, Bucks. was recrystallised twice from an ethanol-water mixture and dried at 50°C under reduced pressure.

Melting point 69-70°C (Literature value 70-71°C)²⁵¹

4,4'-Dimethyl-2,2'-bipyridyl

4,4'-Dimethyl-2,2'-bipyridyl (puriss) supplied by Koch-Light Lab. Ltd., was recrystallised from an ethanol-water mixture. The crystals were dried at 140°C under reduced pressure.

Melting point 171-172°C (Literature value 171-172°C)²⁵²

2,2',2''-Terpyridyl

2,2',2''-Terpyridyl was used as supplied by Koch-Light Lab. Ltd.

4.1.4. Metals

Iron

Iron wire (99.99%) was supplied by B.D.H. London. The wire was first cleaned with fine emery paper and washed with dilute hydrochloric acid. It was then washed thoroughly with distilled water and finally with acetonitrile. It was dried in an oven at 140°C under reduced pressure.

Cobalt

Cobalt sheet (99.99%) was supplied by Koch-Light Lab. Ltd., and was cleaned by the method described above for iron.

Nickel

Nickel sheet (99.99%) was supplied by Koch-Light Lab. Ltd., and was cleaned by the above method.

4.1.5. Preparation of metal(II) polypyridyl complexes

The preparation of metal(II) complexes containing the polypyridyl ligands 2,2'-bipyridyl, 4,4'-dimethyl-2,2'-bipyridyl, and 2,2',2''-terpyridyl, was carried out in three stages:

- (i) Preparation of anhydrous nitrosyl perchlorate.
- (ii) Preparation of hexakis(acetonitrile) metal(II) perchlorate complex, obtained by the reaction of the pure metal with anhydrous nitrosyl perchlorate in acetonitrile.
- (iii) Replacement of co-ordinated acetonitrile by the required polypyridyl ligand.

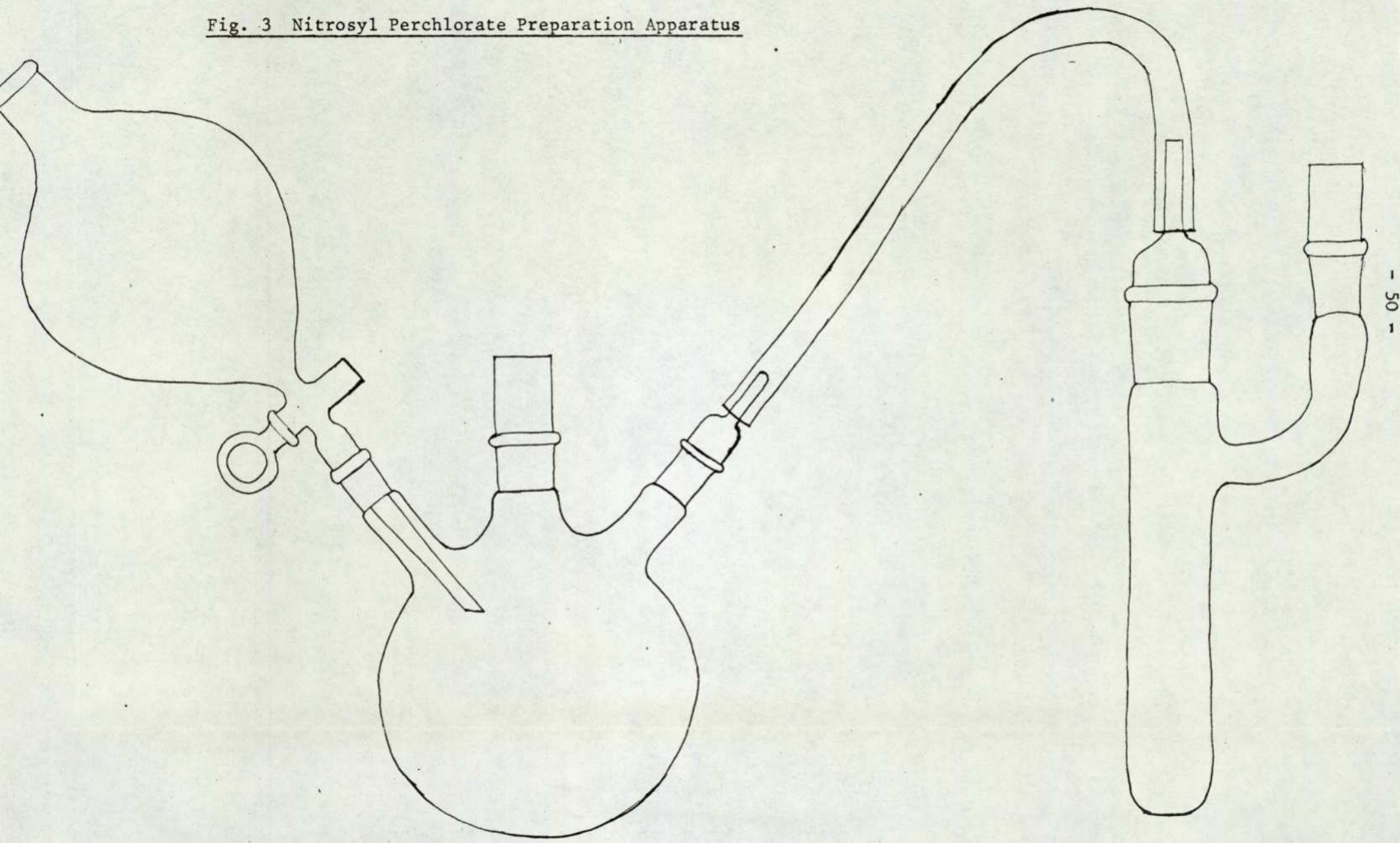
(i) Preparation of nitrosyl perchlorate

Nitrosyl perchlorate (NOClO_4) was first prepared by Hoffmann and Zedtwitz.²⁵³ The existence of the nitrosyl ion (NO^+) in nitrosyl perchlorate and its properties has been established by several groups of workers.²⁵⁴⁻²⁵⁸ A modification of the method of Hoffmann and Zedtwitz²⁵³ was used in the present work.

200cm³ of 70% perchloric acid (G.P.R. grade) was transferred to a 600cm³ reaction tube fitted with a two-necked parallel adapter (B19/26). The tube was connected to a three-necked 500cm³ round-bottomed flask containing 50cm³ of sodium nitrite (G.P.R. grade). A pear shaped 250cm³ dropping funnel containing concentrated nitric acid (G.P.R. grade) was fitted to the flask and the reaction tube was immersed in a Dewar flask. The apparatus is shown in figure 3, page 50.

After flushing the reaction tube with the gas produced by passing the nitric acid dropwise to the sodium nitrite, liquid nitrogen was poured into the Dewar flask. The reaction was continued until sufficient product (oxides of nitrogen) was collected. The reaction tube was disconnected from the flask and 50cm³ of perchloric

Fig. 3 Nitrosyl Perchlorate Preparation Apparatus



acid was added to the reaction mixture. The reaction tube was withdrawn from the Dewar flask and allowed to come to ambient temperature after which the reaction was permitted to proceed for a further 15 minutes.

The reaction product containing white crystals of nitrosyl perchlorate was filtered through a No. 4 sintered filterstick closed by a guard tube packed with phosphorus pentoxide as shown in figure 4, page 52; this process took about 16 hours. The filtered product was washed three times with 15cm³ portions of pure anhydrous acetonitrile, sucked dry on the sinter, and stored in a closed glass tube over phosphorus pentoxide in a dry box.

(ii) Preparation of hexakis(acetonitrile) metal(II) perchlorates

The apparatus used for these preparations is shown in figure 5, page 53. The glassware was cleaned and dried overnight at 140°C in a vacuum oven. A 250cm³ dropping funnel (A) containing 150cm³ anhydrous acetonitrile was fitted with a guard tube (B) packed with phosphorus pentoxide and inserted in neck N of a three-necked 500cm³ round-bottomed flask (C). Neck F was used to connect the system to a vacuum line.

About 5g of the pure metal was transferred to the reaction flask via neck G. 5g of nitrosyl perchlorate was washed twice with anhydrous acetonitrile and transferred to the flask through neck G. The taps T₁ and T₂ were closed and neck G stoppered.

Tap T₂ was opened slightly to reduce the pressure in the reaction flask and by opening tap T₁, about 50cm³ of acetonitrile was added. Taps T₁ and T₂ were adjusted from time to time to give a reduction in pressure just sufficient to remove oxides of

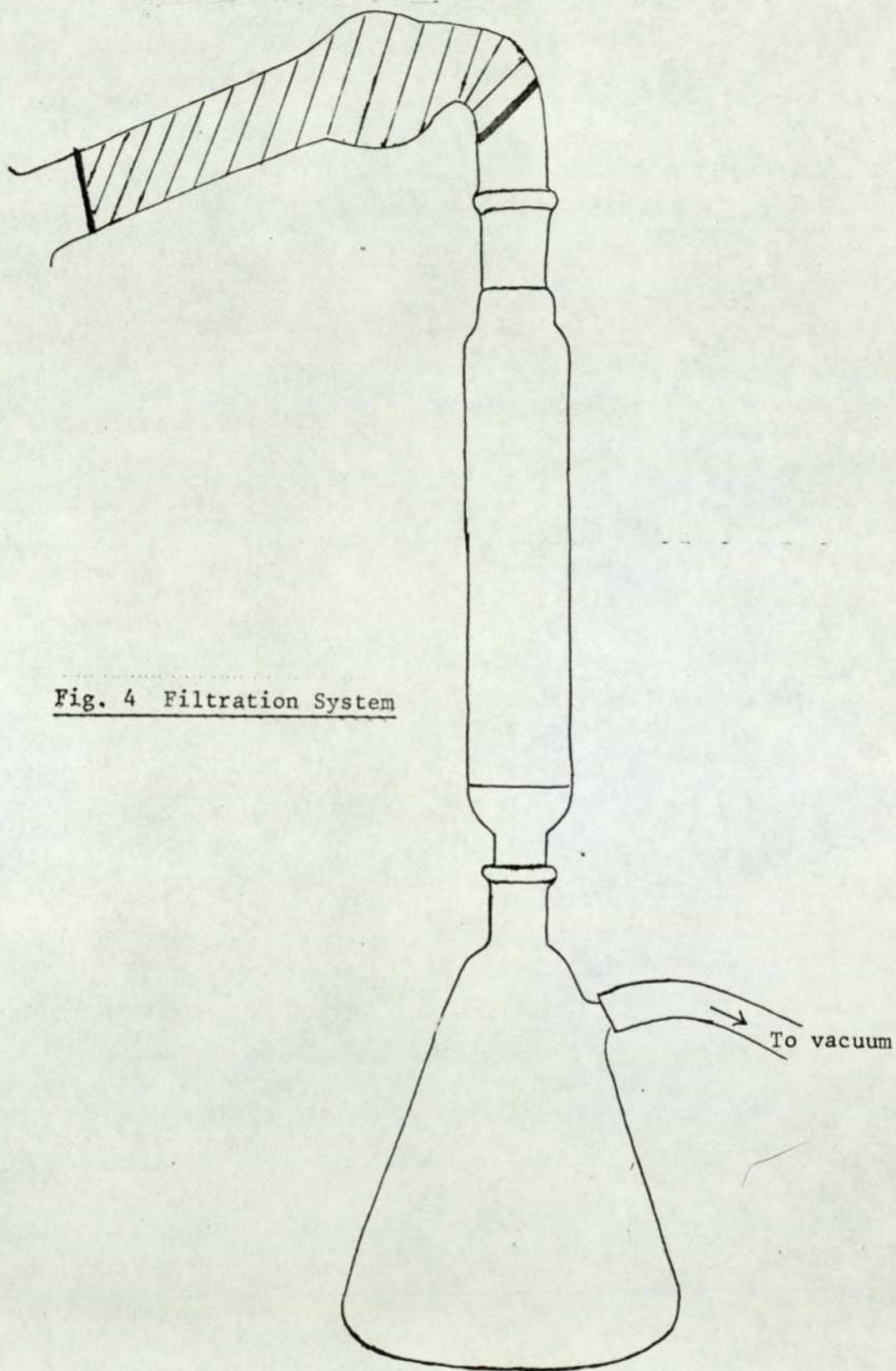
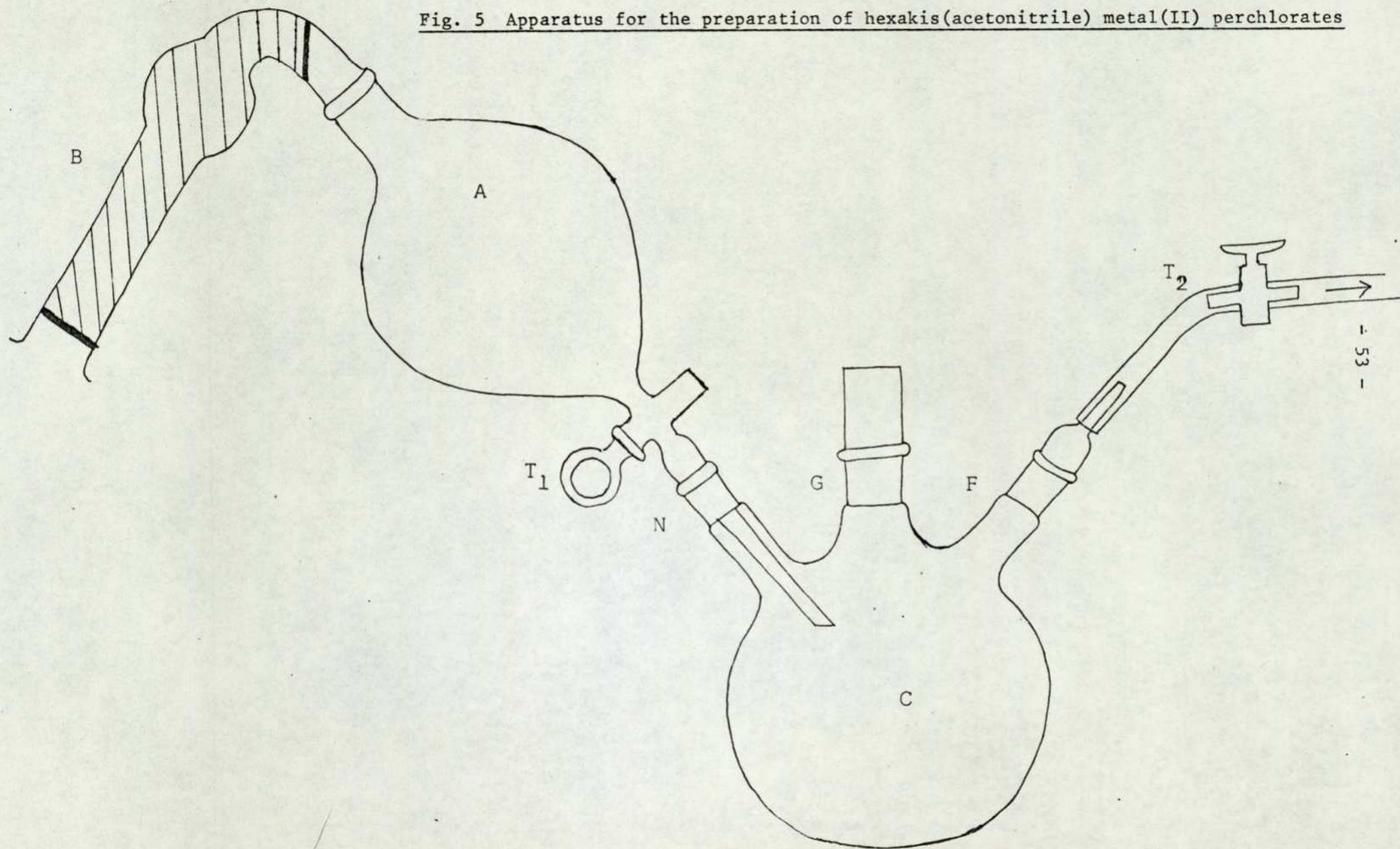


Fig. 4 Filtration System

Fig. 5 Apparatus for the preparation of hexakis(acetonitrile) metal(II) perchlorates



nitrogen and keep the reaction in the flask under control.

Acetonitrile was added from time to time to accelerate the reaction.

When the further addition of acetonitrile did not effect the rate, the reaction was judged to be near completion. The remaining

acetonitrile was then released into the flask which was shaken to

dissolve the crystals of the metal perchlorate complex formed. Tap

T₂ was turned off and the pressure in the reaction vessel was brought to atmospheric pressure by opening tap T₁.

The reaction product (together with unreacted nitrosyl perchlorate and metal) was filtered quickly through a No. 4 sintered filter stick of the type shown in figure 4, page 52. The residue on the sinter was rejected and filtrate containing the product was collected in a 500cm³ conical flask and quickly transferred to a nitrogen filled dry box. 10cm³ portions of anhydrous diethyl ether (dried over sodium metal and stored in the dry box) were then added with constant stirring. Crystals of the metal perchlorate complex soon appeared and were filtered through the filter stick in the dry box. The crystals were washed with two 5cm³ portions of anhydrous acetonitrile and sucked dry for about half an hour. The product was then stored in a sealed glass tube over phosphorus pentoxide in a desiccator kept in a dry box.

Analytical data for the complexes are given below.

$\{\text{Fe}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$. The yield was 15.8g. The off-white coloured complex which gave a negative brown-ring test melted at 85-86°C leaving behind a black residue. The iron content of the complex determined by the method described in section 4.6.2. was found 11.18% and 11.10% for two separate samples. This agrees well

with the theoretical value of 11.15% for $\{\text{Fe}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$.

In the visible and near infra-red region an absorption peak was observed at 11100cm^{-1} having a molar extinction co-efficient of $0.03\text{mol}^{-1}\text{cm}^{-1}$. The infra-red spectrum was recorded using a Nujol mull between sodium chloride plates. Peaks at 2320cm^{-1} (medium), 2290cm^{-1} (sharp), 1090cm^{-1} (broad) and 940cm^{-1} (medium) were observed. The peaks at 1090cm^{-1} and 940cm^{-1} are characteristic of the perchlorate anion.²⁵⁹ The split absorption band with peaks at 2320cm^{-1} and 2290cm^{-1} is associated with C-N stretching modes and indicates the co-ordination of acetonitrile in this complex.²⁵⁹ The shift in the C-N band, normally at 2248cm^{-1} , to a higher frequency is very common for co-ordinated acetonitrile.²⁵⁹⁻²⁶¹ The complex was paramagnetic, the effective magnetic moment being determined as 5.14 B.M. at 20°C using the Gouy method (c.f. 4.4.2.). This value is in agreement with reported values^{259,262} and is consistent with a spin-free octahedral iron(II) complex. A d^6 electron configuration $t_{2g}^4 e_g^2$ would be expected to give a first order orbital contribution which would account for the observed moment exceeding the spin-only value of 4.90 B.M.

$\{\text{Co}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$. The yield of this orange coloured complex was 17.0g. The absence of nitrosyl and nitrate ions was indicated by a negative brown-ring test. The percentage of cobalt metal in the complex, determined by the electrogravimetric method described in section 4.6.2. was found to be 11.72% and 11.76% for two separate samples. These figures are in good agreement with the calculated value of 11.69% for $\{\text{Co}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$.

In the visible and near infra-red region an absorption

peak was observed at 20500cm^{-1} , having a molar extinction coefficient of $15\text{mol}^{-1}\text{cm}^{-1}$, which is in the region reported by Hathaway et al.²⁶³, for the absorption of $\{\text{Co}(\text{CH}_3\text{CN})_6\}(\text{BF}_4)_2$ and assigned as a $A_{2g} \leftarrow T_{1g}$ transition. The infra-red spectrum of this complex showed peaks at 2315cm^{-1} and 2290cm^{-1} which are associated with C - N vibrations. The broad band observed at 1095cm^{-1} with a shoulder at 1040cm^{-1} is characteristic of the ClO_4^- ion according to Hathaway and Underhill.²⁵⁹ The effective magnetic moment was found to be 4.93 B.M. at 20°C . The high value of the magnetic moment of this complex compared with the spin-only value of 3.87 B.M. expected for a $t_{2g}^5 e_g^2$ configuration can be attributed to an expected first order orbital contribution.²⁶²

$\{\text{Ni}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$. The yield of the light purple coloured complex was 16.8g. The nickel content determined by the electrogravimetric method described in section 4.6.2. was found to be 11.66% and 11.61% for two separate samples in agreement with the calculated value of 11.65% for $\{\text{Ni}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$.

The visible spectrum in acetonitrile showed absorption maxima at 17200cm^{-1} and 13950cm^{-1} having molar extinction coefficients of $15.3\text{mol}^{-1}\text{cm}^{-1}$ and $6.8\text{mol}^{-1}\text{cm}^{-1}$ respectively, which are in agreement with previously reported bands.²⁶¹ The infra-red spectrum was similar to those obtained for the iron and cobalt complexes, giving absorption bands which indicated the presence of the C - N group (2290cm^{-1}) and the perchlorate ion (1083cm^{-1} , 1035cm^{-1} and 945cm^{-1}).²⁶¹ The effective magnetic moment was found to be 3.20 B.M. at 20°C which agrees with values previously reported.²⁵⁹⁻²⁶³ This is consistent with an octahedral nickel(II)

complex in which the d configuration is $t_{2g}^6 e_g^2$. The higher value of the magnetic moment over the spin-only value (2.83 B.M.) can be attributed to spin-orbit coupling, first order orbital contribution being absent for this configuration.

(iii) Preparation of polypyridyl metal(II) perchlorate complexes

The complexes were prepared in a dry box having a nitrogen atmosphere. The general procedure for preparing these complexes was as follows:

A weighed amount (about 1g or approximately 2mmol of the hexakis(acetonitrile) metal(II) perchlorate complex was dissolved in about 25cm³ pure anhydrous acetonitrile in a 100cm³ conical flask. This solution was mixed with a solution containing a calculated amount of polypyridyl ligand (to give a slight excess over that required for a 3:1 molar ratio of ligand to metal) in 25cm³ acetonitrile. The resulting solution containing the soluble complex was transferred to the filter stick system shown in figure 4, page 52 and mixed with about 100cm³ anhydrous diethyl ether. Within 3-4 minutes, a precipitate of the polypyridyl complex appeared, settling to the bottom of the filter stick. The filter stick was closed by a guard tube containing phosphorus pentoxide and sucked dry for 2-4 minutes; a completely colourless filtrate indicated the complete removal of the complex from the solvent system. The precipitate was washed twice with 5cm³ portions of acetonitrile and sucked dry for 5-6 minutes after each washing. Finally, the product was sucked dry for about half an hour to remove traces of acetonitrile and water. The complexes were stored in sealed glass tubes over phosphorus pentoxide in a desiccator, which was kept in the dry box.

Analytical data for the complexes are given below:

Tris(2,2'-bipyridyl) iron(II) perchlorate, $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_2$.

The product obtained in 90% yield consisted of red coloured needle shaped hard crystals.

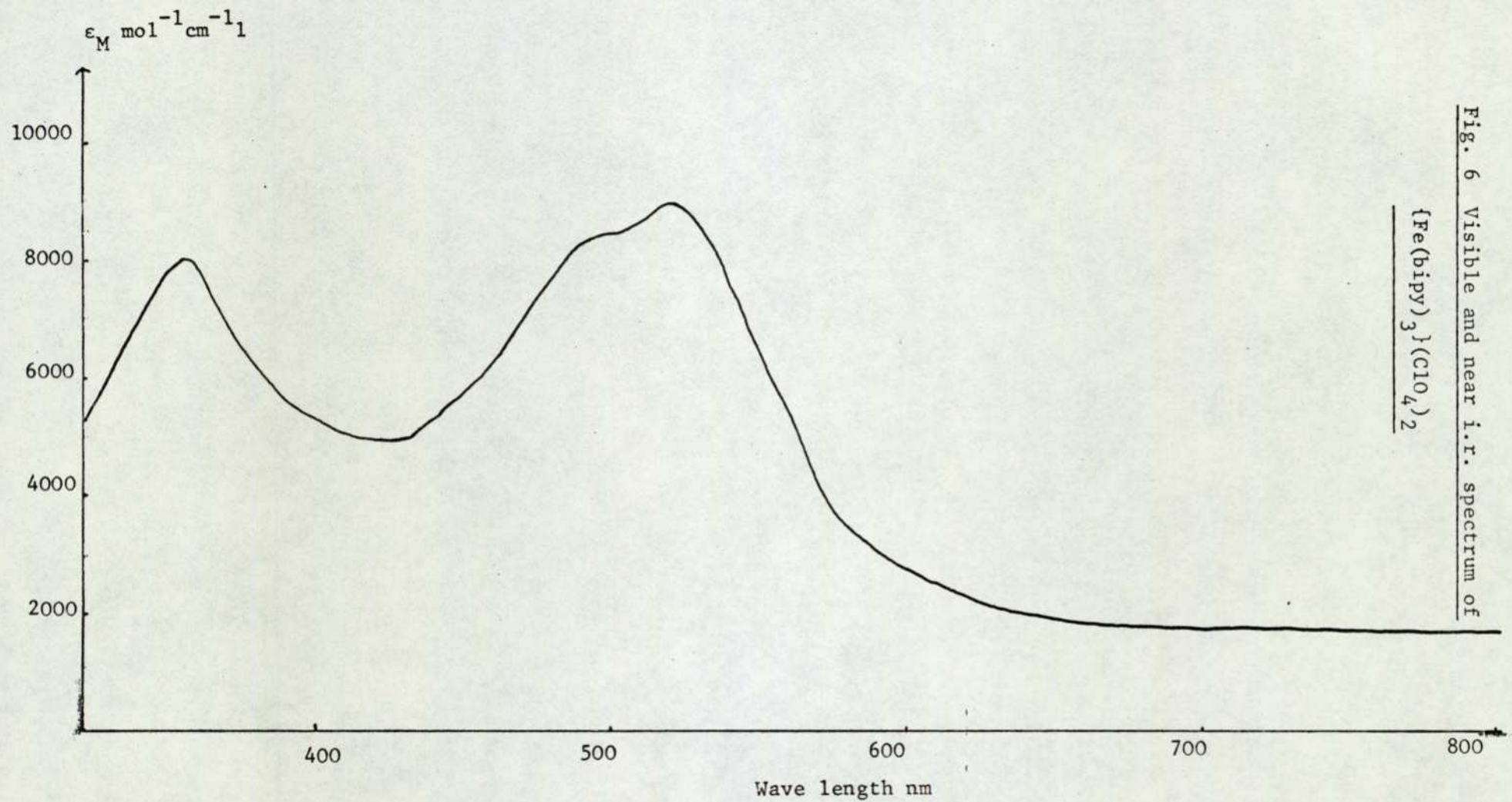
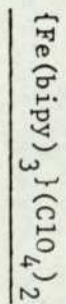
Element	C	H	N	Fe
% Theoretical for above formula	49.77	3.31	11.61	7.72
% Found	49.57	3.86	13.57	7.78

The figures for iron and carbon contents are in good agreement with calculated values. On the other hand, the analytical results for hydrogen and nitrogen are high. Although the adsorption of a small amount of water by the complex, which is hygroscopic in nature, could account for the high hydrogen figure this would not explain the high nitrogen content for which some operating or instrumental error may have been responsible. The spectrum in the visible and near infra-red region is presented in figure 6, page 59. Absorption maxima at 28170cm^{-1} , 20410cm^{-1} and 19150cm^{-1} having extinction co-efficients $8000\text{mol}^{-1}\text{cm}^{-1}$, $8800\text{mol}^{-1}\text{cm}^{-1}$ and $9590\text{mol}^{-1}\text{cm}^{-1}$ respectively are in good agreement with reported data.²⁶⁴⁻²⁶⁹ The first band has been assigned as a ligand to metal charge transfer band, the other two as metal to ligand transitions. In agreement with the work of Burstall and Nyholm²⁷⁰ the complex was found to be diamagnetic at 20°C which indicates a spin paired d^6 configuration.

Tris(4,4'-dimethyl-2,2'-bipyridyl) iron(II) perchlorate,
 $\{\text{Fe}(\text{dimbipy})_3\}(\text{ClO}_4)_2$.

The red needle shaped crystals were obtained in a yield of 86% of the theoretical value. Below are the analytical data for

Fig. 6 Visible and near i.r. spectrum of



carbon, hydrogen, nitrogen and iron contents:

Element	C	H	N	Fe
% Theoretical for above formula	53.53	4.46	10.41	6.92
% Found	51.05	4.63	9.95	6.90

It is seen that both the carbon and nitrogen figures are low, while that of hydrogen is high. This could be accounted for by the presence of water as a contaminant which may have been introduced at some stage during the analytical procedure.

The spectrum observed in the visible and near infra-red region (figure 7, page 61) had bands with maxima at 28170cm^{-1} , 20410cm^{-1} and 18870cm^{-1} with extinction co-efficients of $9000\text{mol}^{-1}\text{cm}^{-1}$, $8860\text{mol}^{-1}\text{cm}^{-1}$ and $9830\text{mol}^{-1}\text{cm}^{-1}$ respectively, data which are similar to those for $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_2$ described above. The complex was diamagnetic in character as expected,²⁷⁰ again indicating a low spin d^6 configuration.

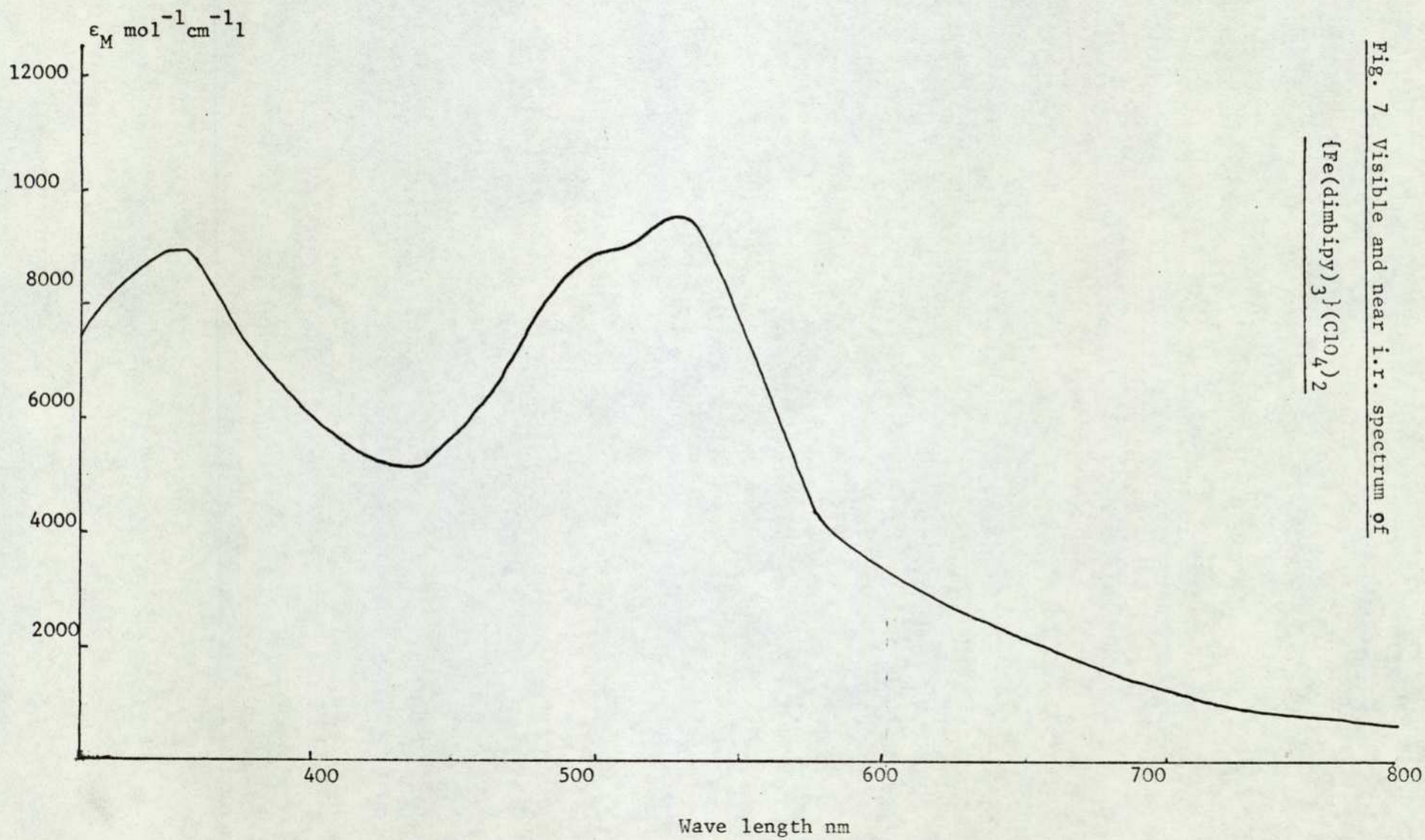
Bis(2,2',2''-terpyridyl iron(II) perchlorate, $\{\text{Fe}(\text{terpy})_2\}(\text{ClO}_4)_2$.

The ash coloured crystals of the diamagnetic complex were produced in a yield of 90% of the theoretical. The analytical data for this complex, given below, are in excellent agreement with the theoretical figures.

Element	C	H	N	Fe
% Theoretical for above formula	49.93	3.05	11.65	7.76
% Found	50.10	3.08	11.61	7.81

Absorption bands in the visible and near infra-red region appeared at 27770cm^{-1} and 18050cm^{-1} with extinction co-efficients of

Fig. 7 Visible and near i.r. spectrum of
 $\text{Fe}(\text{dimbipy})_3(\text{ClO}_4)_2$



8000mol⁻¹cm⁻¹ and 11900mol⁻¹cm⁻¹ respectively as presented in figure 8, page 63. These bands have been attributed to $e_g^* \leftarrow \pi$ $\pi^* \leftarrow t_{2g}$ transitions respectively by Hogg and Wilkins²⁷¹ working in aqueous solution.

Tris(2,2'-bipyridyl) cobalt(II) perchlorate, {Co(bipy)₃}(ClO₄)₂.

A very light yellow soft powder resembling ground mustard seed was obtained. The yield was 85% of the theoretical. Elemental analytical data, given below, are seen to be consistent with the above formula.

Element	C	H	N	Co
% Theoretical for above formula	49.55	3.30	11.56	8.07
% Found	49.50	3.44	11.46	8.10

The visible and near infra-red spectrum showed absorption maxima at 22730cm⁻¹ and 18250cm⁻¹ having extinction co-efficients of 30mol⁻¹cm⁻¹ and 6mol⁻¹cm⁻¹ respectively (figure 9, page 64) in agreement with the values reported by Palmer and Piper.²⁷² The effective magnetic moment was found to be 3.82 B.M. at 20°C consistent with a spin free d⁷ configuration.

Tris(4,4'-dimethyl-2,2'-bipyridyl) cobalt(II) perchlorate,
{Co(dimbipy)₃}(ClO₄)₂.

This complex was slightly darker in colour than {Co(bipy)₃}(ClO₄)₂, but of a similar consistency. The yield was 87% of the theoretical. The analytical results for elemental analysis of three separate batches are given on the following page.

Fig. 8 Visible and near i.r. spectrum of
 $\{\text{Fe(terpy)}_2\}(\text{ClO}_4)_2$

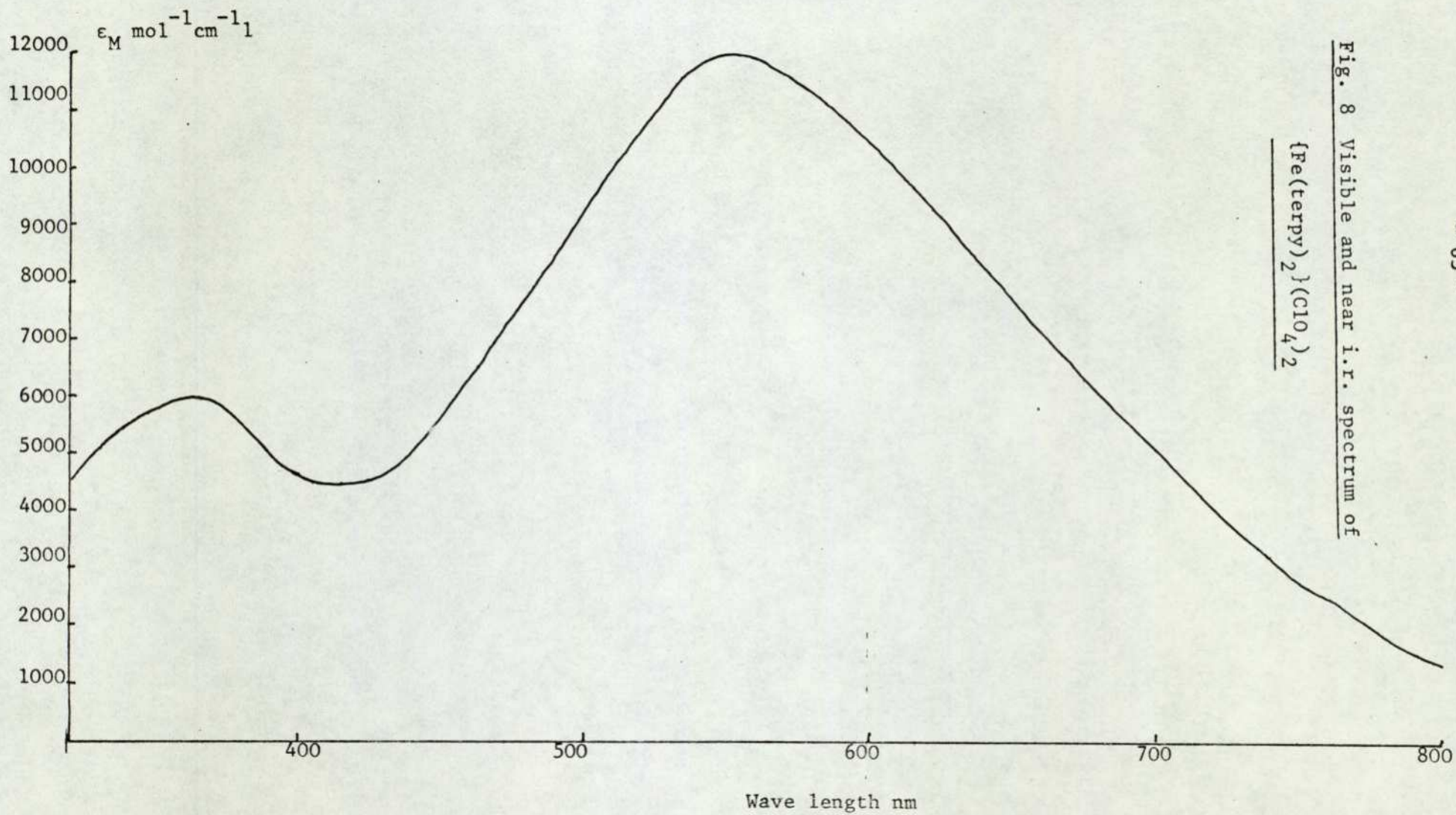
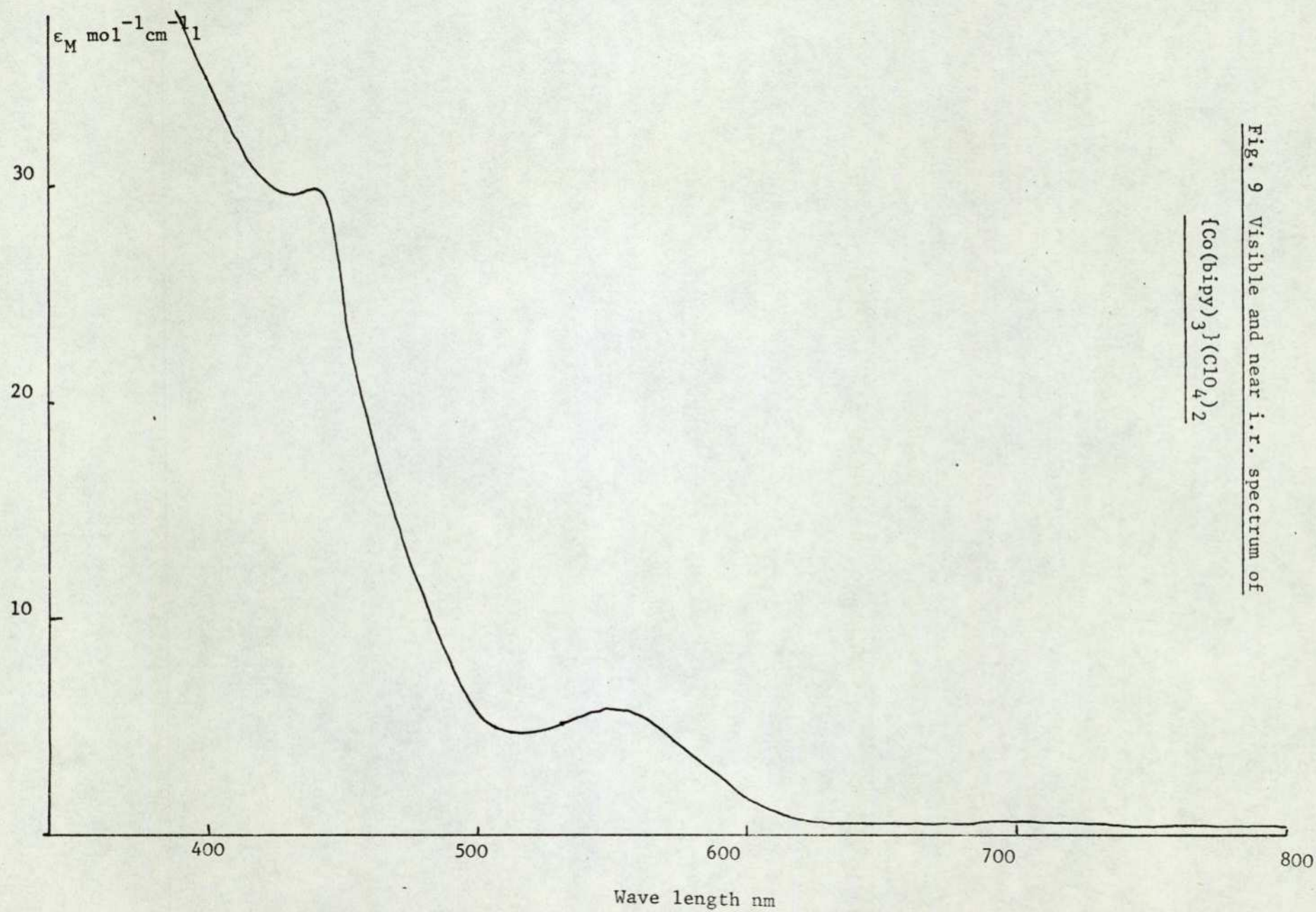


Fig. 9 Visible and near i.r. spectrum of
 $\text{Co(bipy)}_3(\text{ClO}_4)_2$



Element	C	H	N	Co
% Theoretical for above formula	53.30	4.40	10.36	7.36
% Found (1)	53.21	5.23	9.70	7.30
(2)	53.26	5.03	9.40	7.20
(3)	53.44	5.28	10.04	7.28

The analytical data for carbon and cobalt are in very good agreement with the theoretical figures. Again, discrepancies and a certain lack of reproducibility are observed in the hydrogen and nitrogen determinations. This is attributed to the problem of handling the samples in perfectly anhydrous conditions prior to and during the analytical procedures.

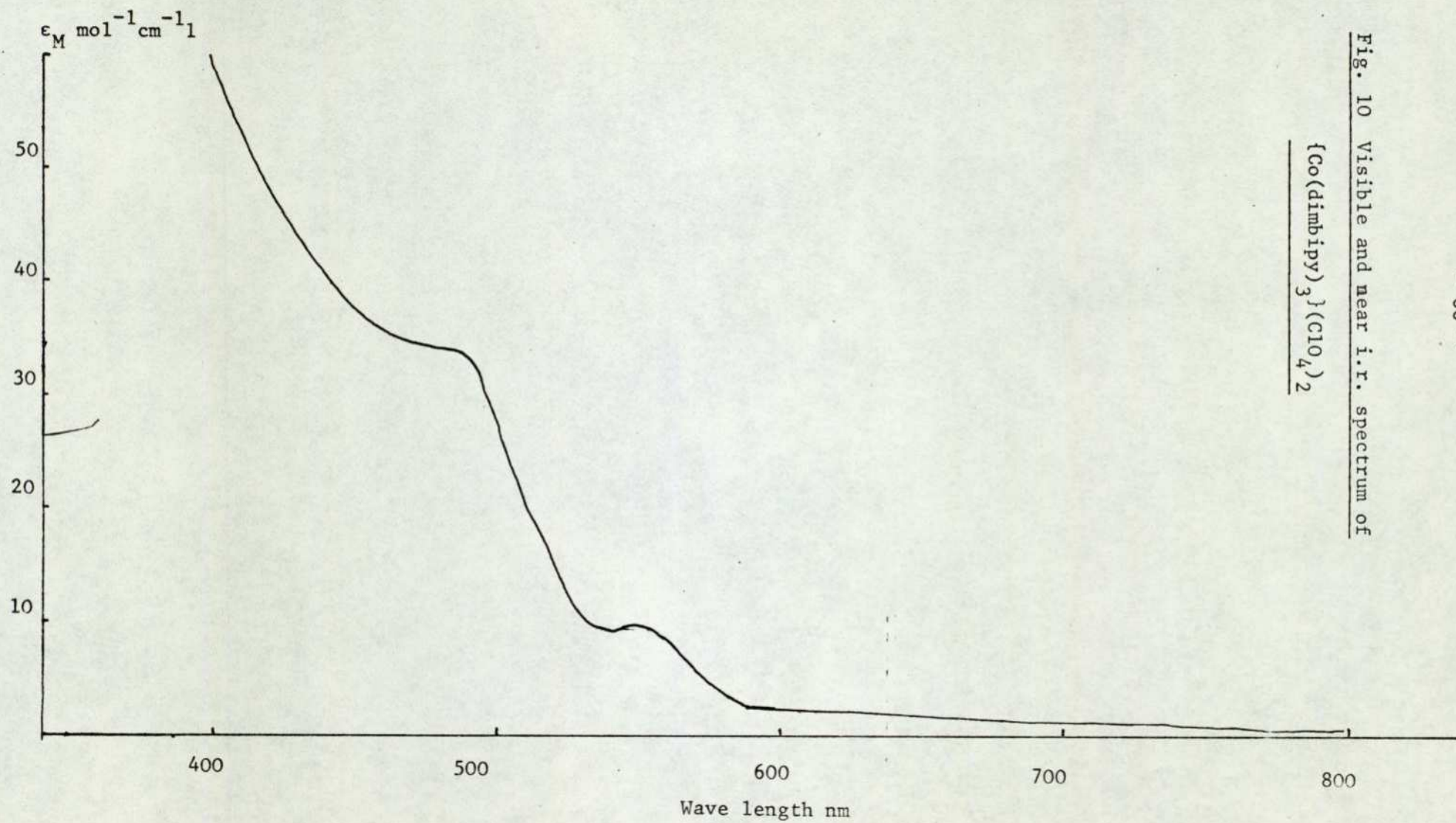
The spectrum recorded in the visible and near infra-red region gave absorption maxima at 23260cm^{-1} and 18520cm^{-1} with extinction co-efficients of $34\text{mol}^{-1}\text{cm}^{-1}$ and $10\text{mol}^{-1}\text{cm}^{-1}$ respectively (figure 10, page 66) similar to those of the $\{\text{Co}(\text{bipy})_3\}(\text{ClO}_4)_2$ complex. The effective magnetic moment of the complex at 20°C was found to be 3.91 B.M., again consistent with a spin free cobalt(II) complex.

Bis(2,2',2''-terpyridyl) cobalt(II) perchlorate, $\{\text{Co}(\text{terpy})_2\}(\text{ClO}_4)_2$.

This compound was obtained as a reddish-yellow soft powder in a yield of 88% of the theoretical. The elemental analysis data are given below:

Element	C	H	N	Co
% Theoretical for above formula	49.77	3.04	11.61	8.11
% Found	49.61	3.31	11.27	8.18

Fig. 10 Visible and near i.r. spectrum of
 $\{\text{Co}(\text{dimbipy})_3\}(\text{ClO}_4)_2$



The analytical results are in good agreement with the calculated values. The spectrum recorded in the visible and near infra-red region gave absorption bands at 27027cm^{-1} , 24096cm^{-1} , 22520cm^{-1} , 19840cm^{-1} and 18120cm^{-1} having extinction co-efficients of $1800\text{mol}^{-1}\text{cm}^{-1}$, $13500\text{mol}^{-1}\text{cm}^{-1}$, $1420\text{mol}^{-1}\text{cm}^{-1}$, $1250\text{mol}^{-1}\text{cm}^{-1}$ and $420\text{mol}^{-1}\text{cm}^{-1}$ respectively (figure 11, page 68). The values of last three bands are in agreement with the figures reported by Hogg and Wilkins²⁷¹ for the spectrum of this complex in aqueous solution. The effective magnetic moment was found to be 4.26 B.M. at 20°C indicating a spin free d^7 configuration as expected.²⁷¹

Tris(2,2'-bipyridyl) nickel(II) perchlorate, $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_2$.

This complex was obtained as a pink coloured soft powder. The yield was about 84% of the theoretical. Analytical data are given below:

Element	C	H	N	Ni
% Theoretical for above formula	49.56	3.30	11.56	8.07
% Found	49.63	3.44	11.43	8.13

These two sets of figures are in very good agreement. The visible and near infra-red spectrum showed absorption maxima at 18980cm^{-1} and 12430cm^{-1} with extinction co-efficients of $96\text{mol}^{-1}\text{cm}^{-1}$ and $21\text{mol}^{-1}\text{cm}^{-1}$ respectively (figure 12, page 69) and fall within the range reported by Piper and Palmer²⁷² and Harris and McKenzie^{273,274} for this complex in aqueous solution. The effective magnetic moment of this complex was found to be 3.2 B.M. at 20°C consistent with the presence of two unpaired electrons in an octahedral d^8 configuration. Values of about 3.2 B.M. are common for the moments of octahedral nickel(II) complexes,²⁶² the difference between the spin only value (2.83 B.M.)

Fig. 11 Visible and near i.r. spectrum of
 $\{\text{Co(terpy)}_2\}(\text{ClO}_4)_2$

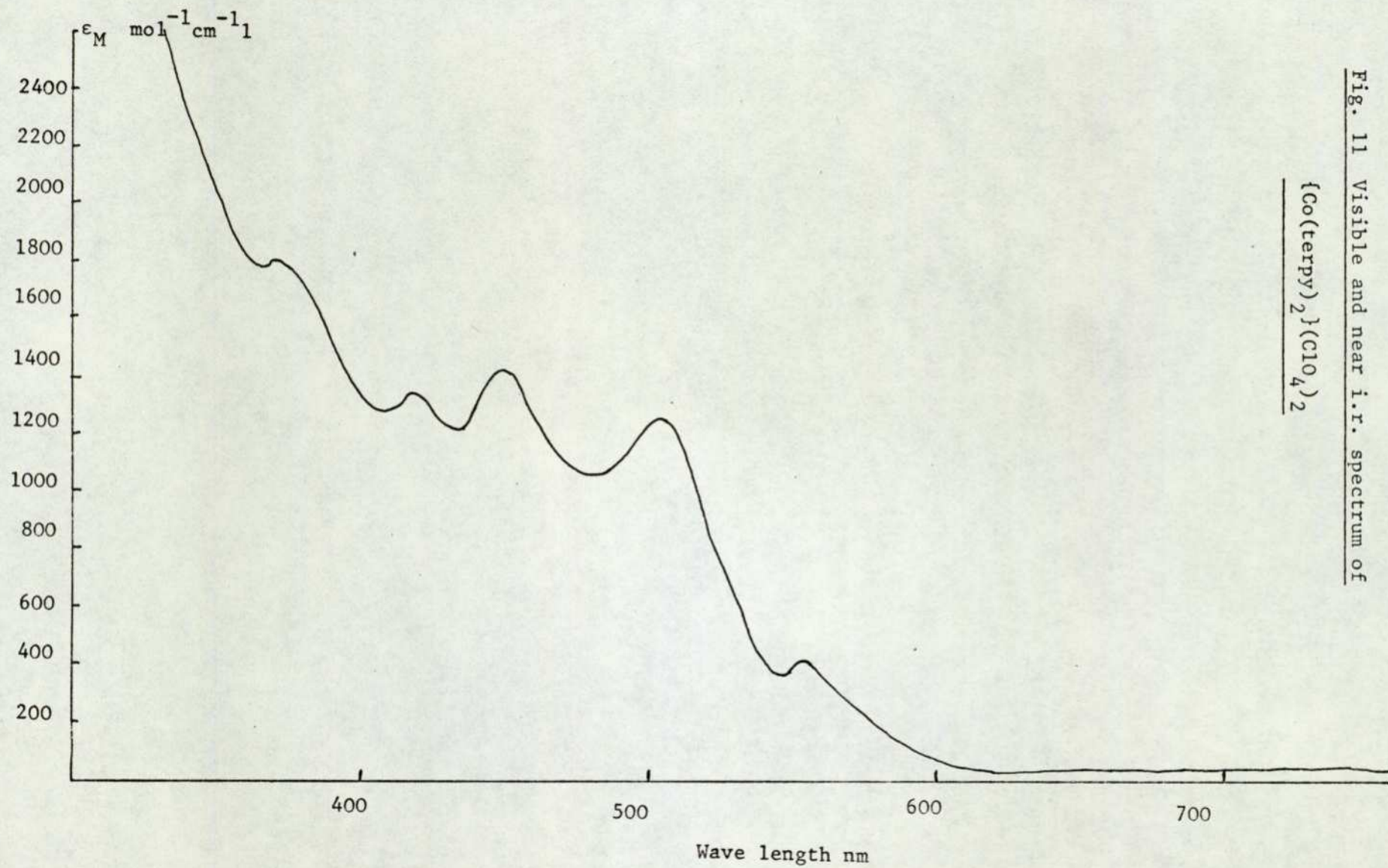
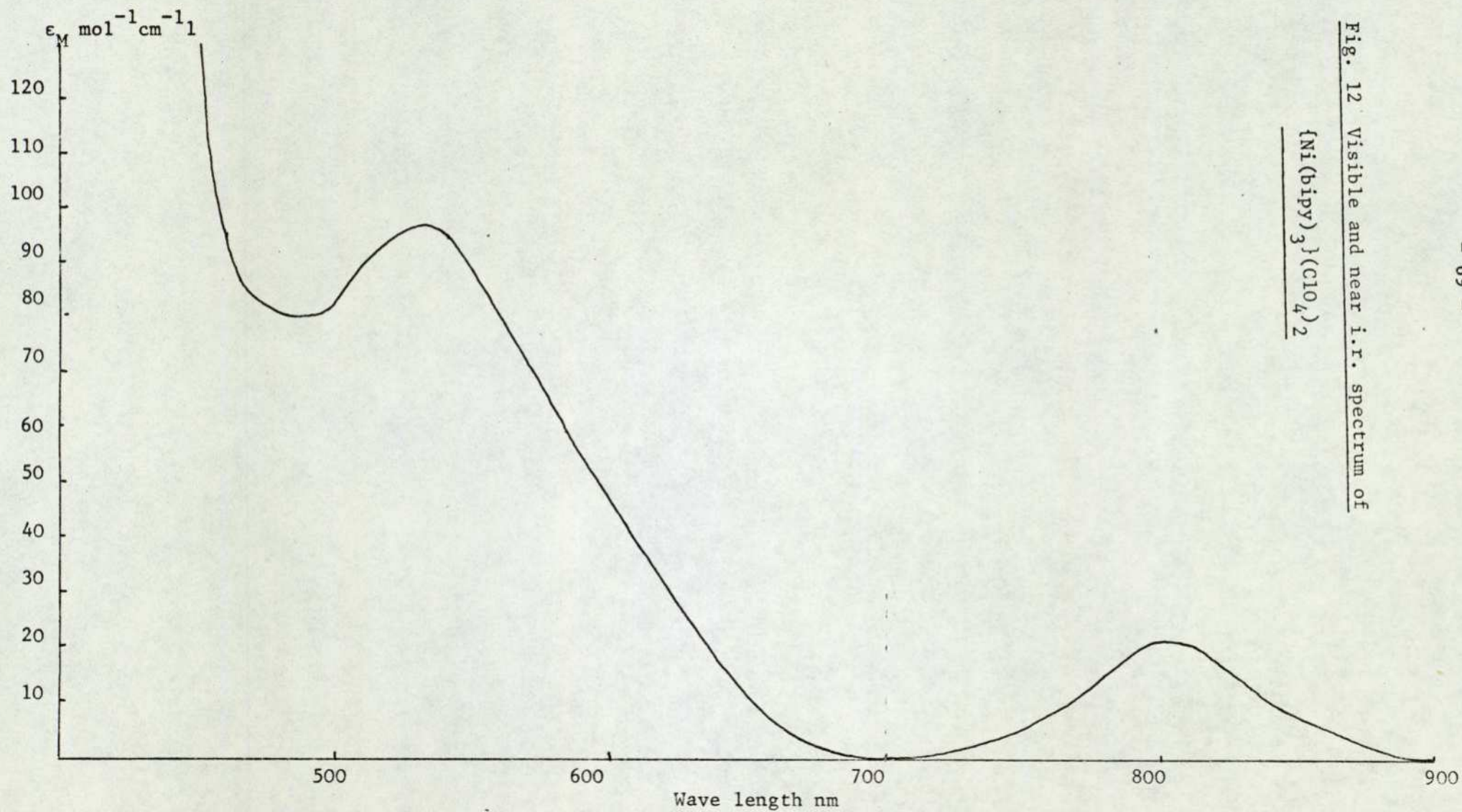
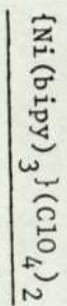


Fig. 12 Visible and near i.r. spectrum of



and the observed figures being attributed to spin-orbit coupling.

Tris(4,4'-dimethyl-2,2'-bipyridyl) nickel(II) perchlorate,
 $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_2$.

This complex was a pinkish powder, darker than $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_2$.

The yield was 88% of the theoretical. The results obtained for the elemental analysis of two samples from separate preparations of this complex were as follows:

Element	C	H	N	Ni
% Theoretical for above formula	53.31	4.44	10.36	7.24
% Found (1)	50.04	4.49	9.94	7.26
(2)	50.30	4.45	10.01	7.30

The low carbon and nitrogen figures are difficult to explain.

In the foregoing discussions of analytical data discrepancies have been attributed to possible water contamination. In this particular case, however, where the carbon content is very low it would appear that other factors, such as incomplete combustion, might be operative. The visible and near infra-red spectrum showed absorption bands at 19270cm^{-1} and 12880cm^{-1} having extinction co-efficients of $107\text{mol}^{-1}\text{cm}^{-1}$ and $25\text{mol}^{-1}\text{cm}^{-1}$ respectively (figure 13, page 71).

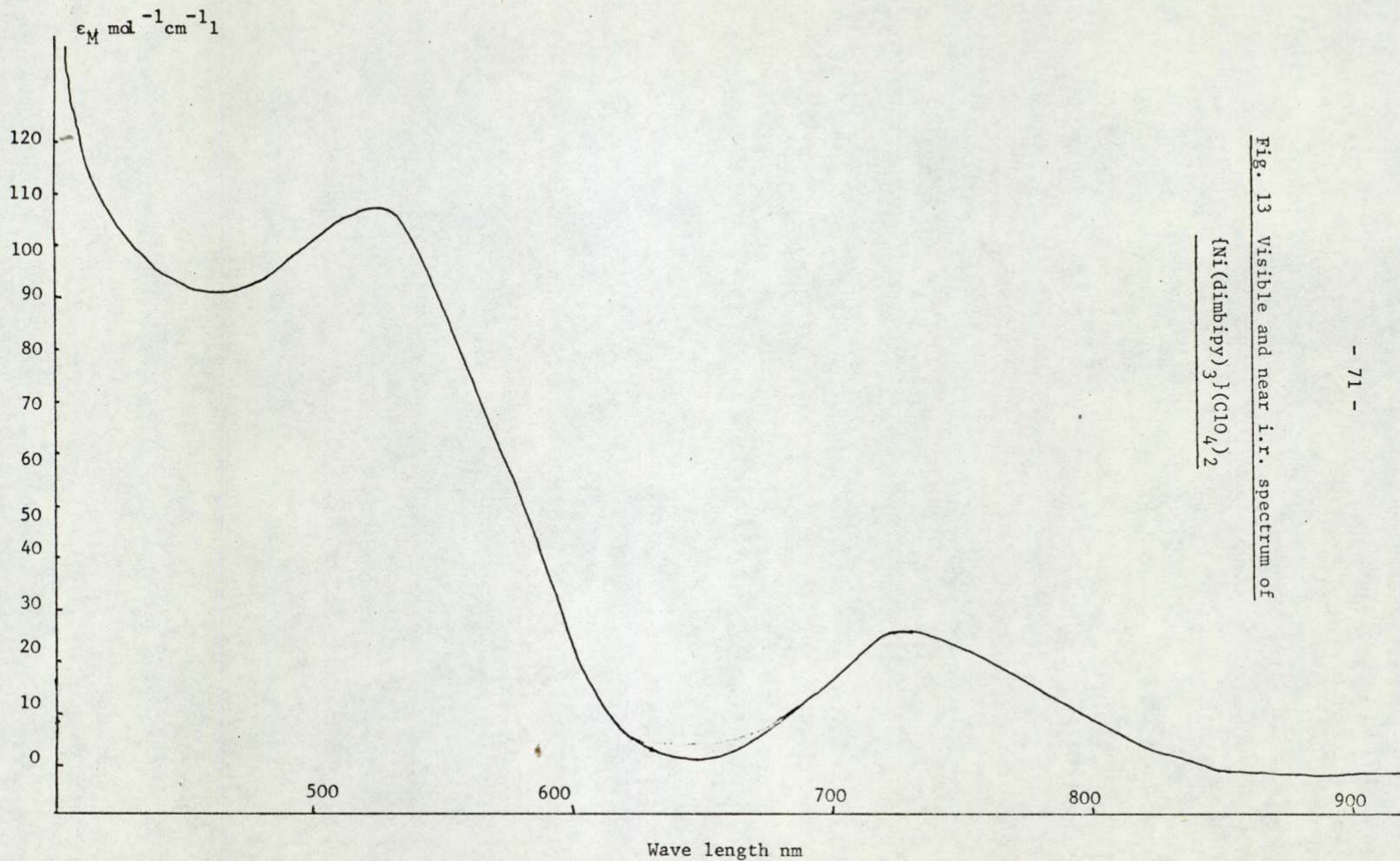
Literature data are not available for this complex for comparison.

The magnetic moment for this complex was found to be 3.2 B.M.

Bis(2,2',2''-terpyridyl) nickel(II) perchlorate, $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_2$.

Off-white coloured needle shaped crystals were obtained. The yield was 93% of the theoretical. The results for elemental analysis are on the following page.

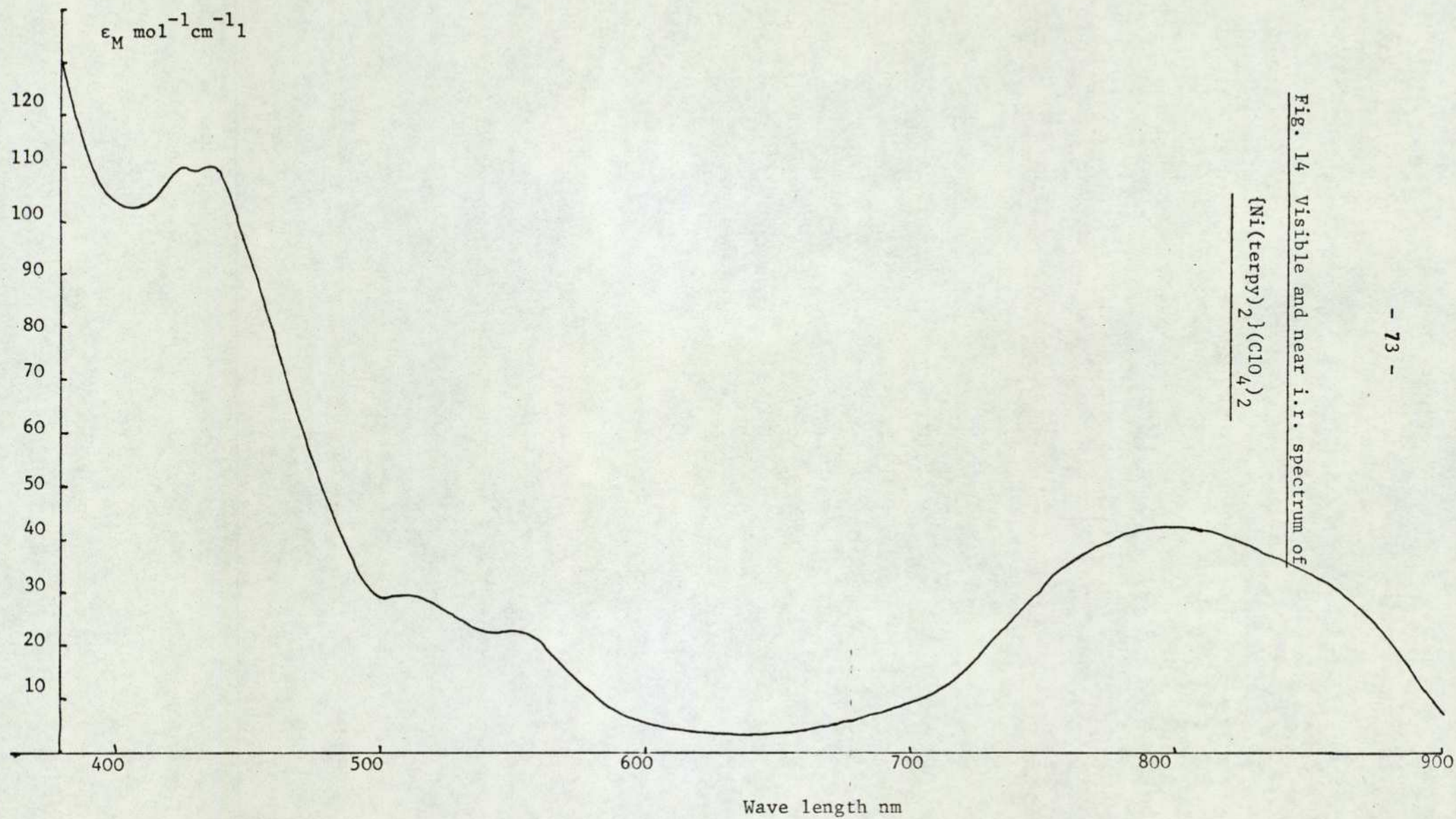
Fig. 13 Visible and near i.r. spectrum of
 $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_2$



Element	C	H	N	Ni
% Theoretical for above formula	49.77	3.04	11.61	8.10
% Found	49.58	3.19	11.60	8.20

Here the agreement between expected and observed figures is very good. In the visible and near infra-red region, absorption maxima at 22470cm^{-1} (centre of split band), 19600cm^{-1} (shoulder), 18180cm^{-1} (shoulder) and 12500cm^{-1} with extinction co-efficients $120\text{mol}^{-1}\text{cm}^{-1}$, $29\text{mol}^{-1}\text{cm}^{-1}$, $21\text{mol}^{-1}\text{cm}^{-1}$ and $42\text{mol}^{-1}\text{cm}^{-1}$ were found respectively (figure 14, page 73). The effective magnetic moment was found to be 3.1 B.M. at 20°C , again consistent with the presence of two unpaired electrons as expected for an octahedral d^8 configuration.

Fig. 14 Visible and near i.r. spectrum of
 $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_2$



4.2. Apparatus

4.2.1. Cyclic voltammeter

The cyclic voltammeter was supplied by Chemtrix Inc. of Beaverton, U.S.A. It comprised a storage oscilloscope, Type 564, incorporating a polarographic time base, Type 205, and a polarographic amplifier, Type 300. The time base provided sweep ranges of 0.5V, 1.0V or 2.0V which could be scanned at rates between 0.3V min^{-1} and 1.200V min^{-1} in either a single sweep or cyclic sweep mode. The direction of the forward sweep could be selected as either anodic or cathodic and the starting potential could be fixed at any value between $\pm 2.0\text{V}$ with respect to the reference electrode of the voltammetry cell. The amplifier provided current sensitivities varying from $0.01\mu\text{A}$ per division to $100\mu\text{A}$ per division on the 10 division graticule of the oscilloscope screen. Voltammograms could either be observed directly on the oscilloscope screen or, alternatively, the output from the amplifier could be fed to an external chart recorder.

In the present work, voltammograms were recorded using a "2700 Series" chart recorder supplied by Bryant Ltd., of Mitcham, Surrey. The time axis of the recorder was synchronised with the voltage sweep of the voltammeter and the chart speed was varied so that one large division on the time axis corresponded to a convenient fraction of the voltage sweep range; this facilitated the measurement of peak potentials. For the purpose of presenting cyclic voltammograms in this thesis, the current-time record was transferred into the normal current-potential curve by folding the

chart paper along a line perpendicular to the time axis corresponding to the switching potential. The reverse wave was then traced on the first half of the record. It was unfortunate that an X-Y recorder was not available which would have given cyclic voltammograms directly.

In setting up the initial potential and checking the sweep range of the instrument, a valve voltmeter, Model 87A, supplied by John Fluke of Seattle, Washington was used.

4.2.2. Potentiostat

The potentiostat was a Wenking, Model 68FR 0.5 instrument having an output of 100V at 100mA and supplied by Gerhard Bank Elektronik of West Germany. It had been specially designed for application in low conductivity electrochemical cells and was ideally suited to the present work. The working electrode in an electrolysis cell could be controlled to within 1mV at any selected potential in the range $\pm 10V$ with respect to the reference electrode, the response time to changes in cell current being of the order of $1\mu S$. The cell current was displayed on a meter having 9 current ranges ($\pm 0.1mA$ to $\pm 1.0A$ for full scale deflection).

Current-time curves were obtained by connecting a chart recorder (a "Speedomax W" model supplied by Leeds and Northrup, Birmingham) across a $0-10^4 \Omega$ decade box (Type RBBG supplied by the Croydon Precision Instrument Co., Croydon, Surrey) in series with the electrochemical cell. The value of the resistance was selected to give the required sensitivity.

4.2.3. Construction of electrochemical cells

All glassware was supplied by Quickfit and Quartz Ltd.

Voltammetry cell

The voltammetry cell is shown in figure 15, page 77.

It consisted of a flat-bottomed tube of 4.4cm in diameter and 12.0cm in length fitted with a B38/44 socket. At about 3cm from the base, connection was made, via a No. 4 sinter, to a smaller diameter tube having a B14/19 socket at the upper end into which the reference electrode could be inserted. A large PTFE stopper having two holes to hold the working and the counter electrodes was fitted into the neck of the main cell compartment.

Coulometry cell

The coulometer cell, shown in figure 16, page 78, had separate compartments for the working and counter electrodes. Each compartment was 4.4cm in diameter and about 11cm deep (capacity 40cm³) with B38/44 necks. The two compartments were connected to each other by a 15mm diameter tube fitted with No. 4 sintered discs at each end. The central compartment was filled via a glass tube containing a tap sealed into the top of the compartment, a similar tube allowing displaced air to be removed.

A pool of mercury formed the counter electrode, connection to which was made by a platinum wire sealed into the base of the compartment. The mercury was stirred by a paddle stirrer powered by a variable speed electric motor. The working electrode compartment was connected near its base through a No. 4 sinterd disc to a 12cm long, 2cm diameter tube having a B14/19 socket at its open end into which the reference electrode could be inserted. The

Fig. 15 Voltammetry Cell

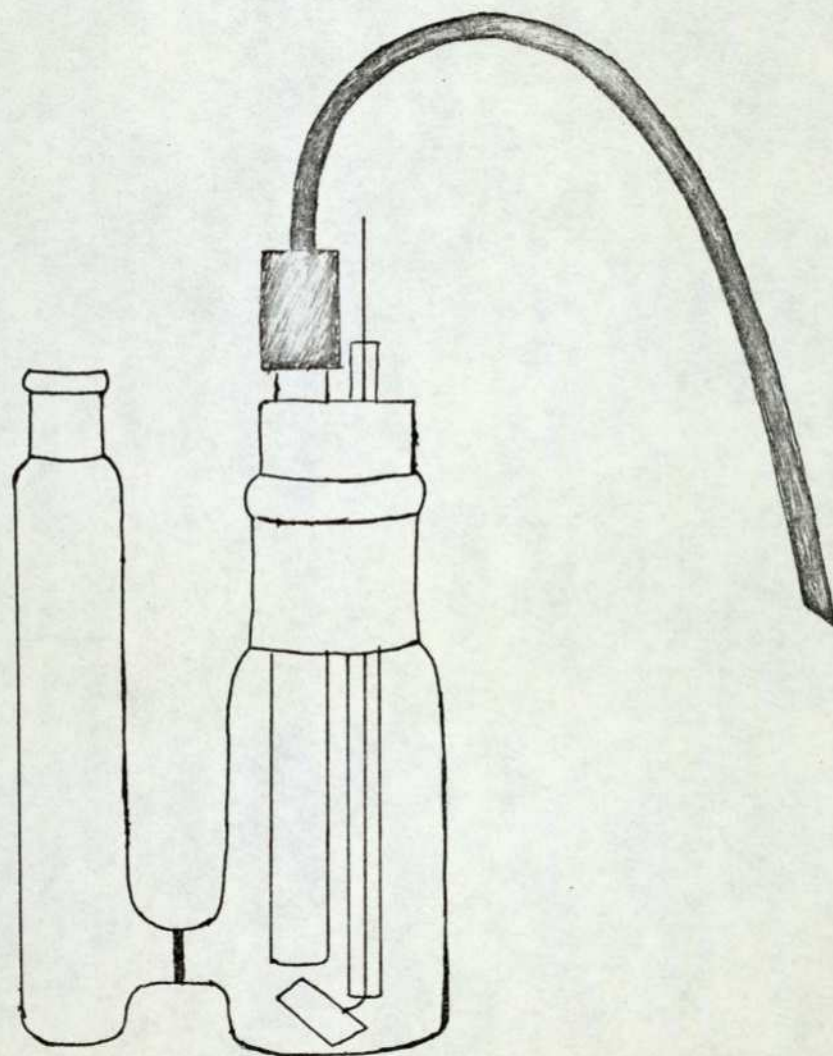
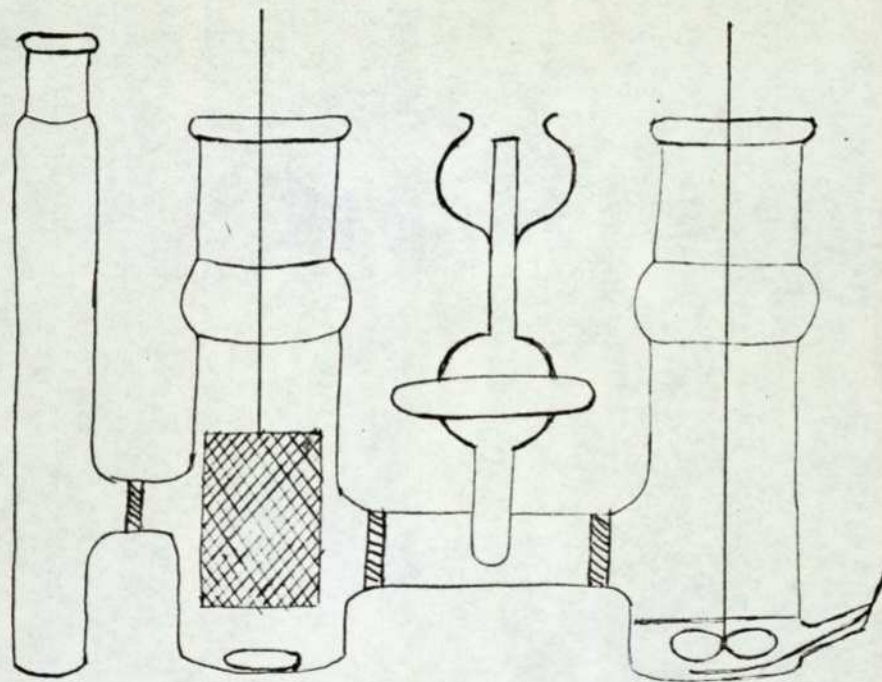


Fig. 16 Coulometry Cell



working electrode was held in a PTFE stopper and the solution in the compartment was stirred by a magnetic stirring bar.

Method of cleaning electrochemical cells

The cells were first cleaned thoroughly using acetone; they were then air dried, filled with fuming nitric acid, and allowed to stand 48 hours. After washing with water, detergent solution and distilled water, the cells were finally rinsed with dry acetonitrile and dried at 140°C in a vacuum oven for about 10 hours and transferred quickly to a dry box.

4.2.4. Preparation of electrodes

Counter Electrode

It was constructed by welding a square of 26 S.W.G. gauge platinum foil, side 2.5cm, to a 4cm long piece of 22 S.W.G. gauge bright platinum wire which was sealed into the bottom of a 15cm long piece of soda-glass tubing of 6mm diameter. The other end of the platinum wire was welded to a 10cm long, 26 S.W.G. gauge copper wire, which was sealed into the top end of the tube.

Working electrode for voltammetry cell

The working electrode for use in the voltammetry cell was a platinum disc electrode of 0.5cm^2 area, supplied by Beckmann, U.S.A. It was cleaned in the following manner:

The electrode was first treated with aqua-regia for 15 minutes and with fuming nitric acid for 3 hours. It was then suspended in a solution of 0.2M iron(II) sulphate in 0.3M sulphuric acid solution for 2 hours to remove any oxide coating. After washing thoroughly with distilled water, the electrode was

anodised at a current of about 100mA. After washing the electrode thoroughly with twice-distilled water and finally with acetonitrile several times, it was dried in a vacuum oven at about 50°C for 4-5 hours and stored in the dry box.

Working electrode for coulometry cell

This electrode was a cylindrical mesh platinum electrode (4.5cm in length and 2.5cm in diameter) supplied by Johnson and Mathey, London. After an initial soak for 48 hours in dilute sulphuric acid, the electrode was cleaned in the same way as the working electrode used in the voltammetry cell.

The silver/silver nitrate reference electrode

The reference electrode was constructed by the method given below by Kratochvil et al.²⁷⁵

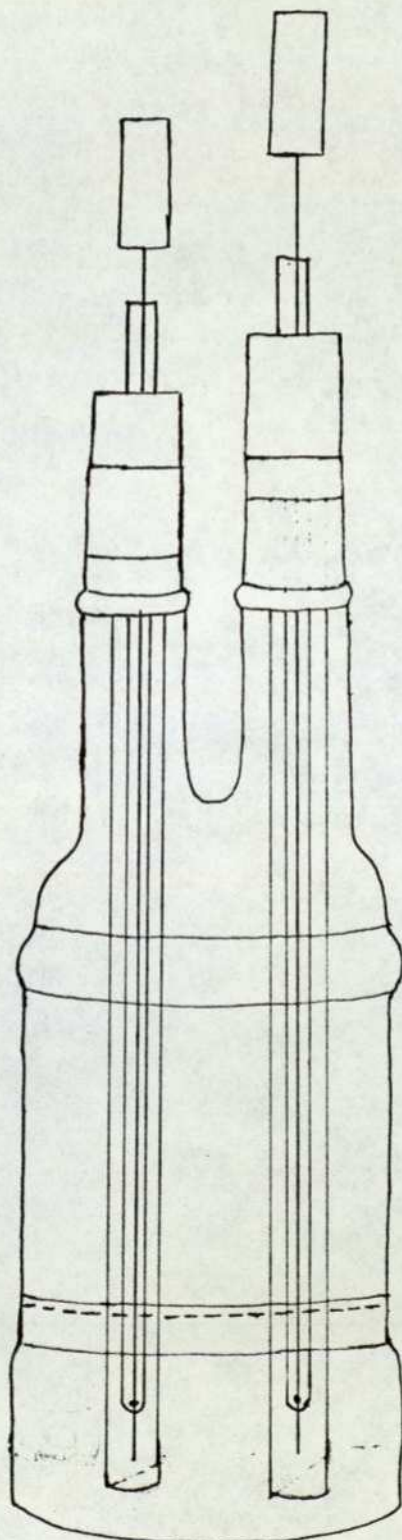
A 4cm long piece of 22 S.W.G. gauge bright platinum wire was first welded to a piece of 22 S.W.G. copper wire 25cm in length. The platinum wire was then sealed into the end of a 15cm long piece of soda-glass tube of 6mm diameter, so that about 1cm of the platinum wire protruded from the seal. In preparing the reference electrode, the platinum wire was first cleaned by treatment with aqua-regia for 15 minutes, followed by immersion in boiling concentrated nitric acid for about 3 hours. The platinum was then washed well with distilled water, anodised in fresh concentrated nitric acid solution for 20 minutes at a current of about 150mA and finally washed with twice-distilled water. The clean platinum electrode was then silvered by making it the cathode in a cell containing silver cyanide complex as the electrolyte and passing a current of 7mA for an hour. (The silver cyanide solution was made up by

dissolving 1.69g silver nitrate (Analytical Reagent grade) in 100cm³ de-ionised water, adding 1.3g of potassium cyanide (Analytical Reagent grade) and stirring until a clear solution was obtained).

The silvered electrode was soaked in twice-distilled water for two days, dried in a vacuum oven at about 50°C for 4-5 hours and transferred to a dry box where the reference electrode (figure 17, page 82) was assembled.

The silver electrode was held by means of a PTFE stopper inside a piece of glass tube of 1cm diameter, and 10cm length, having a B14/19 cone at the top end and a section of a No. 4 sintered disc sealed into the bottom end. The tube was filled with a solution containing silver nitrate(0.01M), and tetra-n-butylammonium perchlorate (0.1M) in purified acetonitrile. The reference electrode, when not in use, was stored in a holder of the type shown in figure 17, page 82, which comprised of two B14/19 sockets sealed into the top of a B55/44 cone fitting into the top of a jar of about 150cm³ capacity containing the same silver nitrate solution as used for the reference electrode. Two reference electrodes, one of which was used in the electrochemical experiments, the other being used only to check the condition of the first electrode were stored in the same holder. When the potential difference between the used electrode and the control electrode exceeded 5mV, the used electrode was judged to be no longer satisfactory and a fresh electrode was prepared.

Fig. 17 The Silver/Silver Nitrate Reference Electrode Cell



4.2.5. Spectrophotometers

U.V., visible and near infra-red spectra were recorded using a spectrophotometer Model EPS-3T supplied by Hitachi Perkin-Elmer.

Infra-red spectra were recorded using Model "Infracord" and Model "1457" spectrophotometers supplied by Perkin-Elmer.

An atomic absorption spectrophotometer Model 290B supplied by Perkin-Elmer was used to determine iron, cobalt and nickel in polypyridyl complexes.

4.2.6. Gouy balance

The Gouy balance consisted of a Stanton Model SM12 semi-micro balance from the left hand pan of which was suspended, by means of a nylon thread, a stoppered specimen tube, 10cm long, and of internal diameter 2mm. The tube was held by an aluminum collar hanging from a copper hook tied to the lower end of the suspension thread. A permanent magnet of field strength 5,000 gauss could be positioned so that the bottom of the specimen tube was at the centre of the 2cm gap between the 4cm diameter pole pieces. The suspension thread and specimen tube were surrounded by a glass sheath to exclude draughts.

4.3. Experimental procedures in voltammetry, coulometry and preparative scale constant potential electrolysis

All the weighings and operations involved in making up the solutions of known concentrations were carried out inside the dry box under an atmosphere of dry nitrogen.

4.3.1. Setting up the voltammetry cell

The supporting electrolyte solution, 0.1M tetra-n-butylammonium perchlorate in acetonitrile, was made-up by dissolving the calculated amount of the salt in purified, anhydrous acetonitrile and making up to 250.0cm³. 50cm³ of this solution was transferred by a pipette to the main compartment of the voltammetry cell illustrated in figure 15, page 77. The reference electrode compartment was filled with the same solution until the level was about 3-4cm below that in the main compartment. The silver/silver nitrate reference electrode prepared as described in section 4.2.4., page 80, was then inserted. The volumes of the solutions in the reference cell and the reference cell compartment were such that when the cell assembly was complete the solution levels in these tubes and in the main compartment were the same. The position of the working electrode was finally adjusted so that its lower end was as close as possible to the sintered disc leading to the reference electrode compartment.

An accurately known weight of the complex under investigation was transferred into the main compartment. When the complex had completely dissolved, connections were made to the voltammeter and cyclic voltammograms were recorded for selected operating parameters (c.f. section 4.2.1., page 74).

4.3.2. Setting up the coulometry cell

About 40cm³ of the supporting electrolyte solution (prepared as described in the last section) was first added to each of the main cell compartments of the coulometry cell (figure 16, page 78). In electrochemical reduction experiments where metal(I) complexes which were very sensitive to molecular oxygen were produced, the supporting electrolyte solution was first de-gassed for a few minutes with dry nitrogen. The central compartment was then filled carefully so that all gas bubbles were expelled. About 5cm³ of clean dry mercury metal was added to the auxillary electrode compartment and the cylindrical platinum mesh electrode was positioned in the working electrode compartment which contained a magnetic stirring bar. The reference electrode was inserted into the reference electrode compartment in which the volume of supporting electrolyte was adjusted so that the final levels of the solutions in the two tubes were the same and equal to that in the main compartments.

An accurately known weight of the complex under investigation was added to the working electrode compartment and the speeds of the magnetic and paddle stirrers were adjusted to the required rates. When the complex had completely dissolved, connections were made to the potentiostat and the solution was electrolysed at the chosen fixed potential. The current sensitivity of the chart recorder was selected so that the initial current gave a large deflection; when the current had decreased to less than 10% of its initial value, the sensitivity was increased by a factor of 10X and the electrolysis was continued until the current corresponded to less than 1% of the

initial value. Again the sensitivity was increased and the electrolysis was stopped when the current had dropped to at least 0.1% of the initial value. The three sections of the current-time curve were cut out and weighed separately, correction being made for residual current. The area of each section was determined by comparing its weight with that of a known area of the same chart paper. Since the number of coulombs corresponding to unit area of each section was known, the total number of coulombs passed during electrolysis could be calculated. The number of electrons transferred per molecule in the electrode reaction was then determined from the following relationship:

$$n = \frac{Q \cdot M}{F \cdot W}$$

where

n = number of electrons transferred per molecule,

Q = quantity of the electricity consumed by the process (coulombs),

M = molecular weight of the complex under investigation,

F = the Faraday (96,493 coulombs),

W = the weight of complex (g).

4.3.3. Controlled potential electrolysis on a preparative scale

The cell used for coulometric studies (figure 16, page 78) was also used for preparative scale electrolyses and was set up in the same way as described above. Since larger quantities of the complex were involved, the time required for completion of each electrolysis was much greater than in coulometric experiments. Although a record of the variation of current with time was not required for

preparative experiments, the chart recorder was kept in the circuit, running at a very slow speed (30 inches hour⁻¹), so that the approach of complete electrolysis could be easily ascertained. After electrolysis, the solution in the working electrode compartment was transferred by pipette to a 250cm³ round-bottomed stoppered flask for storage and subsequent isolation.

In the preparation of metal(I) complexes where the products were extremely soluble in acetonitrile and could not be readily isolated from the supporting electrolyte, a different procedure was sometimes adopted. Tetra-n-butylammonium perchlorate was omitted from the cell solutions; instead, a correspondingly larger quantity of the metal(II) complex, which then acted as its own supporting electrolyte, was used. This method had the great disadvantage that the amount of metal(II) complex required was so large (~5g) that it could not be used on the grounds of excessive cost when the ligand involved was expensive.

Methods of product isolation

The following methods of isolation were used. Method A was attempted in cases where (n-Bu)₄NClO₄ was present as the supporting electrolyte. Method B was used when tetra-n-butylammonium perchlorate was absent.

Method A

The stopper of the flask containing the electrolysed solution was replaced by an adapter, incorporating a vacuum tap, for connection to a vacuum line. The sealed flask was then removed from the dry box, attached to the line, and the solution evaporated under reduced pressure until the product started to crystallise.

After disconnecting from the line, the flask was returned to the dry box and the product was collected on a No. 4 sintered filter stick closed by a guard tube packed with phosphorus pentoxide.

In the attempted isolation of the oxygen sensitive metal(I) complexes by this method, the guard tube was replaced by a cone and tap which was connected via a phosphorus pentoxide trap to a cylinder of white spot nitrogen used to maintain an oxygen-free atmosphere in the filter stick. The crystals were washed three times with 5cm³ portions of anhydrous, purified acetonitrile to remove any trace of supporting electrolyte. The product was then sucked dry for about an hour to remove any traces of water and finally transferred to a dry sample tube which was sealed and stored over phosphorus pentoxide in a desiccator.

Method B

This method was used in the attempted isolation of metal(I) complexes only. All operations were carried out in the dry box.

Air-free anhydrous diethyl ether was added to the product solution in the flask until the product precipitated. It was then filtered through a No. 4 sintered filter stick closed by a tap connected to the dry oxygen-free nitrogen supply described above. After washing twice with air-free, anhydrous acetonitrile and sucking dry under reduced pressure for 2-3 hours the product was collected in a sealed tube and stored in the same way as described in Method A.

4.4. Experimental procedures in spectral and magnetic studies

4.4.1. Determination of visible and infra-red spectra

Solutions for the determination of visible and near infra-red spectra were prepared and transferred to the optical cells in the dry box under an atmosphere of nitrogen. The lids of the cells were sealed with "Sellotape". In cases where a wide variation in peak absorptions was observed it was necessary to use cells of different length and/or different concentrations of complex to obtain satisfactory spectra. For this reason, visible and near infra-red spectra are presented as plots of molar extinction co-efficient versus wavelength.

The preparation of "Nujol" mulls and the assembly of infra-red cells was also carried out in the dry box.

4.4.2. Magnetic susceptibility determinations

Mercuric tetracyanato cobaltate(II) was used to calibrate the Gouy tube. The filling of the stoppered tube with a polypyridyl complex was carried out in the dry box. In the calculation of the effective magnetic moment of the metal ion,²⁷⁶ diamagnetic corrections for the ligand molecules were made using the molar susceptibility data given by Figgis and Lewis.²⁶²

4.5. Oxidising and reducing properties of polypyridyl complexes

4.5.1. Oxidising property of a metal(III) polypyridyl complex

The complex under investigation was dissolved in a small amount of pure acetonitrile free from any reducible and oxidisable impurities. It was added to an aqueous iodide solution containing a very small amount of starch. The development of a deep blue colour indicated the oxidation of iodide to iodine.

4.5.2. Reducing property of a metal(I) polypyridyl complex

The apparatus required for this test was constructed by connecting two tubes to each other by a tap, the open ends of the tubes being fitted with stoppers. A solution of the complex in pure acetonitrile was transferred to one of the tubes in the dry box. The apparatus was brought out of the dry box and 20cm³ of a solution of dilute sulphuric acid containing 1mg potassium dichromate and sodium diphenylamine sulphonate indicator was transferred to the second compartment. The violet coloured solution was de-aerated for about 5 minutes using oxygen-free nitrogen and the compartment was closed with a stopper. The complex solution was then added to the dichromate solution dropwise by opening the tap. Disappearance of the intense violet colour indicated the reduction of the dichromate ion.

4.6. Analytical determinations

4.6.1. C, H and N analysis

Carbon, hydrogen and nitrogen determinations were carried out by the National Physical Laboratory, Teddington, Middlesex. Samples for analysis were capsulated in aluminum capsules in the dry box. The analyses were performed using a Perkin-Elmer 240 autoanalyser.

4.6.2. Fe, Co and Ni analysis

Classical methods were used to determine the metallic elements in hexakis(acetonitrile) metal(II) perchlorate complexes, large amounts of the complexes being available. Iron(II) was determined by titrating the acidified complex solution with standard potassium permanganate solution. Cobalt and nickel were determined using electrogravimetric methods.

The metallic element contents of polypyridyl complexes, of which only small amounts were available, were determined using atomic absorption spectrophotometry.

Iron in $\{\text{Fe}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$

An accurate weight of the sample (about 100mg) was transferred to a 100cm³ conical flask and dissolved in about 20cm³ of a solution of 0.1M sulphuric acid. It was titrated against standardised 0.002M potassium permanganate solution. The end point was reached when one drop of the titrant gave a permanent pink colouration.

Iron in polypyridyl complexes of iron(I), iron(II) and iron(III) perchlorate

About 20mg of the sample was accurately weighed on a

micro-analytical balance and transferred to a 200cm^3 beaker. The sample was dissolved in about 5cm^3 of acetonitrile. 2cm^3 of 71% perchloric acid (atomic absorption grade, supplied by Hopkin and Williams, Chadwell Heath, Essex) was added slowly. The solution was simmered for about 10 minutes to evaporate the acetonitrile and break down the ligand. The cooled solution was diluted to 50.00cm^3 in a grade 'A' measuring flask. A standard iron solution was prepared by following the above procedure but starting with the requisite amounts of iron(II) ammonium sulphate (Analytical Reagent grade) to give a solution of about 100 p.p.m. iron. Solutions in the range 2 p.p.m. to 10 p.p.m. were prepared by dilution. A blank solution was similarly prepared, but without the addition of the iron(II) salt.

Standard solutions and the sample solution were fed in turn into the air/acetylene flame of the atomic absorption spectrophotometer (slit width 0.2nm) and the absorption of each solution at 248.3nm (iron resonance line) was measured against the blank solution. The concentration of iron was interpolated from the calibration curve.

Cobalt in $\{\text{Co}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$

About 100mg of the complex was accurately weighed on a micro-analytical balance and transferred to a 200cm^3 beaker. About 2cm^3 of concentrated sulphuric acid (Analytical Reagent grade) were added. The solution was simmered for about 15 minutes to remove acetonitrile. 3g of ammonium sulphate and 35cm^3 of concentrated ammonium solution were added and the solution was diluted to about 120cm^3 with distilled water. The addition of about 0.2g of hydrazine sulphate to the solution prevented any deposition of cobalt oxide

at the anode during the subsequent electrolysis.

The solution was electrolysed by immersing two concentric cylindrical rhodium plated electrodes in the solution and passing a current of 1A for 2 hours, using the "Electrolytic Analysis Apparatus", supplied by Baird and Tatlock, Chadwell Heath, Essex. The weight of cobalt in the sample was determined by weighing the cathode before and after the electrolysis. Electrolysis was assumed to be complete when no pink or reddish colour was observed on evaporating about 5cm^3 of solution with about 15mg of phenyl thiohydantoic acid in a porcelain crucible.

Cobalt in polypyridyl complexes of cobalt(I), cobalt(II) and cobalt(III) perchlorate

The same procedure as for the determination of iron by spectrophotometry was used. Standard solutions of cobalt in the concentration range 2 p.p.m. to 10 p.p.m. were prepared using a standard 1000 p.p.m. cobalt solution supplied by Hopkin & Williams, Chadwell Heath, Essex. Absorption was determined at a wavelength of 240.7nm (cobalt resonance line) using a slit width of 0.2nm.

Nickel in $\{\text{Ni}(\text{CH}_3\text{CN})_6\}(\text{ClO}_4)_2$

The determination of nickel in this complex was carried out using the electrogravimetric method described for cobalt. In this case of nickel, however, no hydrazine sulphate was added to the solution before electrolysis.

Electrolysis was assumed to be complete when no pink colour was observed on the addition of a small volume of a solution of dimethylglyoxime was added to about 5cm^3 of the electrolysed solution.

Nickel in polypyridyl complexes of nickel(I), nickel(II) and nickel(III) perchlorates

The same procedure as for the determination of iron and cobalt in polypyridyl complexes by atomic absorption was used. Standard solutions in the range 2 p.p.m. to 10 p.p.m. nickel were prepared using a standard 1000 p.p.m. nickel solution supplied by Hopkin & Williams, Chadwell Heath, Essex. The wavelength selected was 230.0nm (resonance line for nickel) and the slit width was 0.2nm.

5. RESULTS AND DISCUSSION

All potentials quoted in this section are relative to the standard electrode, Ag/AgNO_3 (0.01M), $0.1\text{M}(\text{n-Bu})_4\text{NClO}_4$ in acetonitrile, unless otherwise stated.

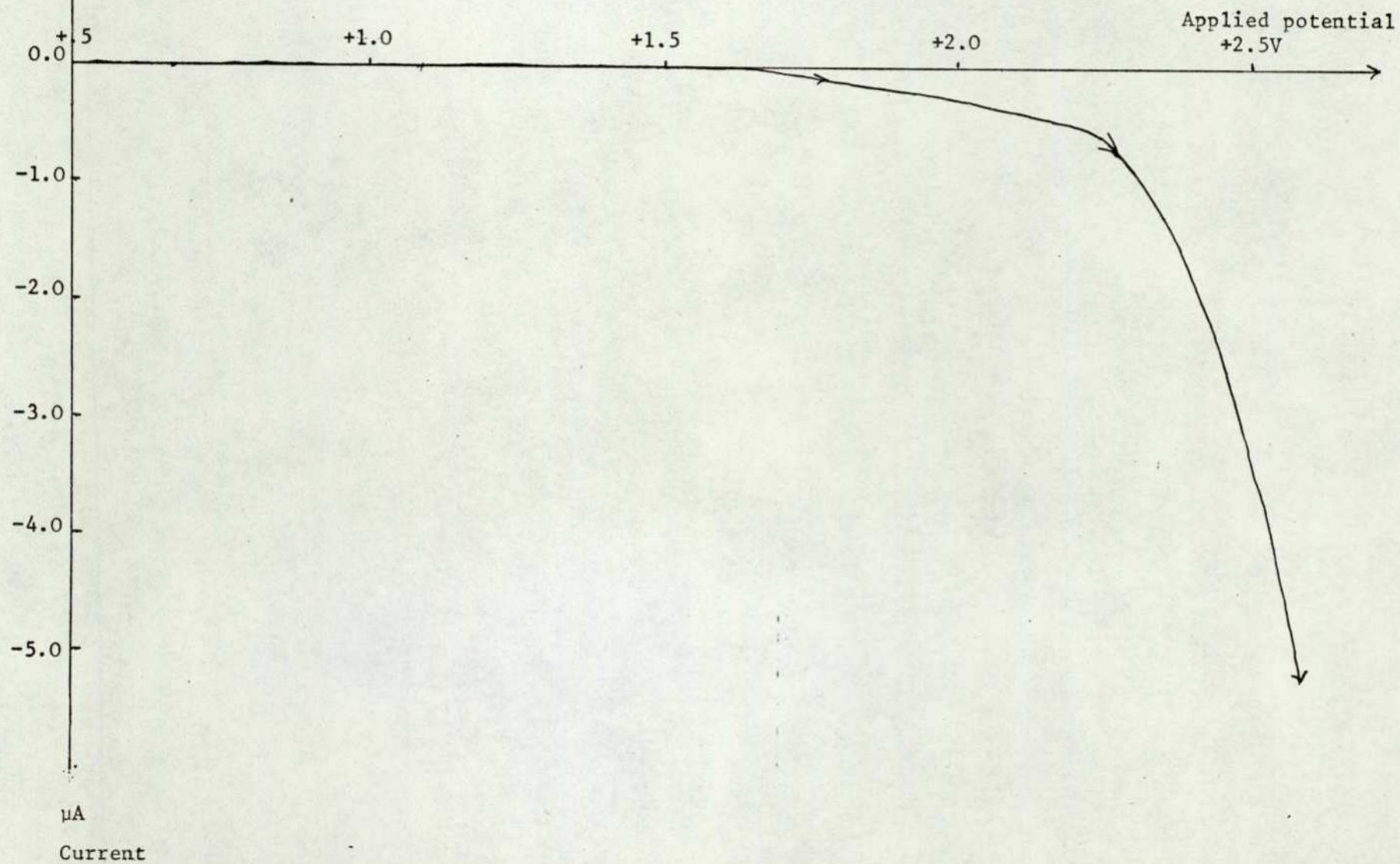
5.1. Oxidation and reduction limits of supporting electrolyte

The cyclic voltammogram of a 0.1M solution of tetra-n-butylammonium perchlorate for an anodic single sweep range of +0.50V to 2.50V at a scan-rate of 0.2V sec^{-1} is shown in figure 18, page 97. The anodic limit, defined according to the arbitrary definition of Lord and Rogers²⁹⁹ as the potential corresponding to an anodic current of $1\mu\text{A}$ was +2.25V. Similar voltammograms for 0.2M, 0.3M and 0.4M solutions of tetra-n-butylammonium perchlorate were found to be very similar to that of the 0.1M solution, the anodic limit being virtually unaffected by changes in the concentration of the supporting electrolyte in the range investigated.

The cyclic voltammogram of a 0.1M solution of tetra-n-butylammonium perchlorate for a cathodic sweep range of 0.0V to -3.0V at a scan-rate of 0.2V sec^{-1} was also observed. The cathodic limit of the solvent system (i.e. the potential corresponding to a cathodic current of $1\mu\text{A}$) was found to be more negative than -3.0V. As was the case for the anodic sweeps, no changes in the voltammograms were observed when higher concentrations of supporting electrolyte (0.2M, 0.3M and 0.4M) were used.

Acetonitrile, first produced on a commercial scale in 1952 is now established as a noble solvent for voltammetric studies,

Fig. 18 Cyclic Voltammogram (Forward single anodic sweep) of tetra-n-butylammonium perchlorate

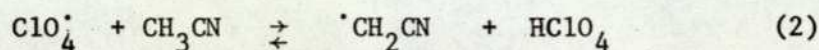
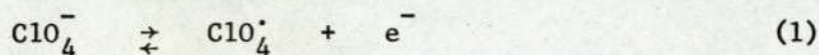


being a weaker base²⁷⁷⁻²⁸³ and much weaker acid^{284,285} than water. The main advantage of this solvent is that it has a much greater range than water, Kolthoff and Coetzee²⁴⁹ reported the range to be from +1.8V to -1.5V versus the saturated calomel electrode at a rotating platinum micro-electrode and from +0.6V to -2.8V at a dropping mercury electrode, using tetraethylammonium perchlorate as the supporting electrolyte. Olson and Vasilveskis²⁸⁶ reported the range as +0.3V to -3.2V at a dropping mercury electrode and +2.0V to -2.5V at a spherical platinum electrode (versus the $\text{Ag}/10^{-2}\text{M AgNO}_3$ electrode) in the presence of 0.2M tetraethylammonium perchlorate. These values compare with the range of +2.25V to -3.0V at a stationary platinum disc electrode as determined in the present work. In addition to its great resistance to reduction and oxidation, acetonitrile has other properties which makes it most suitable as a non-aqueous solvent medium. Its dielectric constant (38 at 25°C) is high enough to permit the strong electrolyte behaviour of salts such as quaternary ammonium perchlorate. The liquid range of the solvent (-45.7°C to 81.6°C) makes it suitable for room temperature solution studies and permits kinetic studies to be made over an adequate range of temperature. The low viscosity of acetonitrile (3.39 mpoise at 25°C) enables analytical operations such as filtration and centrifugation to be carried out without difficulty.

Attempts to improve the anodic limit of acetonitrile systems by changing the nature of the electrolyte have not been successful. The use of tetra-n-butylammonium tetrafluoroborate and tetra-n-butylammonium hexafluorophosphate to replace tetra-n-butylammonium

perchlorate has not been found to give any significant increase in the anodic limit,^{1,286} although this has been claimed by Osa et al.²⁸⁷ and by Fleischmann and Pletcher.²⁸⁸ A disadvantage of using quaternary ammonium tetrafluoroborate and hexafluorophosphate is that the presence of water even at the concentration of 150 p.p.m. gives high residual currents at potentials well within the normal anodic limit resulting in the formation of carbon dioxide, acetamide and methanol.²³⁸

Studies of the reactions occurring at the limiting potentials of quaternary ammonium perchlorates in acetonitrile have been mainly concerned with the oxidation of the solvent system. The following mechanism for reactions taking place at the anodic limit, involving the oxidation of the perchlorate ion as the first step, has been put forward by Schmidt and Noak:²⁸⁹



The work of Billion^{290,291} supports the above mechanism. Billion^{290,291} described a method for the coulometric determination of organic bases in which the bases were neutralised by hydrogen ions generated in step (2) by the anodic oxidation of solutions of anhydrous lithium perchlorate in acetonitrile. This disputed the claim of Streulli,^{292,293} also employing a coulometric technique

but using lithium perchlorate trihydrate, that the generation of hydrogen ions arose from the oxidation of water according to the reaction: $2\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$. Maki and Geske²⁹⁴ have provided further evidence for this mechanism from e.s.r. studies; a hyperfine structure of four equally spaced lines of equal intensity was observed which was interpreted as due to the perchlorate radical. The first step of the mechanism has been universally accepted. However, the second step is disputed by Koyama et al.,²⁹⁵ who detected small amounts of chloride ion but were unable to detect the presence of succinonitrile after prolonged electrolysis of acetonitrile solutions containing perchlorate salts. Russell²⁹⁶ supports Koyama et al.²⁹⁵ and suggests that the second step in the reaction mechanism is the chemical oxidative attack of perchlorate radicals on the solvent, a fraction of perchlorate radicals being reduced to chloride ion, the formation of which has been reported by other workers.^{295,297}

Although the reaction mechanism involving the oxidation of the perchlorate ion in acetonitrile at a platinum anode is not yet fully understood, the suitability of quaternary ammonium perchlorates as supporting electrolytes is not in question since the reaction only interferes at potentials above the anodic limit.

A further advantage of using a quaternary ammonium perchlorate as an electrolyte is that when a platinum electrode is used as the anode, the platinum is anodised by the perchlorate reaction. This is an effective method of cleaning the electrode (although some dissolution of the platinum can be expected²⁹⁸) and so provides a reproducible electrode surface.

5.2. Cyclic voltammetry of polypyridyl complexes of iron(II), cobalt(II) and nickel(II) perchlorates

The characteristics of cyclic voltammograms of solutions of polypyridyl complexes of iron(II), cobalt(II) and nickel(II) perchlorate of the type $\{ML_3\}(ClO_4)_2$ (L = bipy, dimbipy) and $\{ML_2\}(ClO_4)_2$ (L = terpy) in the presence of 0.1M tetra-n-butylammonium perchlorate as supporting electrolyte are given in Tables I to VI, pages 102 to 113. Tables I to III give data for cyclic voltammograms obtained with anodic forward sweeps; Tables IV to VI refer to experiments in which forward cathodic sweeps were used. For each metal(II) complex system, data are given for voltammograms in which different concentrations of complex and different sweep rates were employed. Included in the Tables are values of the difference in forward and reverse peak potentials (c.f. equation 7, page 40). Figures 19 to 36 give representative cyclic voltammograms for each system studied for both anodic and cathodic forward sweep conditions.

For a particular concentration of electroactive species and a given scan rate, the reproducibility of the peak potentials of any cyclic voltammogram was about $\pm 5mV$ and forward sweep peak currents could be determined with a reproducibility of $\pm 5\%$. The reverse wave peak currents were less reproducible (about $\pm 5-10\%$) because of the difficulty of fixing the reference current level at the start of the reverse wave; this should be taken as the steady current which develops after the forward peak has been past. In some instances, however, the sweep direction was changed before this steady current had time to develop fully and the steady current had

continued on page 132

Table I

Anodic forward sweep cyclic voltammetry of polypyridyl complexes of iron(II) perchlorate

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipa	ipc	Epa	Epc		
			(μ A)	(μ A)	V	V		
Fe(bipy) ₃ ²⁺	0.4	0.1	21	20	+0.795	+0.711	84	+0.767
	0.8	0.1	45	45	+0.804	+0.723	81	+0.776
	1.2	0.1	63	65	+0.801	+0.721	80	+0.773
	1.6	0.1	85	90	+0.798	+0.711	87	+0.770
	2.0	0.1	105	95	+0.795	+0.711	84	+0.767
	2.0	0.01	31	30	+0.790	+0.729	61	+0.762
	2.0	0.1	100	105	+0.794	+0.711	83	+0.766
	2.0	0.5	220	230	+0.810	+0.714	96	+0.782
Fe(dimbipy) ₃ ²⁺	0.4	0.1	18	18	+0.643	+0.592	51	+0.615
	0.8	0.1	37	40	+0.648	+0.592	56	+0.620
	1.2	0.1	55	55	+0.648	+0.590	58	+0.620
	1.6	0.1	70	75	+0.649	+0.592	57	+0.621

cont/d ...

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipa	ipc	Epa	Epc		
			(μA)	(μA)	V	V		
Fe(dimbipy) ₃ ²⁺	2.0	0.1	92	95	+0.650	+0.594	56	+0.622
	2.0.	0.01	30	30	+0.651	+0.591	60	+0.623
	2.0	0.1	95	100	+0.649	+0.592	58	+0.621
	2.0	0.5	210	200	+0.653	+0.590	63	+0.625
Fe(terpy) ₂ ²⁺	0.4	0.1	26	26	+0.328	+0.270	58	+0.300
	0.8	0.1	53	50	+0.327	+0.273	54	+0.299
	1.2	0.1	76	80	+0.329	+0.270	59	+0.301
	1.6	0.1	102	100	+0.327	+0.272	55	+0.299
	2.0	0.1	125	120	+0.327	+0.273	54	+0.299
	2.0	0.01	40	38	+0.331	+0.271	60	+0.303
	2.0	0.1	120	125	+0.327	+0.273	54	+0.299
	2.0	0.5	280	290	+0.324	+0.273	51	+0.296

Table II

Anodic forward sweep cyclic voltammetry of polypyridyl complexes of cobalt(II) perchlorate

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipa	ipc	Epa	Epc		
			(μ A)	(μ A)	V	V		
Co(bipy) ₃ ²⁺	0.4	0.1	31	30	+0.016	-0.047	63	-0.012
	0.8	0.1	61	60	+0.018	-0.048	66	-0.010
	1.2	0.1	88	90	+0.019	-0.047	66	-0.009
	1.6	0.1	120	125	+0.016	-0.048	64	-0.012
	2.0	0.1	155	160	+0.016	-0.047	63	-0.012
	2.0	0.01	56	55	+0.012	-0.046	58	-0.016
	2.0	0.1	155	160	+0.017	-0.047	64	-0.011
	2.0	0.5	350	330	+0.020	-0.049	69	-0.008
Co(dimbipy) ₃ ²⁺	0.4	0.1	30	28	-0.094	-0.159	65	-0.122
	0.8	0.1	55	53	-0.095	-0.160	65	-0.123
	1.2	0.1	82	85	-0.095	-0.159	64	-0.123

cont/d ...

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		E _{pa} -E _{pc} mV	E _{1/2} V
			ipa	ipc	E _{pa}	E _{pc}		
			(μA)	(μA)	V	V		
Co(dimbipy) ₃ ²⁺	1.6	0.1	105	100	-0.098	-0.159	61	-0.126
	2.0	0.1	135	140	-0.100	-0.163	63	-0.128
	2.0	0.01	43	45	-0.100	-0.159	59	-0.128
	2.0	0.1	140	135	-0.102	-0.159	57	-0.130
	2.0	0.5	310	320	-0.092	-0.157	64	-0.120
Co(terpy) ₂ ²⁺	2.0	0.01	32	30	+0.015	-0.047	62	-0.013
	2.0	0.1	102	98	+0.010	-0.050	60	-0.018
	2.0	0.5	230	220	+0.009	-0.047	56	-0.019

Table III

Anodic forward sweep cyclic voltammetry of polypyridyl complexes of nickel(II) perchlorate

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipa	ipc	Epa	Epc		
			(μ A)	(μ A)	V	V		
Ni(bipy) ₃ ²⁺	0.4	0.05	19	20	+1.483	+1.385	98	+1.455
	0.8	0.05	35	33	+1.480	+1.385	95	+1.452
	1.2	0.05	55	52	+1.482	+1.390	92	+1.454
	1.6	0.05	75	70	+1.483	+1.385	98	+1.455
	2.0	0.05	90	90	+1.483	+1.389	94	+1.455
	2.0	0.005	28	27	+1.483	+1.423	60	+1.455
	2.0	0.05	95	90	+1.480	+1.385	98	+1.452
	2.0	0.25	210	200	+1.489	+1.374	115	+1.461
Ni(dimbipy) ₃ ²⁺	0.4	0.05	20	20	+1.375	+1.280	95	+1.337
	0.8	0.05	39	38	+1.375	+1.289	86	+1.337
	1.2	0.05	58	60	+1.374	+1.285	89	+1.336

cont/d ...

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		E _{pa} -E _{pc} mV	E _{1/2} V
			ipa	ipc	E _{pa}	E _{pc}		
			(μA)	(μA)	V	V		
Ni(dimbipy) ₃ ²⁺	1.6	0.05	80	75	+1.375	+1.289	86	+1.337
	2.0	0.05	98	105	+1.375	+1.289	86	+1.337
	2.0	0.005	27	28	+1.375	+1.316	59	+1.337
	2.0	0.05	96	102	+1.375	+1.284	91	+1.337
	2.0	0.25	190	180	+1.375	+1.274	101	+1.337
Ni(terpy) ₂ ²⁺	0.4	0.05	17	19	+1.400	+1.305	95	+1.372
	0.8	0.05	35	37	+1.398	+1.306	92	+1.370
	1.2	0.05	53	50	+1.402	+1.300	102	+1.374
	1.6	0.05	68	65	+1.398	+1.300	98	+1.370
	2.0	0.05	80	85	+1.402	+1.301	101	+1.374
	2.0	0.005	24	23	+1.400	+1.332	68	+1.372
	2.0	0.05	76	80	+1.403	+1.300	103	+1.375
	2.0	0.25	170	165	+1.412	+1.294	118	+1.384

Table IV

Cathodic forward sweep cyclic voltammetry of polypyridyl complexes of iron(II) perchlorate

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipc	ipa	Epc	Epa		
			(μ A)	(μ A)	V	V		
Fe(bipy) ₃ ²⁺	0.4	0.05	13	12	-1.719	-1.658	61	-1.691
	0.8	0.05	25	27	-1.718	-1.653	65	-1.690
	1.2	0.05	39	36	-1.718	-1.657	61	-1.690
	1.6	0.05	52	55	-1.720	-1.658	62	-1.692
	2.0	0.05	65	60	-1.719	-1.658	61	-1.691
	2.0	0.005	21	20	-1.708	-1.650	58	-1.680
	2.0	0.05	63	65	-1.719	-1.658	61	-1.691
	2.0	0.25	150	145	-1.720	-1.657	63	-1.692
Fe(dimbipy) ₃ ²⁺	0.4	0.05	18	19	-1.659	-1.605	54	-1.631
	0.8	0.05	35	36	-1.658	-1.603	55	-1.630
	1.2	0.05	56	55	-1.659	-1.603	56	-1.631
	1.6	0.05	74	70	-1.658	-1.605	53	-1.630

cont/d ...

Complex	Concentration	Scan-rate	Peak currents		Peak potentials		Epa-Epc	E _{1/2}
	mM	V sec ⁻¹	ipc	ipa	Epc	Epa	mV	V
			(μA)	(μA)	V	V		
Fe(dimbipy) ₃ ²⁺	2.0	0.05	88	95	-1.659	-1.603	56	-1.631
	2.0	0.005	30	30	-1.657	-1.605	52	-1.629
	2.0	0.05	92	90	-1.660	-1.605	55	-1.632
	2.0	0.25	210	220	-1.659	-1.600	59	-1.631
Fe(terpy) ₂ ²⁺	0.4	0.05	14	15	-1.621	-1.558	63	-1.593
	0.8	0.05	28	27	-1.621	-1.559	62	-1.593
	1.2	0.05	41	38	-1.622	-1.558	64	-1.594
	1.6	0.05	53	55	-1.621	-1.559	62	-1.593
	2.0	0.05	65	70	-1.622	-1.561	61	-1.594
	2.0	0.005	21	20	-1.620	-1.559	61	-1.592
	2.0	0.05	63	60	-1.621	-1.553	68	-1.593
	2.0	0.25	145	155	-1.623	-1.554	69	-1.595

Table V

Cathodic forward sweep cyclic voltammetry of polypyridyl complexes of cobalt(II) perchlorate

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipc	ipa	Epc	Epa		
			(μ A)	(μ A)	V	V		
Co(bipy) ₃ ²⁺	0.4	0.05	13	13	-1.288	-1.221	67	-1.260
	0.8	0.05	25	25	-1.290	-1.223	67	-1.262
	1.2	0.05	43	40	-1.288	-1.220	68	-1.260
	1.6	0.05	52	55	-1.288	-1.221	67	-1.260
	2.0	0.05	65	70	-1.285	-1.221	64	-1.257
	2.0	0.005	23	23	-1.284	-1.216	58	-1.256
	2.0	0.05	74	70	-1.288	-1.221	67	-1.260
	2.0	0.25	165	170	-1.294	-1.222	77	-1.266
Co(dimbipy) ₃ ²⁺	0.4	0.1	35	35	-1.353	-1.290	63	-1.325
	0.8	0.1	66	65	-1.352	-1.290	62	-1.324
	1.2	0.1	100	105	-1.361	-1.295	66	-1.333
	1.6	0.1	130	125	-1.354	-1.287	67	-1.326

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipc	ipa	Epc	Epa		
			(μA)	(μA)	V	V		
Co(dimbipy) ₃ ²⁺	2.0	0.1	155	160	-1.353	-1.291	62	-1.325
	2.0	0.01	43	45	-1.361	-1.203	58	-1.333
	2.0	0.1	150	145	-1.353	-1.290	63	-1.325
	2.0	0.5	330	350	-1.350	-1.284	66	-1.322
Co(terpy) ₂ ²⁺	2.0	0.01	48	50	-1.064	-1.008	56	-1.036
	2.0	0.1	155	150	-1.068	-1.011	57	-1.040
	2.0	0.5	340	350	-1.071	-1.013	58	-1.043

Table VI

Cathodic forward sweep cyclic voltammetry of polypyridyl complexes of nickel(II) perchlorate

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipc	ipa	Epc	Epa		
			(μA)	(μA)	V	V		
Ni(bipy) ₃ ²⁺	0.25	0.1	20	20	-1.576	-1.495	81	-1.548
	0.49	0.1	47	50	-1.575	-1.495	80	-1.547
	1.23	0.1	115	120	-1.576	-1.495	81	-1.548
	1.23	0.01	34	35	-1.578	-1.520	58	-1.550
	1.23	0.1	120	125	-1.576	-1.548	81	-1.548
	1.23	0.5	270	280	-1.581	-1.470	111	-1.550
	2.68	0.1	250	245	-1.578	-1.508	70	-1.550
Ni(dimbipy) ₃ ²⁺	0.4	0.05	24	25	-1.416	-1.359	57	-1.388
	0.8	0.05	52	50	-1.416	-1.360	56	-1.388
	1.2	0.05	70	75	-1.418	-1.360	58	-1.390
	1.6	0.05	105	100	-1.416	-1.360	56	-1.388
	2.0	0.05	110	115	-1.416	-1.360	56	-1.388

cont/d ...

Complex	Concentration mM	Scan-rate V sec ⁻¹	Peak currents		Peak potentials		Epa-Epc mV	E _{1/2} V
			ipc	ipa	Epc	Epa		
			(μA)	(μA)	V	V		
Ni(dimbipy) ₃ ²⁺	2.0	0.005	43	40	-1.416	-1.359	57	-1.388
	2.0	0.05	115	110	-1.428	-1.368	60	-1.400
	2.0	0.25	270	280	-1.428	-1.351	77	-1.400
Ni(terpy) ₂ ²⁺	3.8	0.005	44	45	-1.558	-1.499	59	-1.530
	3.8	0.05	145	140	-1.558	-1.501	57	-1.530
	3.8	0.25	360	375	-1.560	-1.500	60	-1.532

Fig. 19 Cyclic voltammogram (forward anodic sweep) of tris(2,2'-bipyridyl) iron(II) perchlorate

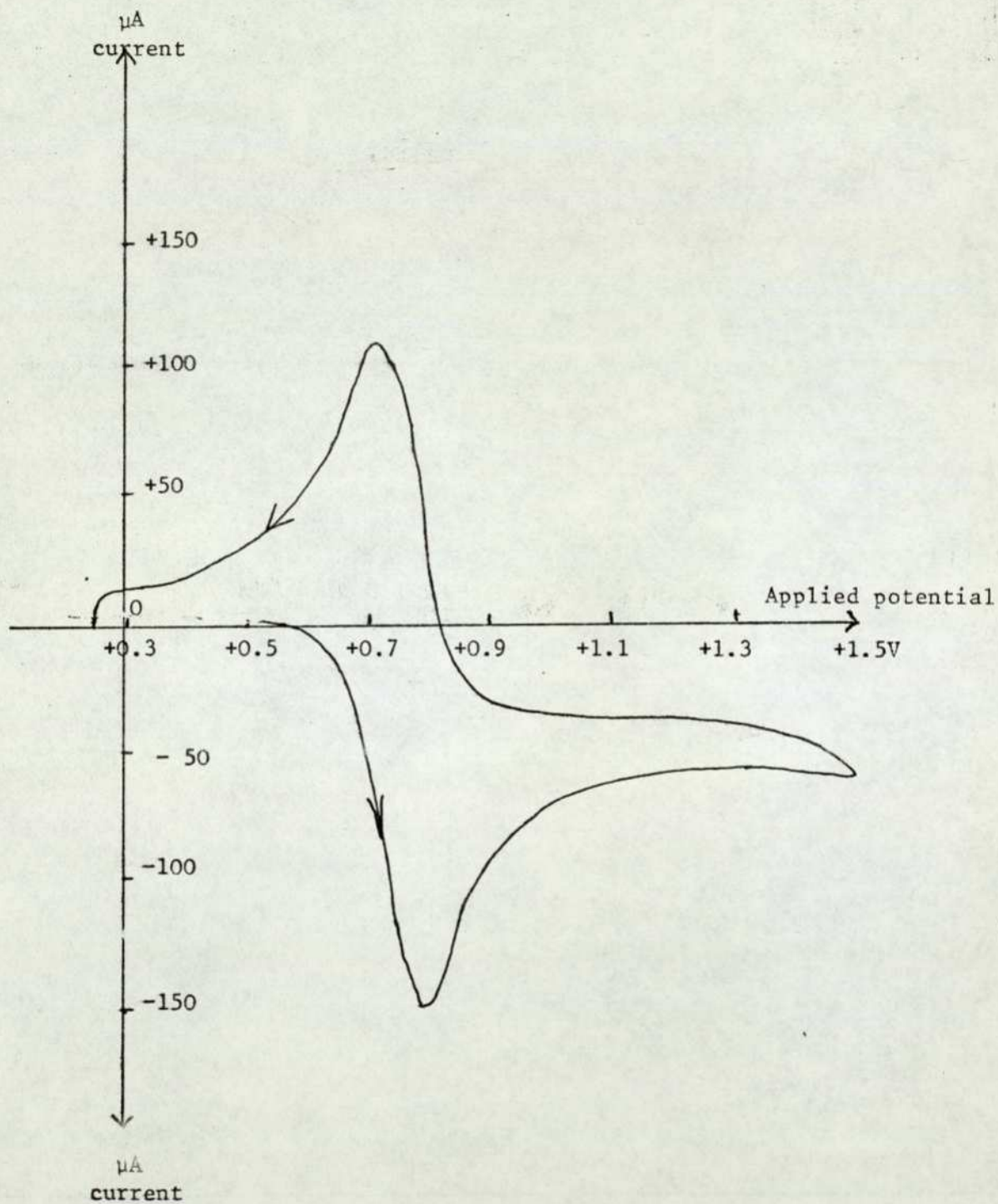


Fig. 20 Cyclic voltammogram (forward anodic sweep) of tris(4,4'-dimethyl-2,2'-bipyridyl) iron(II) perchlorate

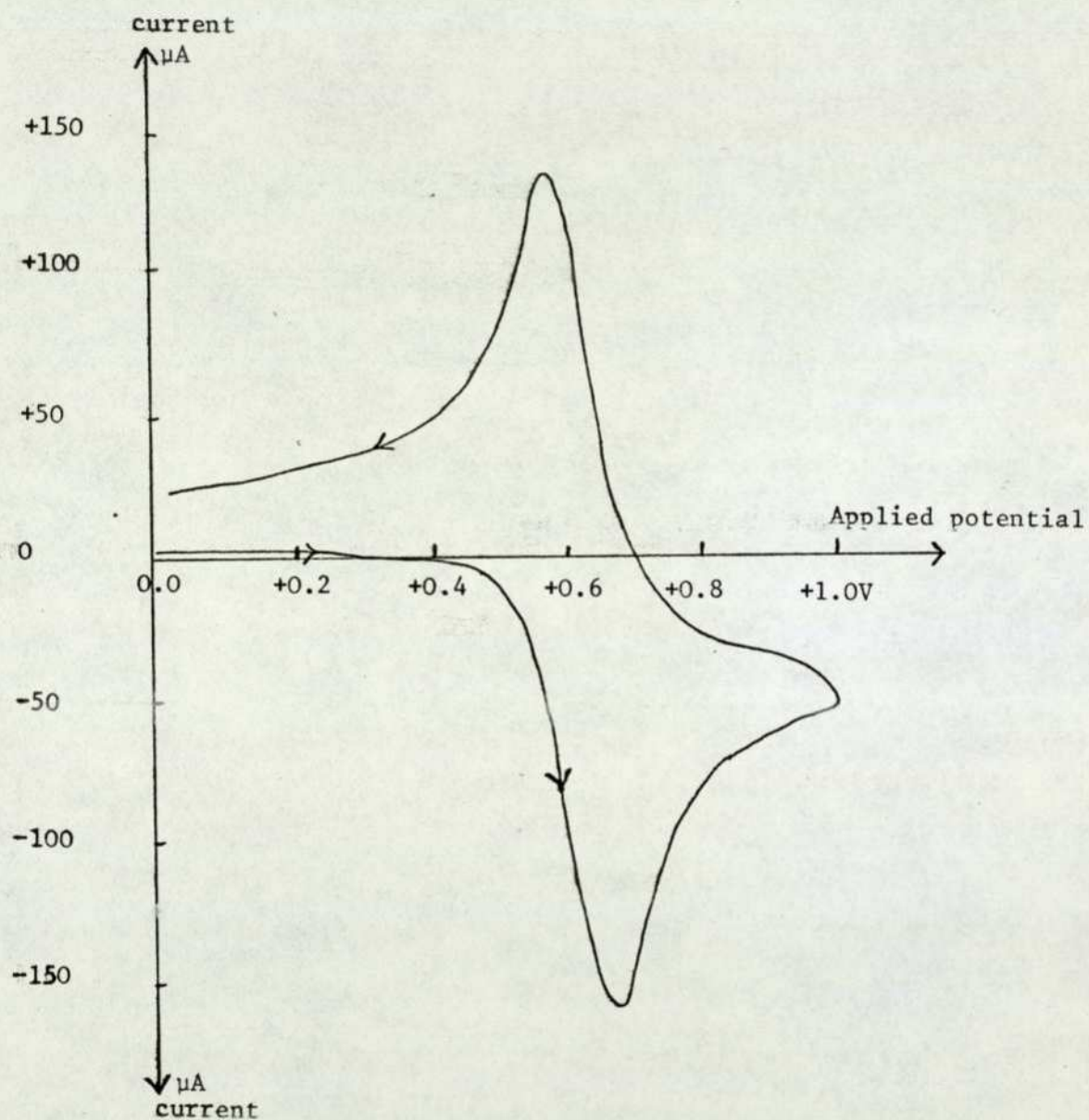


Fig. 21 Cyclic voltammogram (forward anodic sweep) of
bis(2,2',2''-terpyridyl) iron(II) perchlorate

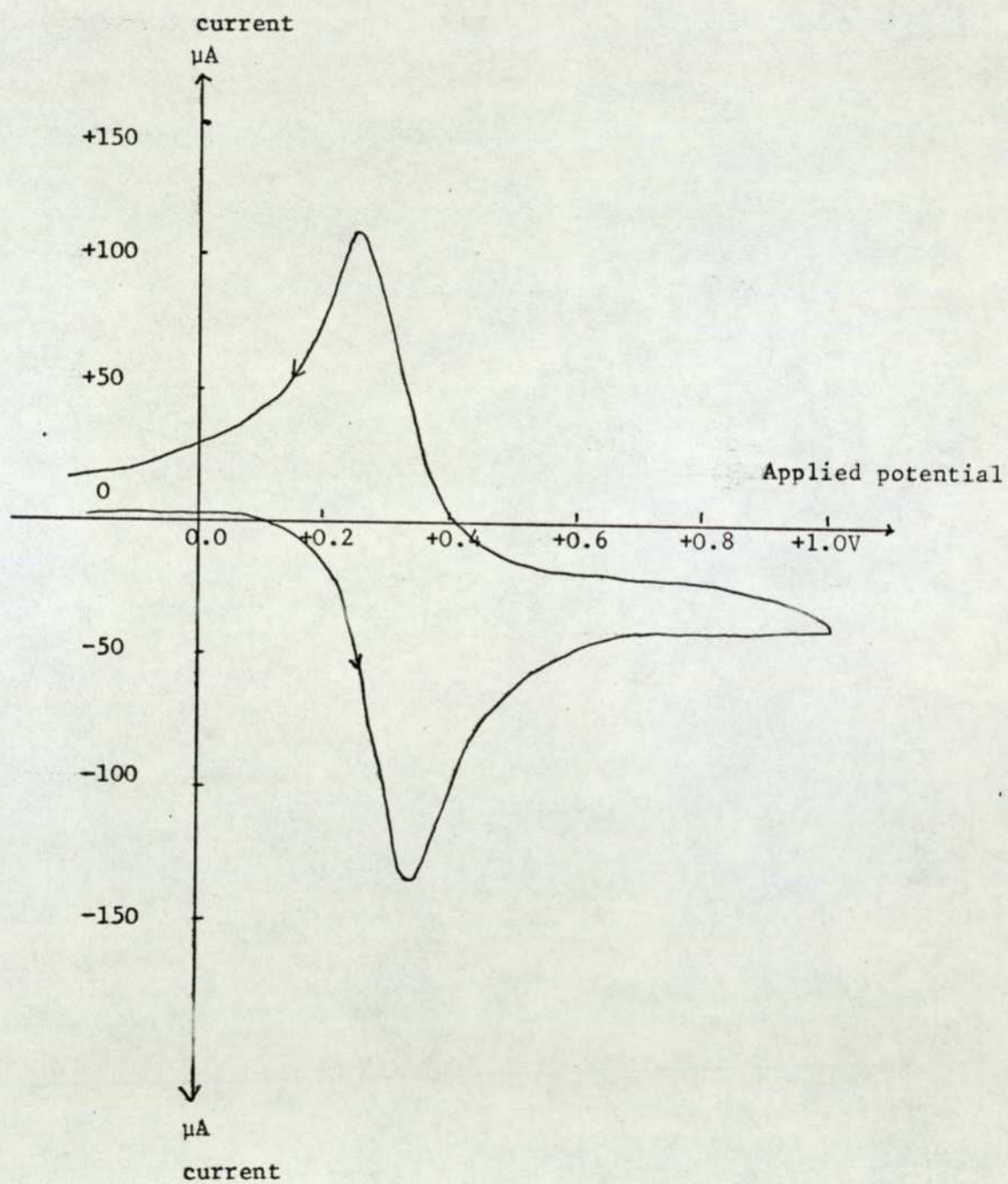


Fig. 22 Cyclic voltammogram (forward anodic sweep) of tris(2,2'-bipyridyl) cobalt(II) perchlorate

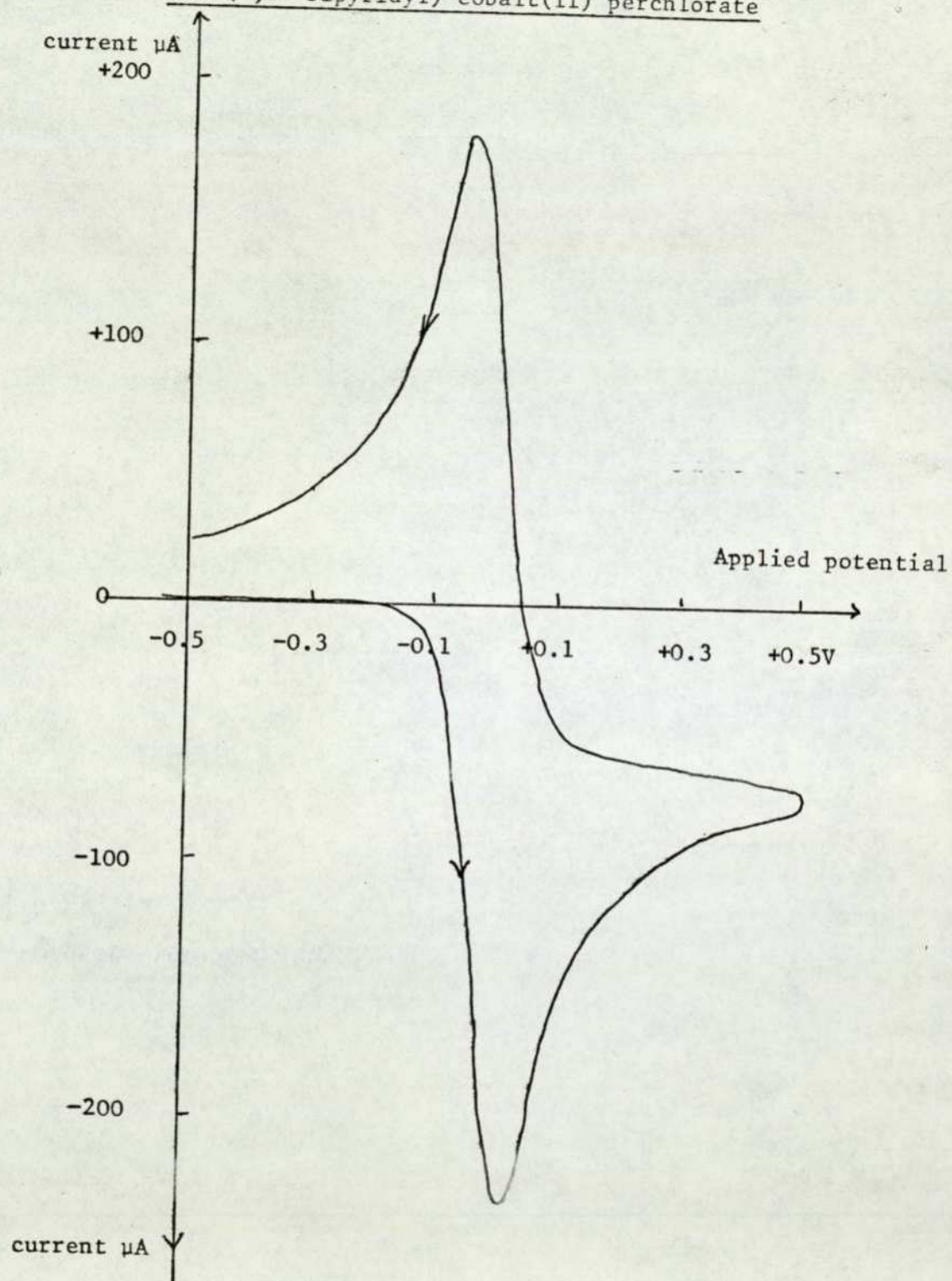


Fig. 23 Cyclic voltammogram (forward anodic sweep) of
tris(4,4'-dimethyl-2,2'-bipyridyl) iron(II) perchlorate

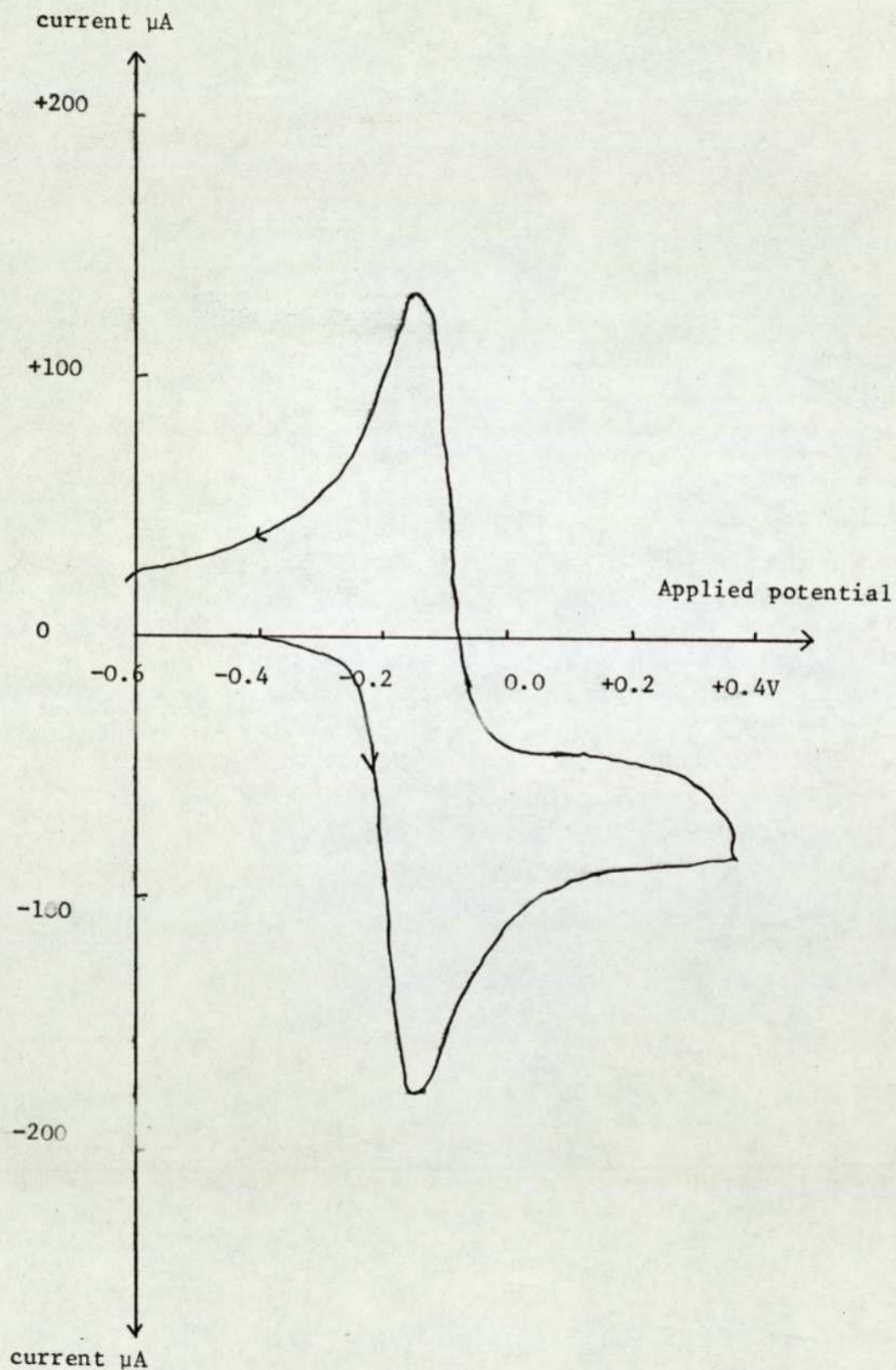


Fig. 24 Cyclic voltammogram (forward anodic sweep) of
bis(2,2',2'',-terpyridyl) cobalt(II) perchlorate

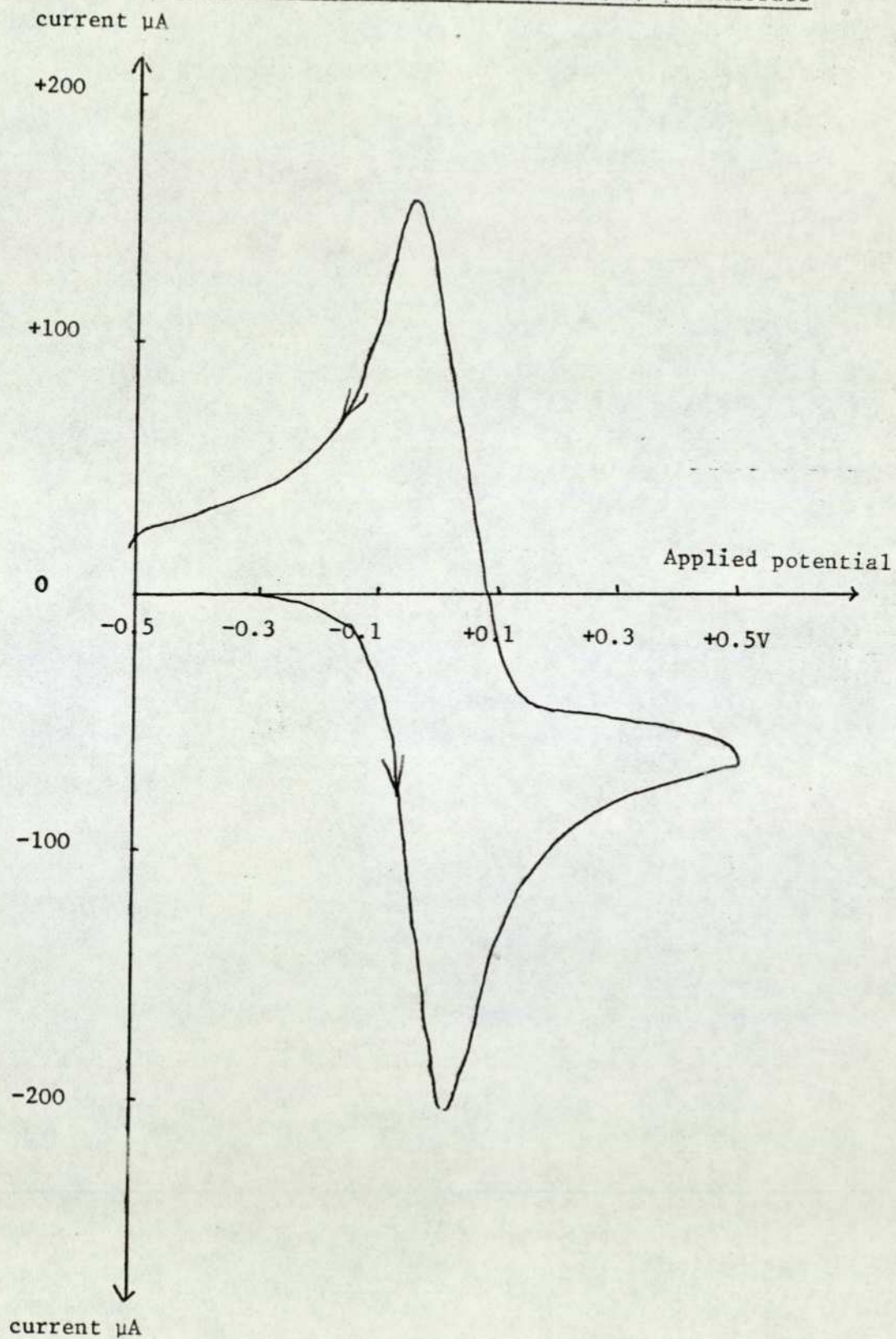


Fig. 25 Cyclic voltammogram (forward anodic sweep) of tris(2,2'-bipyridyl) nickel(II) perchlorate

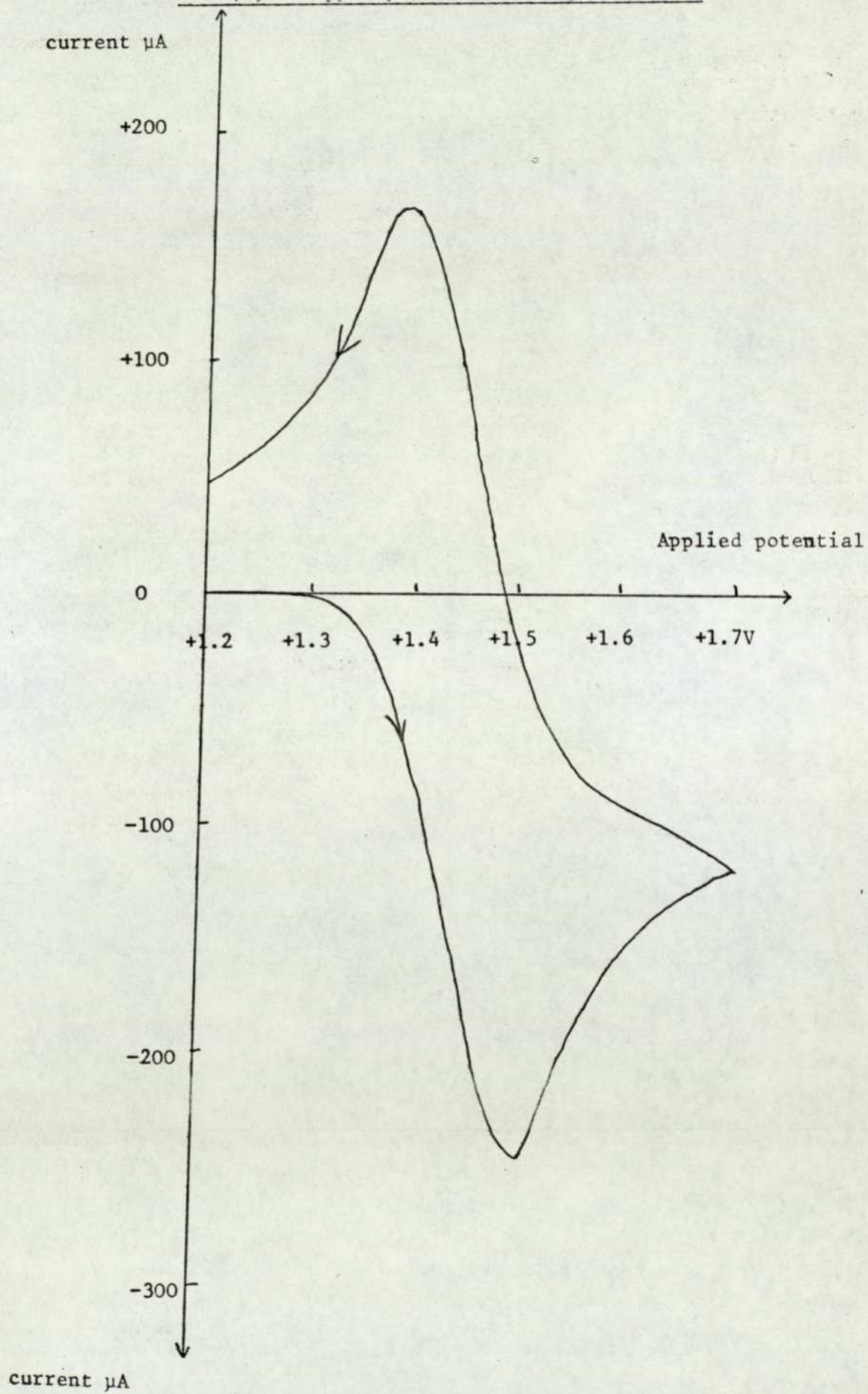


Fig. 26 Cyclic voltammogram (forward anodic sweep) of
tris(4,4'-dimethyl-2,2'-bipyridyl) nickel(II) perchlorate

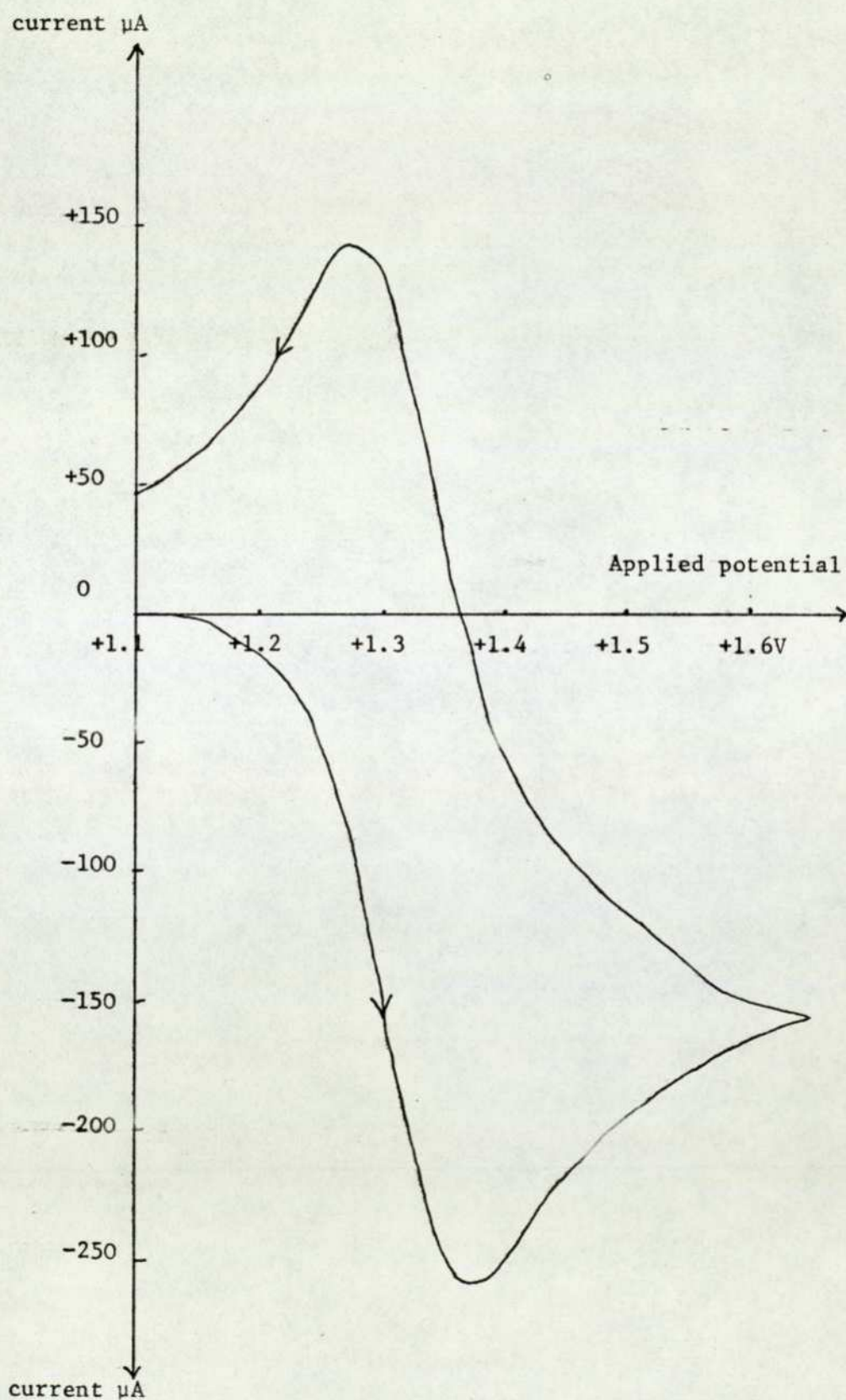


Fig. 27 Cyclic voltammogram (forward anodic sweep) of bis(2,2',2'',-terpyridyl) nickel(II) perchlorate

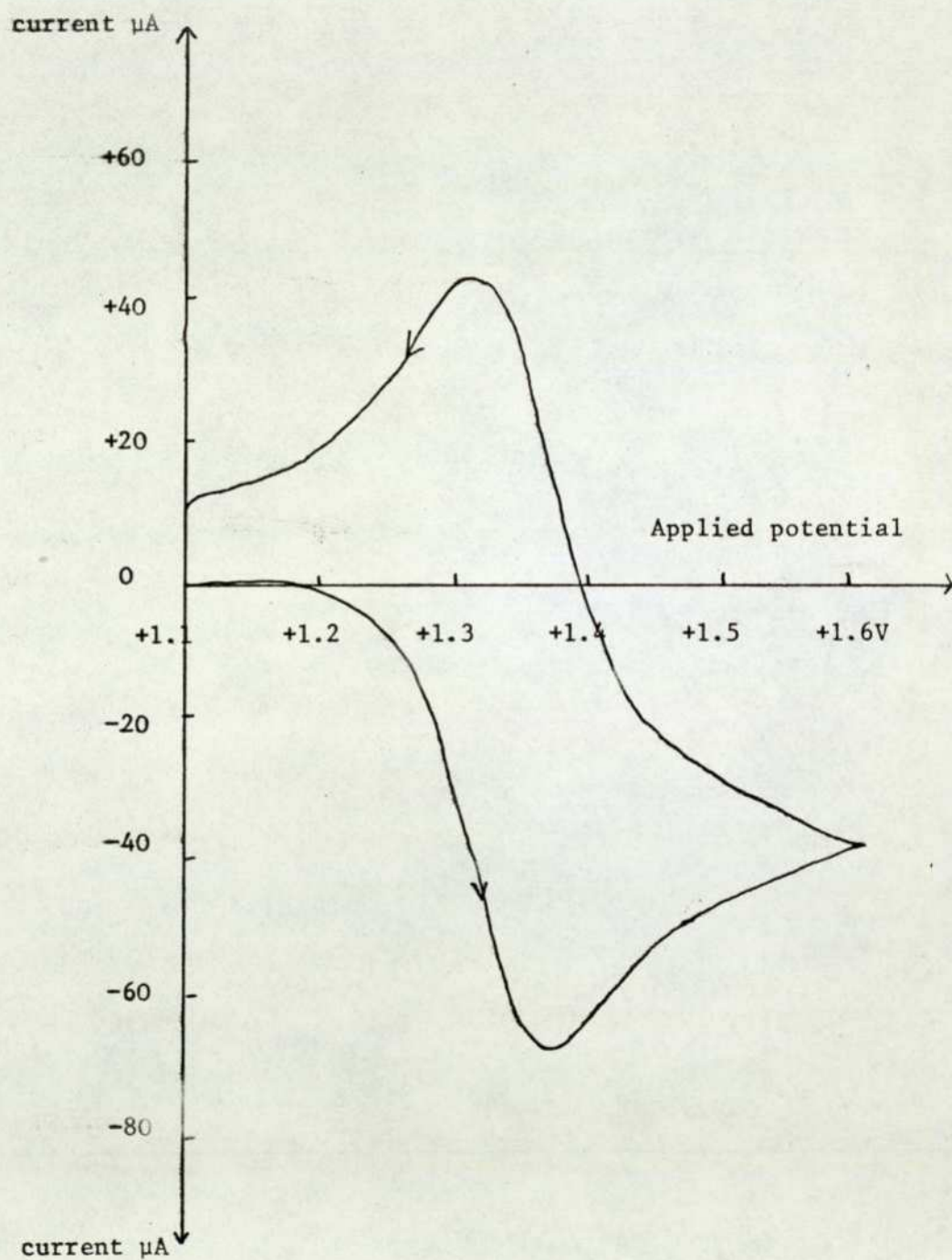


Fig. 28 Cyclic voltammogram (forward cathodic sweep) of
tris(2,2'-bipyridyl) iron(II) perchlorate

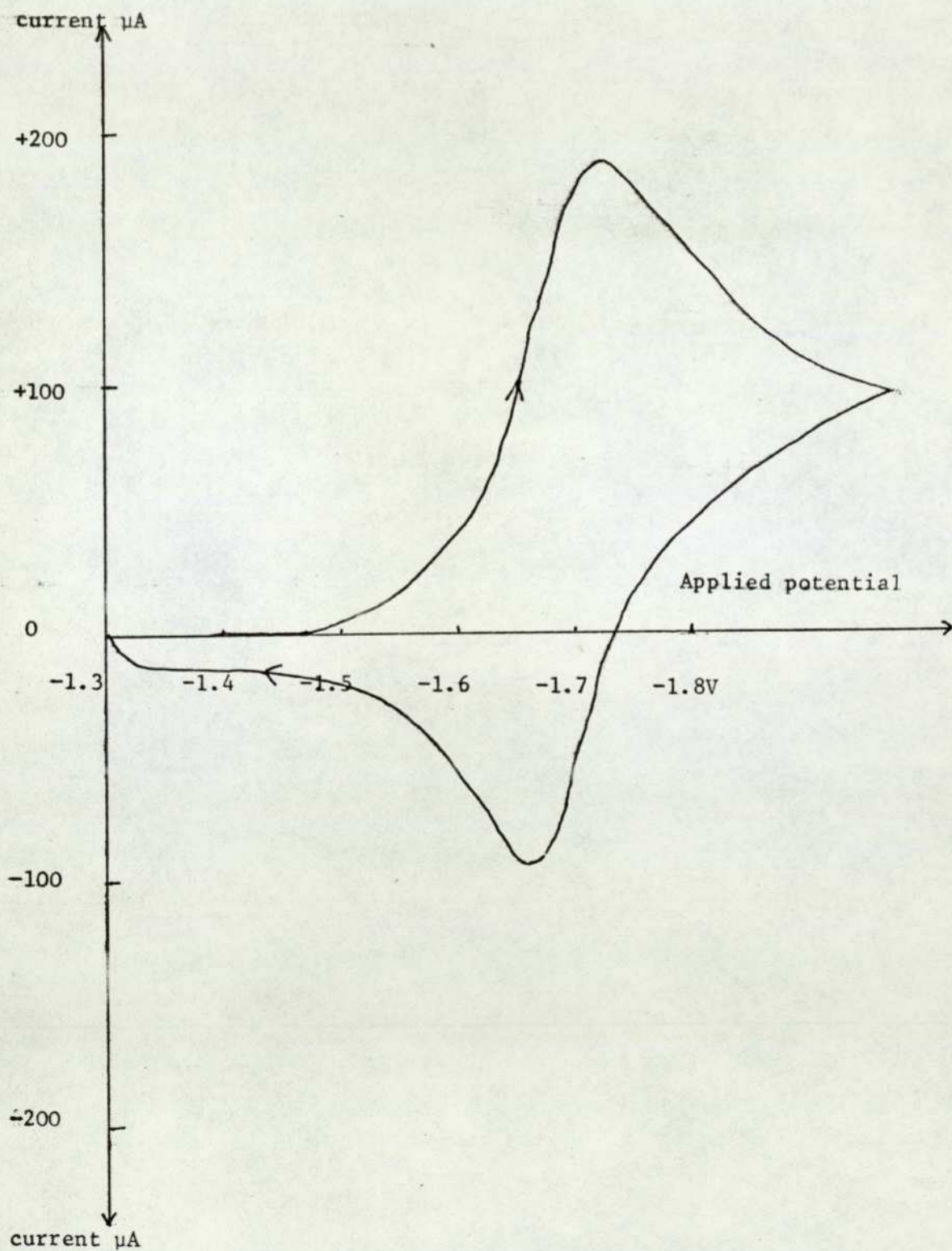


Fig. 29 Cyclic voltammogram (forward cathodic sweep) of
tris(4,4'-dimethyl-2,2'-bipyridyl) iron(II) perchlorate

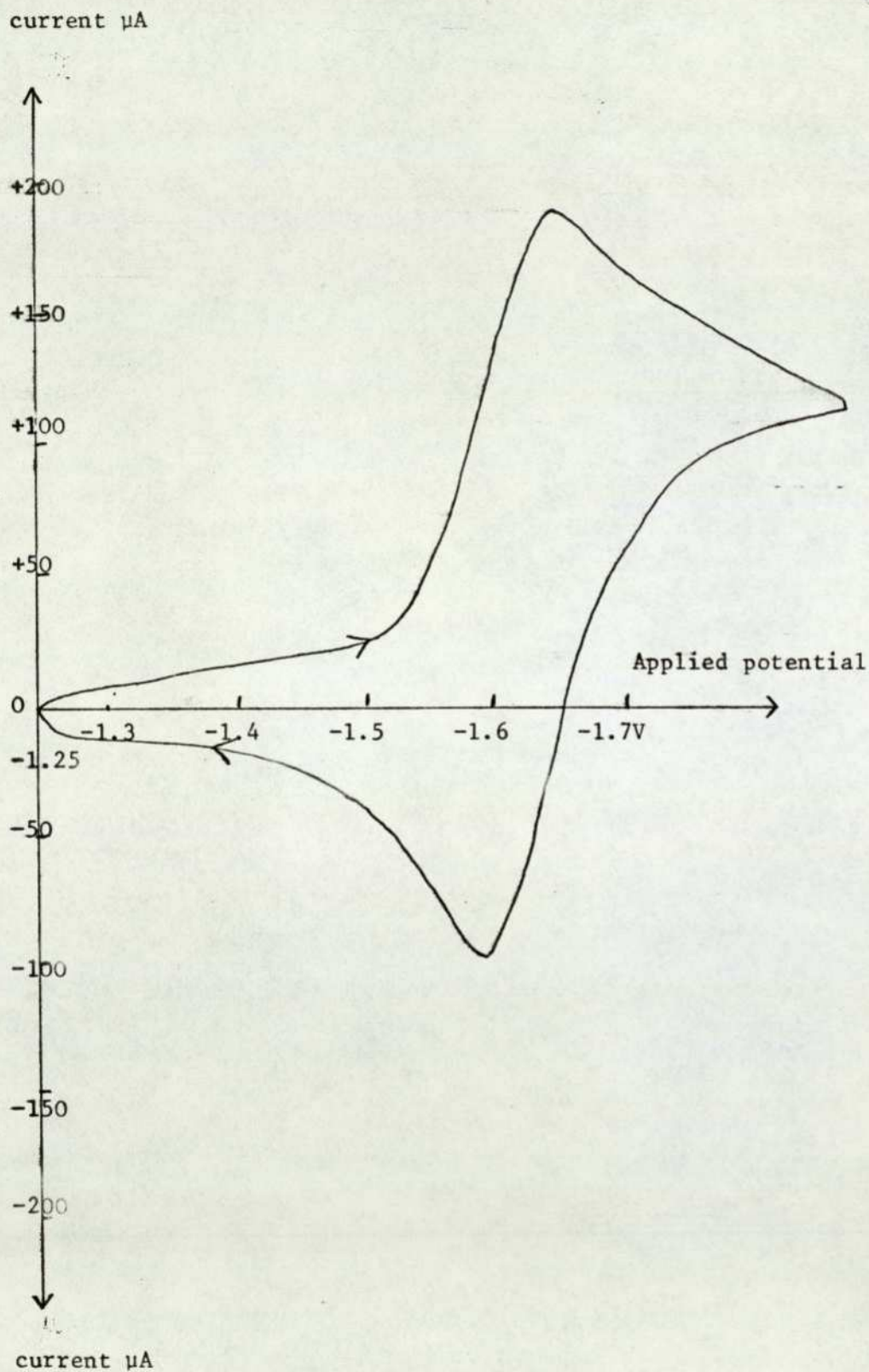


Fig. 30 Cyclic voltammogram (forward cathodic sweep) of bis(2,2',2''-terpyridyl) iron(II) perchlorate

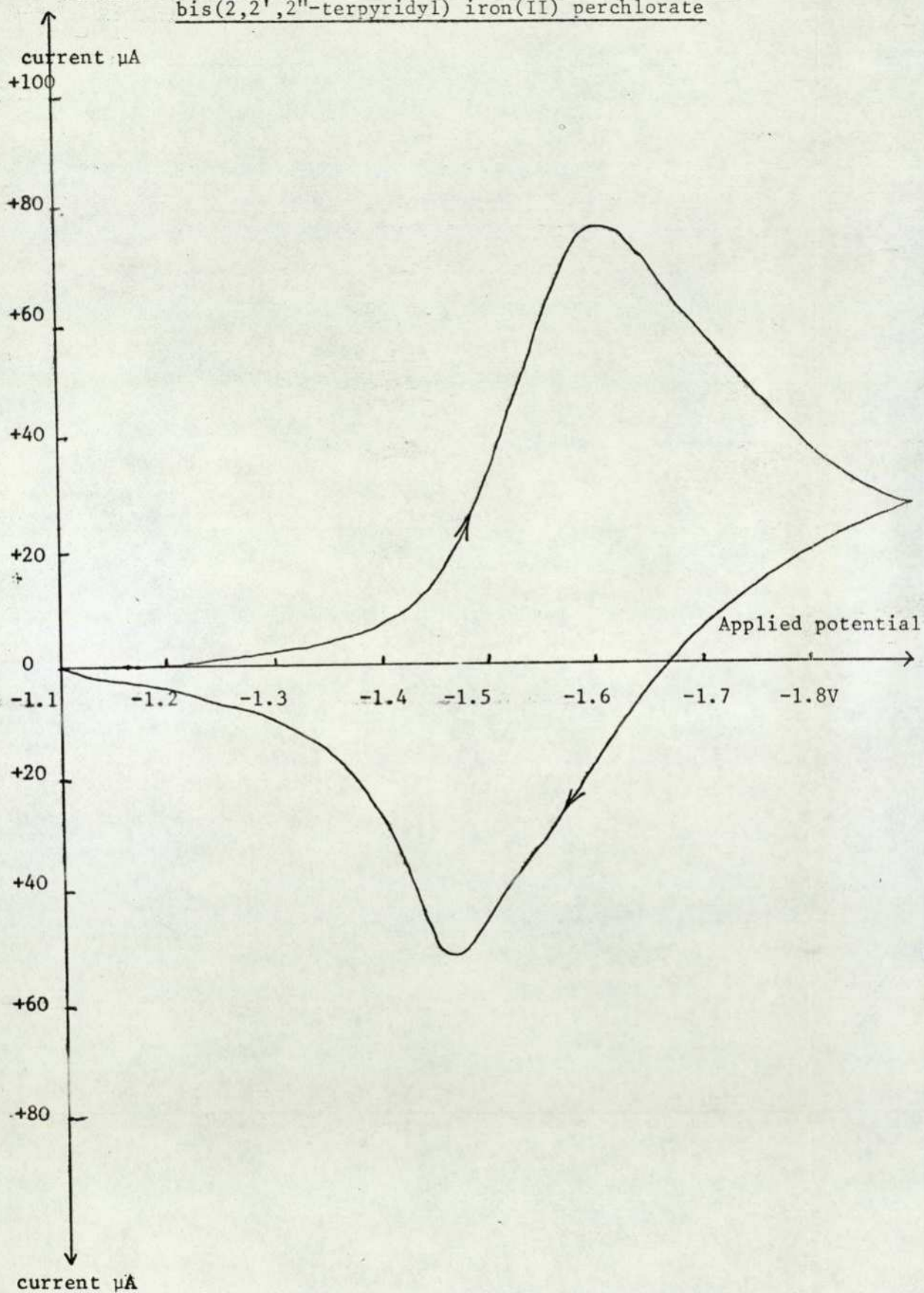


Fig. 31 Cyclic voltammogram (forward cathodic sweep) of tris(2,2'-bipyridyl) cobalt(II) perchlorate

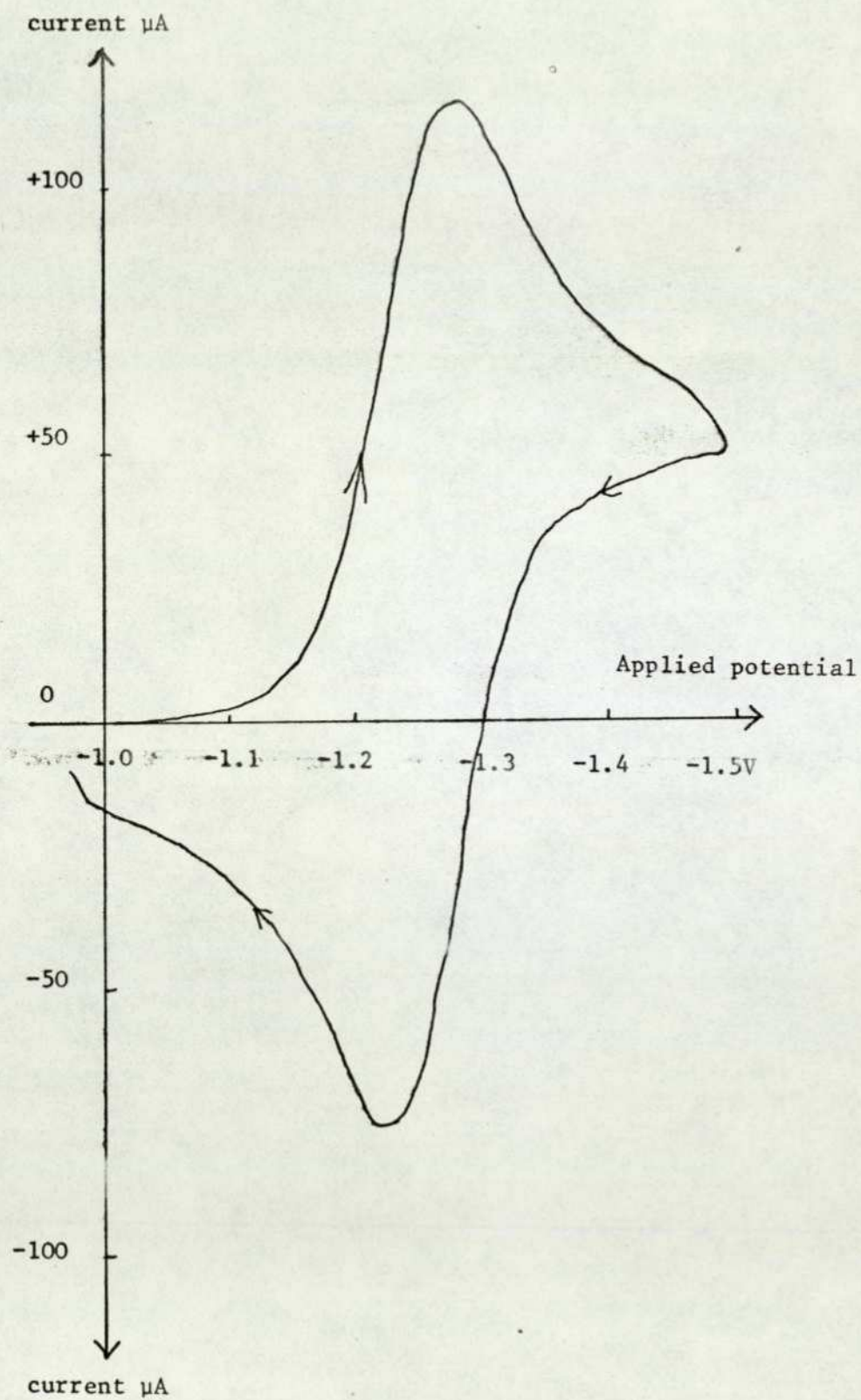


Fig. 32 Cyclic voltammogram (forward cathodic sweep) of
tris(4,4'-dimethyl-2,2'-bipyridyl) cobalt(II) perchlorate

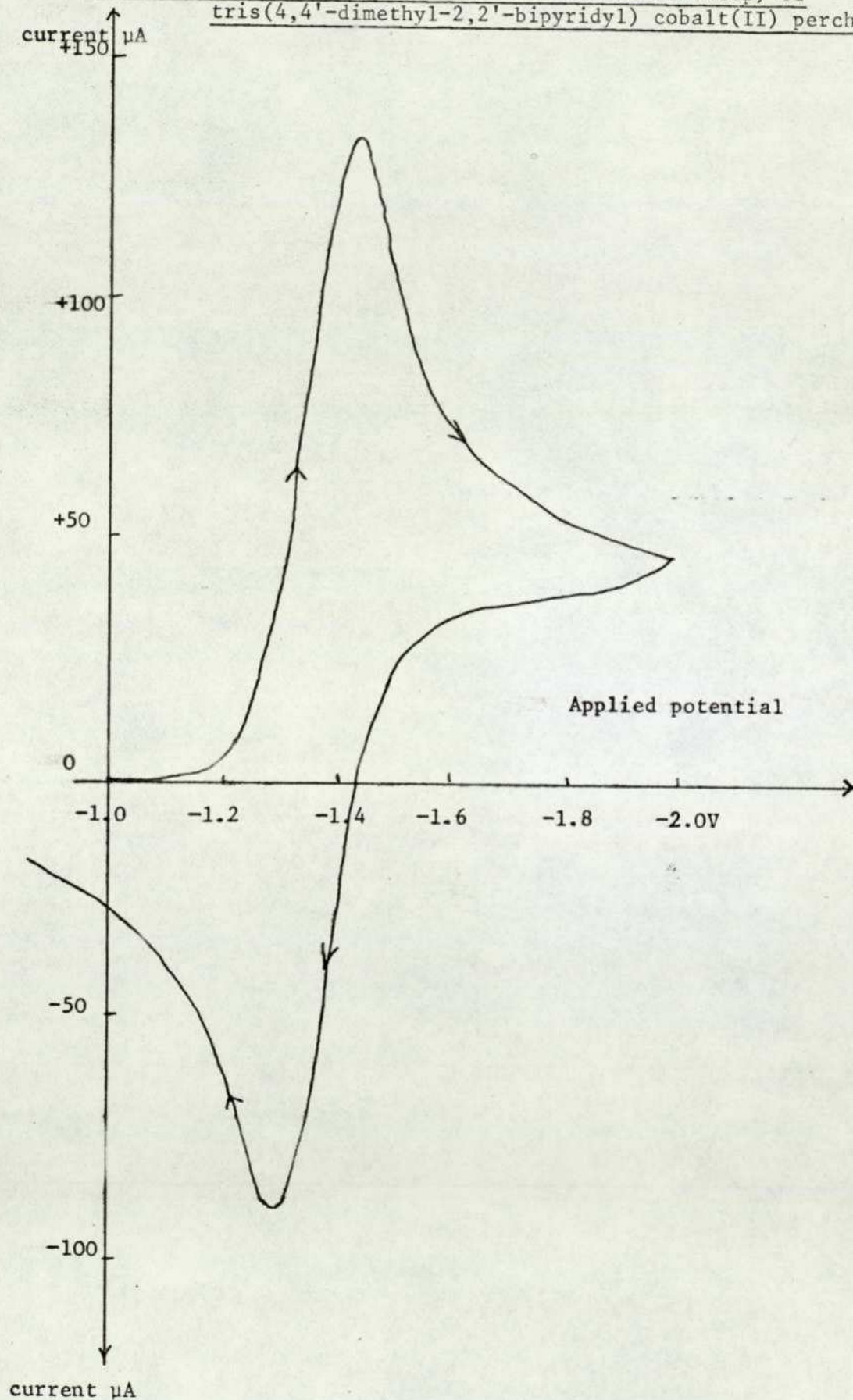


Fig. 33 Cyclic voltammogram (forward cathodic sweep) of bis(2,2',2''-terpyridyl) cobalt(II) perchlorate

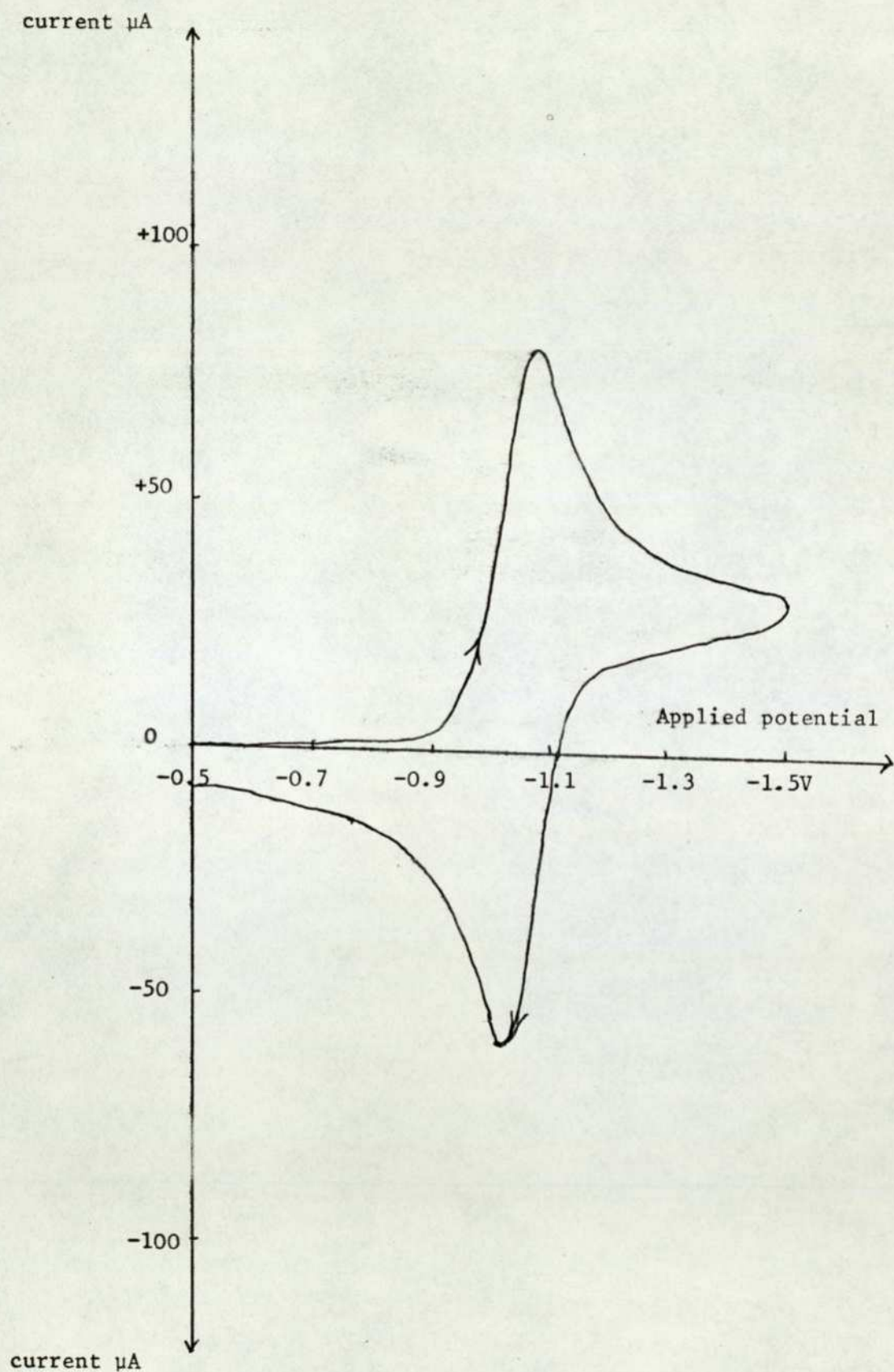


Fig. 34 Cyclic voltammogram (forward cathodic sweep) of tris(2,2'-bipyridyl) nickel(II) perchlorate

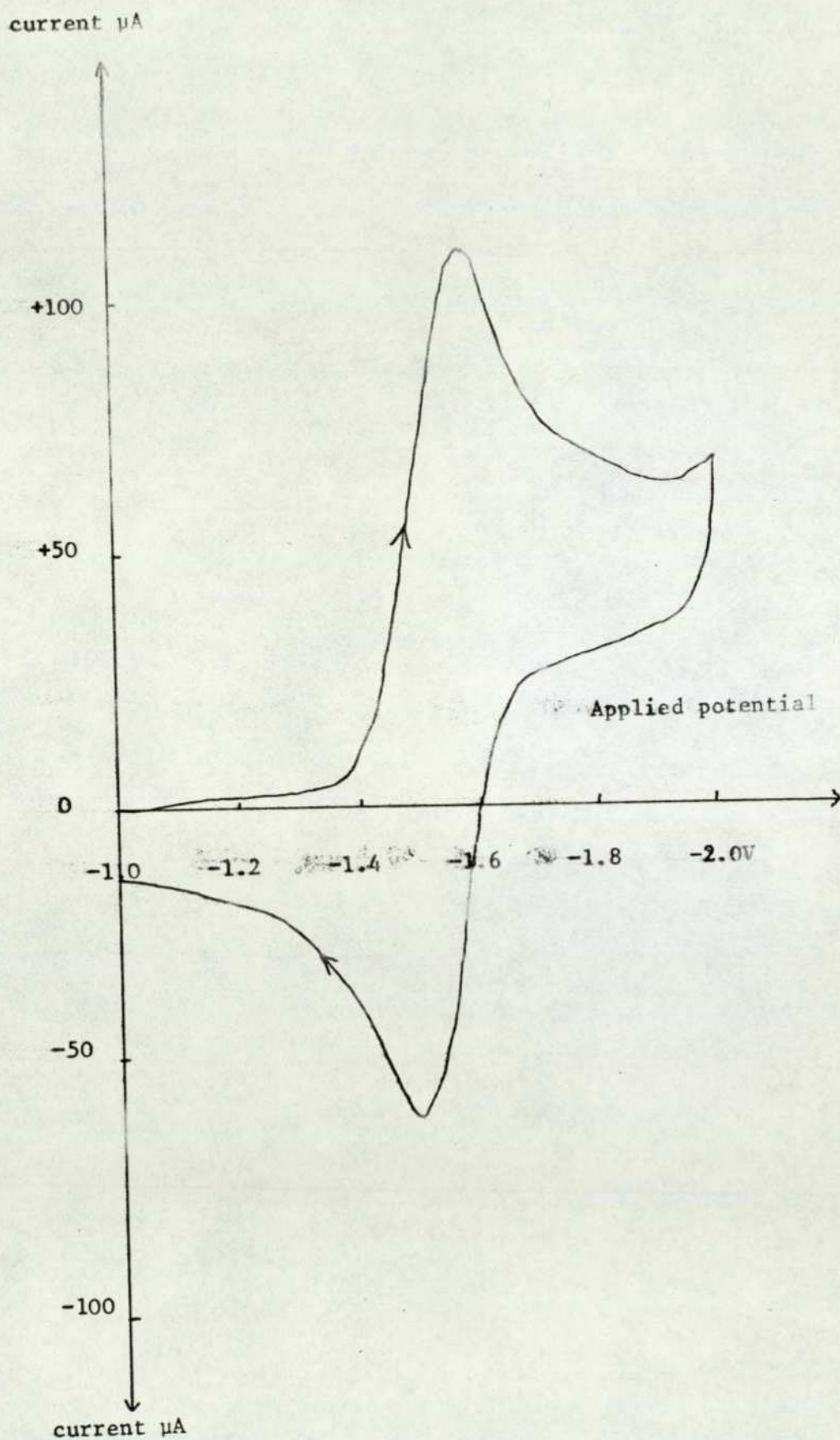


Fig. 35 Cyclic voltammogram (forward cathodic sweep) of tris(4,4'-dimethyl-2,2'-bipyridyl) nickel(II) perchlorate

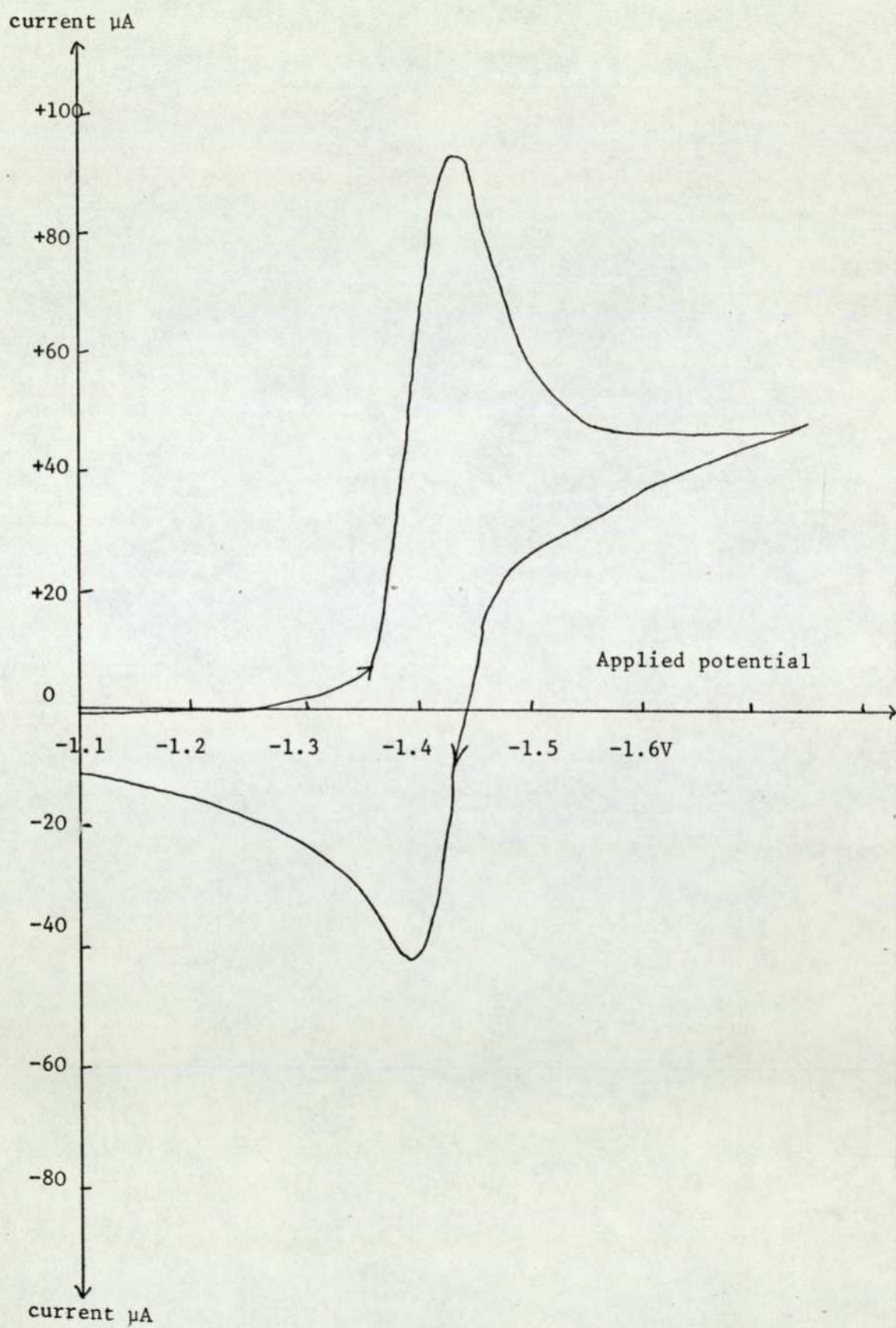
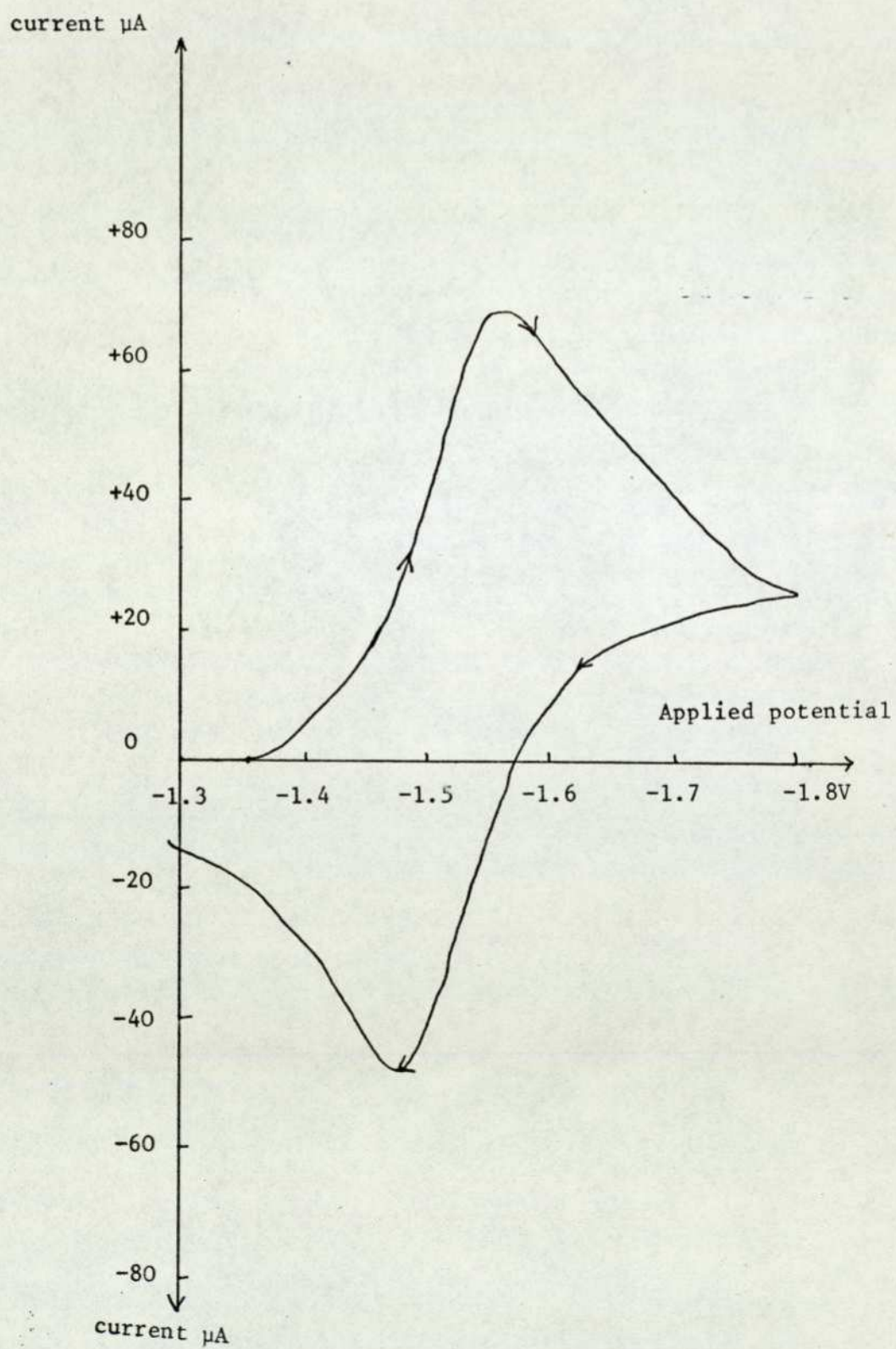


Fig. 36 Cyclic voltammogram (forward cathodic sweep) of
bis(2,2',2''-terpyridyl) nickel(II) perchlorate



to be estimated by extrapolation of the current-voltage curve past the end of the forward sweep. The same difficulty did not apply to forward peak currents since the current at the start of a forward sweep was always zero.

The data for waves obtained with a forward cathodic sweep refer to the first of two reduction waves observed in all the systems studied. Figure 31, page 126 shows a typical voltammogram of the first wave for the reduction of the Co(II)/bipy complex. This will be confirmed later as due to reduction to the corresponding Co(I) complex. Figure 1, page 39 shows the second reduction wave which was assumed to be due to reduction to the metal(0) state since the peak separation was 63mV, indicating a one electron transfer (c.f. section 3, page 40). Similar peak separations were observed for the second waves of the iron(II) and nickel(II) complex systems. The second reduction waves were not studied in detail.

The cyclic voltammetry data for all metal(II) complex systems studied indicate that reversible one electron oxidation and reduction processes (c.f. section 3, page 40) are operative. This is evident from the data given in Tables I to VI from which it can be seen that the following relationships hold:

- (i) The forward peak potentials are independent of sweep rates in all cases. For different sweep rates and for different concentrations the forward peak potentials do not vary by more than $\pm 5\text{mV}$.
- (ii) The forward peak current is proportional to the concentration of the electroactive species in solution. Figures 37 to 51, pages 153 to 167 show plots of i_p against concentration which

are linear.

- (iii) The forward peak current is proportional to $V^{\frac{1}{2}}$ as indicated by the graphs in figures 57 to 69, pages 173 to 185. These data are somewhat limited but, nevertheless, support the reversibility criterion.
- (iv) The ratio of the forward and reverse peak currents is unity within the limits of experimental error.
- (v) In all cases, at the slowest sweep rates used, it is seen that the separation of the peak potentials is of the order of 50-60mV. This means that the electron transfer processes involve one electron (the calculated separation for a reversible system is $\frac{57\text{mV}}{n}$ at 25°C (c.f. section 3, page 40)).

It will be noted that in many voltammograms obtained for sweep rates above 0.005V sec^{-1} , the separation of the peak potentials exceeds 60mV and that the separation increases with increasing scan rate. This was first thought to be due to some degree of irreversibility, but one important factor indicates that this is not the case. Even when the separation is as large as 100mV the forward peak potential remains the same as that observed at slower sweeps and it is only the reverse potential that shifts with sweep rate. These symptoms are exactly those described⁵ for the situation where the switch in sweep direction occurs at potentials too close to the forward peak which results (in the case of a forward anodic wave) in incomplete oxidation of the reduced form which has diffused to the electrode. The concentration of the oxidised form present for reduction in the reverse wave will, therefore, be less than the initial bulk concentration of the reduced form. This results in the reverse

wave occurring at potentials less anodic than would normally be the case and the effect increases with sweep rate. It seems from the data given in Tables I to VI that in some cases this effect was operative although the accompanying effect of a smaller reverse peak current could not be detected within the limits of experimental error.

An important conclusion which can be drawn from the voltammetric data is that within the time scale of the experiments, the metal(III) and metal(I) species which are formed are stable; there is no evidence of coupled chemical reactions. It will be seen later that while the metal(III) and metal(II) polypyridyl complexes are six co-ordinate, the two metal(I) complexes, which it was possible to isolate ($\{\text{Ni}(\text{bipy})_2\}\text{ClO}_4$ and $\{\text{Co}(\text{bipy})_2\}\text{ClO}_4$) appeared to be four co-ordinate. In these cases, reduction of the corresponding metal(II) complexes must involve a follow up chemical reaction in which a ligand molecule is lost; presumably this reaction is slow compared to the voltammetric time scale otherwise the effect would be expected to modify the reverse sweep characteristics.

Since the systems investigated behave reversibly, the data can be used to calculate values of $E_{\frac{1}{2}}$ and these are included in Tables I to VI. $E_{\frac{1}{2}}$ values were calculated from the forward peak potentials (c.f. equation 8, page 40) because of the effect discussed above, of the shift in the reverse peak in certain cases. The $E_{\frac{1}{2}}$ value is a good approximation to the E^0 value as seen by reference to equation 2, page 35.

Tables VII and VIII give a summary of mean values of $E_{\frac{1}{2}}$ for both the M(III)/M(II) and M(II)/M(I) couples.

Table VII

$E_{\frac{1}{2}}$ values for the metal(III)/metal(II) couple

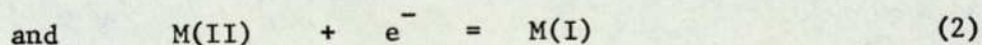
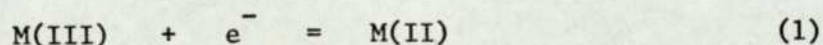
Metal Ligand	Iron	Cobalt	Nickel
bipy	+0.770V	-0.011V	+1.455V
dimbipy	+0.621V	-0.125V	+1.337V
terpy	+0.300V	-0.017V	+1.374V

Table VIII

$E_{\frac{1}{2}}$ values for the metal(II)/metal(I) couple

Metal Ligand	Iron	Cobalt	Nickel
bipy	-1.690V	-1.261V	-1.549V
dimbipy	-1.631V	-1.327V	-1.391V
terpy	-1.593V	-1.040V	-1.531V

The E^0 values corresponding to the two sets $E_{\frac{1}{2}}$ values given above refer to the processes:



The magnitude of E^0 can be regarded as being a measure of the ease of reduction of the oxidised form or, conversely, the difficulty of oxidising the reduced form. Since the 2nd and 3rd Ionisation potentials of the free metal atom measure the difficulty of oxidising M^+ and M^{2+} respectively in the gaseous state then a proportionality would be expected between the E^0 value (and hence $E_{\frac{1}{2}}$) for the

metal(II)/metal(I) couple and the 2nd I.P. and between the E^0 value for the metal(III)/metal(II) couple and the 3rd I.P. of the metal atom. Figures 70 and 71, pages 186 and 187 give plots of $E_{\frac{1}{2}}(M^{3+}/M^{2+})$ versus 3rd I.P. and $E_{\frac{1}{2}}(M^{2+}/M^+)$ versus 2nd I.P. respectively for the three metals and for each complex system. Both sets of data show a marked lack of proportionality; this can be related in qualitative terms to crystal field effects in the following way:

It has already been shown from magnetic properties (c.f. section 4.1.5.) that the bipy, dimbipy and terpy complexes of iron(II), cobalt(II) and nickel(II) have the following d configurations:

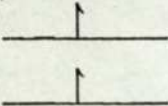
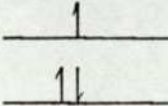
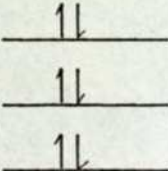
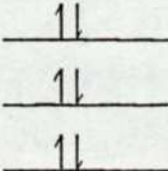
	Fe(II)	Co(II)	Ni(II)
e_g	_____ _____	1 1	1 1
t_{2g}	1↓ 1↓ 1↓	1 1↓ 1↓	1↓ 1↓ 1↓

It will be shown later (section 5.3) that the corresponding metal(III) configurations are as shown on the next page.

	Fe(III)	Co(III)	Ni(III)	
	All ligands	All ligands	bipy dimbipy	terpy
e_g	<u> </u> ° <u> </u>	<u> </u> <u> </u>	<u> </u> 1 <u> </u>	<u>1</u> <u>1</u>
t_{2g}	<u>↑</u> <u>↑↓</u> <u>↑↓</u>	<u>↑↓</u> <u>↑↓</u> <u>↑↓</u>	<u>↑↓</u> <u>↑↓</u> <u>↑↓</u>	<u>1</u> <u>↑↓</u> <u>↑↓</u>

Thus in the oxidation of iron(II) polypyridyl complexes a t_{2g} electron is removed. Cobalt(II) complexes, on the other hand lose an e_g electron as do the bipy and dimbipy complexes of nickel(II). This means that the effect of the crystal field is to increase the difficulty of oxidising iron(II) complexes compared to Co(II) and Ni(II) complexes (other than Ni(II)/terpy). The oxidation of cobalt(II) complexes must also involve a gain in crystal field stabilisation energy, since after removal of an e_g electron, the remaining e_g electron drops into the t_{2g} set; this will increase the ease of oxidation. The experimental data for the M(III)/M(II) couples are in broad agreement with these arguments, $E_{1/2}$ values for the Fe(III)/Fe(II) couples being higher than those for the Co(III)/Co(II) couples. $E_{1/2}$ values for the nickel(III)/nickel(II) couples are the highest of the series as expected. On a similar basis it would be expected that of the nickel(III)/nickel(II) couples, the terpyridyl system would have the highest $E_{1/2}$ value since oxidation of the Ni(II)-terpy complex involves the removal of a t_{2g} electron. However, this is not the case.

Correlation of the M(II)/M(I) couple data with crystal field effects is limited to the Co(II)/Co(I)-bipy and Ni(II)/Ni(I)-bipy systems owing to a lack of magnetic data for other systems. Even in these cases, the stereochemistry of the metal(I) complexes is not known (c.f. section 5.4.2.). However, assuming an octahedral environment, magnetic data are consistent with the following configurations:

	Co(I)/bipy	Ni(I)/bipy
e_g		
t_{2g}		

Comparing these configurations with those of the corresponding metal(II) complexes, reduction of the Co(II)-bipy complex will involve the addition of an electron to t_{2g} orbital whereas the Ni(II)-bipy complex will accept an electron into an e_g orbital. Crystal field effects will thus facilitate the reduction of the Co(II) complex which is in agreement with the data of figure 71; it is seen that Co(II) complexes are, in fact, more easily reduced than the corresponding nickel(II) complexes.

Previous studies of polypyridyl complexes of iron, cobalt and nickel in acetonitrile have incorporated classical d.c. and a.c. techniques and have been restricted to 2,2'-bipyridyl complexes; cyclic voltammetry data are not available for comparison. The present $E_{1/2}$ values are in good agreement with $E_{1/2}$ values reported in the literature

as the figures compared in Table IX indicate.

Table IX

Bipy complex system	$E_{\frac{1}{2}}$	
	Present work	Literature values
Fe(III)/Fe(II)	+0.770V	+0.75V ^{300,301}
Co(III)/Co(II)	-0.011V	-0.017V ³⁰² -0.005V ³⁰⁰
Fe(II)/Fe(I)	-1.690V	-1.71V ³⁰¹
Co(II)/Co(I)	-1.261V	-1.23V ³⁰²
Ni(II)/Ni(I)	-1.549V	-1.46V ³⁰³

The value of $E_{\frac{1}{2}} = -1.46V$ quoted by Tanaka and Sato³⁰³ for the nickel system is claimed to refer to the Ni(II)/Ni(0) couple. However, this was not confirmed by coulometric studies and it seems likely that the reduction wave observed was in fact the Ni(II)-Ni(I) wave of the present work. Tanaka and Sato³⁰³ have also observed second reduction waves in all three systems which are claimed to correspond to the Fe(I)/Fe(0),³⁰¹ Co(I)/Co(-I),³⁰² and Ni(0)/Ni(-I),³⁰³ couples. It would appear that these waves are, in fact, associated with the metal(I)/metal(0) couples as is indicated for the second reduction waves obtained in the present work. However, a more detailed examination of the second reduction waves backed up by constant potential coulometry, will be necessary before the number of electrons transferred in the second reduction steps can be completely resolved.

5.3. Controlled potential coulometry of polypyridyl complexes of iron(II), cobalt(II) and nickel(II) perchlorate

The results of controlled potential coulometry experiments (c.f. section 4.3.2., page 85), in which polypyridyl complexes of iron(II), cobalt(II) and nickel(II) were oxidised and reduced are given in Tables X and XI (pages 141 to 144) respectively. The potential at which each complex was oxidised or reduced was in the vicinity of the peak potential of the forward sweep wave of the corresponding cyclic voltammogram (section 5.2.). The number of electrons transferred per molecule of electrochemical species was calculated in each case from the equation given in section 4.3.2., page 86.

The two sets of data give calculated values of n , the number of electrons transferred, close to unity. In most cases the values are within the expected experimental error of about $\pm 5-10\%$. In general, the data for electrochemical oxidations are better than those for electrochemical reductions. This might be due to the fact that in the latter type of experiment, for reasons which cannot be explained, a larger amount of metal(II) complex (in excess of about 0.05g) had to be used; otherwise, the initial current was so disproportionately small and the electrolysis time so long that a useful current-time curve could not be obtained. The use of a large amount of complex increased the possibility of errors due to deposition of product species on the electrode giving reduced efficiency and producing irregularities in the current-time curve. Another feature of the reduction experiments was that a heating effect was observed which must have led to increased mixing of the solutions of the different cell compartments. Again, it

Table X

Coulometric data for electro-oxidation of metal(II) complexes

Complex	Weight mg	Applied potential V	Initial current mA	Duration of electrolysis min.	Quantity of electricity consumed C	Number of electrons transferred n	Observation
Fe(bipy) ₃ ⁺²	43.1	+0.78	47	20	5.8	1.00	Dark red to blue ditto
	14.2	+0.76	18	15	1.9	1.00	
Fe(dimbipy) ₃ ⁺²	13.4	+0.62	15	35	1.6	1.00	
	23.0	+0.64	18	30	1.6	1.06	
Fe(terpy) ₂ ⁺²	10.3	+0.30	17	20	1.4	1.01	
	13.4	+0.30	16	15	1.4	0.98	
Co(bipy) ₃ ⁺²	27.0	+0.03	35	15	3.4	0.94	From light yellow to dark yellow No distinct change in the colour ditto
	25.2	+0.04	42	10	3.7	1.07	
Co(dimbipy) ₃ ⁺²	25.0	-0.105	37	15	2.9	0.97	
	57.0	-0.102	44	20	6.9	1.01	
Co(terpy) ₂ ⁺²	21.5	+0.002	18	10	2.9	1.00	
	14.7	+0.004	20	6	1.9	0.97	

cont/d ...

Complex	Weight mg	Applied potential V	Initial current mA	Duration of electrolysis min.	Quantity of electricity consumed C	Number of electrons transferred n	Observation
$\text{Ni}(\text{bipy})_3^{+2}$	25.2	+1.48	34	30	3.6	1.07	[Pink colour of Ni(II) complex turned green as the electrolysis proceeded]
	112.0	+1.40	75	65	16.5	1.10	
	101.2	+1.45	96	50	12.7	0.95	
$\text{Ni}(\text{dimbipy})_3^{+2}$	5.0	+1.35	15	30	6.0	1.00	[Green colour formed]
	75.0	+1.37	29	25	8.9	0.99	
$\text{Ni}(\text{terpy})_2^{+2}$	65.4	+1.35	30	25	7.9	0.90	[Very light green colour from light yellow]
	94.5	+1.36	74	35	14.2	1.12	

Table XI

Coulometric data for electro-reduction of metal(II) complexes

Complex	Weight mg	Applied potential V	Initial current mA	Duration of electrolysis min.	Quantity of electricity consumed C	Number of electrons transferred n	Observation
Fe(bipy) ₃ ⁺²	183.0	-1.70	43	70	28.1	1.15	Product turned from dark red to blue-violet
	214.9	-1.70	51	75	28.5	0.99	
Fe(dimbipy) ₃ ⁺²	104.2	-1.66	51	45	12.9	1.04	ditto
	108.1	-1.65	48	50	13.0	1.00	
Fe(terpy) ₂ ⁺²	146.2	-1.60	75	90	23.7	1.18	
	231.9	-1.58	84	80	30.2	0.94	
Co(bipy) ₃ ⁺²	154.5	-1.28	80	60	23.5	1.14	Product turned from yellow to green to dark blue
	100.8	-1.30	75	50	12.6	0.96	
Co(dimbipy) ₃ ⁺²	140.0	-1.54	120	55	14.3	1.00	ditto
	100.5	-1.44	78	65	12.0	1.00	
Co(terpy) ₂ ⁺²	48.0	-1.54	37	35	7.1	1.10	Product turned from light red to dark blue
	108.8	-1.52	79	70	16.0	1.09	

cont/d ...

Complex	Weight mg	Applied potential V	Initial current mA	Duration of electrolysis min.	Quantity of electricity consumed C	Number of electrons transferred n	Observation
Ni(bipy) ₃ ⁺²	69.0	-1.54	42	35	9.0	0.97	Product turned pink to yellow to bright blue
	190.4	-1.55	65	60	28.3	1.05	
	50.0	-1.56	52	20	6.3	0.95	
Ni(dimbipy) ₃ ⁺²	100.0	-1.43	87	40	12.1	1.01	
	85.0	-1.42	71	30	10.5	1.03	
Ni(terpy) ₂ ⁺²	118.8	-1.54	51	60	18.0	1.13	Product turned from light green to dark blue
	112.0	-1.55	70	50	16.5	1.10	

is difficult to offer an explanation for this effect. Perhaps changes in cell resistance occurred during electrolysis; against this argument, however, the initial resistance of the cell was the same as that in electro-oxidation experiments (about $1K\Omega$).

These data thus confirm the results of the cyclic voltammetry experiments which indicated one electron oxidation and one electron reduction processes. In addition, the coulometric studies showed that the product species must have an appreciable stability (of the order of hours) and that preparative scale electrolyses were feasible.

There have been few previously reported coulometric studies on complexes of iron(II), cobalt(II) and nickel(II) with nitrogen-donor ligands in non-aqueous solvents with which the present data can be compared. Nemec et al.³⁰⁰ attempted the oxidative constant potential coulometry of tris-bipyridyl iron(II) perchlorate but the results were inconclusive. However, the same authors observed one electron transfer in the electro-reduction of the complex ions $\{Co(bipy)_3\}^{3+}$ and $\{Fe(bipy)_3\}^{3+}$ at a rotating platinum electrode. No data are available for nickel(II) polypyridyl complexes. Two groups of workers, Olson and Vasilveskis^{107,145,211} and Busch et al.^{186,304} have carried out coulometric studies on iron(II), cobalt(II) and nickel(II) complexes containing square-planar amine ligands in acetonitrile and have found one electron oxidation and reduction processes to be operative.

5.4. Electrosynthesis and properties of metal(III) and metal(I) polypyridyl complexes of iron, cobalt and nickel

5.4.1. Preparation of polypyridyl complexes of iron(III), cobalt(III), and nickel(III) perchlorates by electro-oxidation of the corresponding metal(II) complexes

The main interest in this series of electrochemical syntheses lies in the uncommon nickel(III) polypyridyl complexes of which $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_3$, $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_3$ and $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_3$ have not been previously reported. Although the electrosyntheses of iron(III) and cobalt(III) polypyridyl complexes are of lesser importance, these have been included, since they provided a check on the technique by giving stable known products. The electrosynthesis of cobalt(III) complexes was also considered to be of interest by allowing a comparison to be made with more common chemical methods of preparation.

Table XII, page 147 gives the experimental details of the electrochemical preparations carried out by the method described in section 4.3.3., page 86. The controlled potential applied in each anodic oxidation was the same as that of the corresponding coulometric experiment (c.f. Table X, pages 141, 142). Magnetic susceptibility data (c.f. section 4.4.2., page 89) are also included.

The analysis and properties of each product are now discussed. Although electronic spectral data will be included here, a more detailed discussion, including attempts to make assignments for d - d transitions, will be given later in section 5.6.

Tris(2,2'-bipyridyl) nickel(III) perchlorate, $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_3$

The bright green needle shaped crystals appeared to be stable provided that care was taken to exclude moisture, exposure to the

Table XII

Metal(III) complex	Weight of metal(II) complex taken	Anodic potential	Method of isolation	% yield theoretical	Nature of product	Effective magnetic moment
	g	V				B.M.
(i) {Fe(bipy) ₃ }(ClO ₄) ₃	1.0	+1.480	A	70	blue	2.18
(ii) {Fe(dimbipy) ₃ }(ClO ₄) ₃	1.0	+0.560	A	70	blue	2.36
(iii) {Fe(terpy) ₂ }(ClO ₄) ₃	1.0	+0.300	A	85	blue-ash	2.12
(iv) {Co(bipy) ₃ }(ClO ₄) ₃	2.0	+0.040	A	80	yellow	diamagnetic
(v) {Co(dimbipy) ₃ }(ClO ₄) ₃	1.0	-0.105	A	80	yellow	diamagnetic
(vi) {Co(terpy) ₂ }(ClO ₄) ₃	1.0	+0.003	A	70	orange	diamagnetic
(vii) {Ni(bipy) ₃ }(ClO ₄) ₃	2.0	+1.480	A	70	green	2.10
(viii) {Ni(dimbipy) ₃ }(ClO ₄) ₃	1.0	+1.370	A	72	green	1.95
(ix) {Ni(terpy) ₂ }(ClO ₄) ₃	1.0	+1.350	A	91	grey-ash	4.90

atmosphere resulting in a colour change to the pink of the nickel(II)-bipyridyl complex. The oxidising properties of the product were shown by its ability to react with iodine(-I) to give iodine(0) in the test described in section 4.5.1., page 90.

Elemental analysis of the product was consistent with the formula $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_3$ as shown by the good agreement between the two sets of data given below:

Element	C	H	N	Ni
% Theoretical for the above formula	43.59	2.90	10.17	7.10
% Found	43.39	3.30	10.34	7.11

The somewhat high figure for the hydrogen content might indicate the presence of small amount of water. Of the analytical figures quoted, that of nickel is probably the most reliable since it was determined immediately after the preparation, allowing little chance of water contamination. The excellent agreement of the nickel figures suggests that if water was present as a contaminant it must have been introduced at some stage between the time the product was packed into a small sample tube in the glove-box and its eventual analysis at the National Physical Laboratories, Teddington.

The visible and near infra-red spectrum of the product in acetonitrile is presented in figure 72, page 188 and shows maximum absorbances at 25900cm^{-1} and 16590cm^{-1} having corresponding molar extinction co-efficients $106\text{mol}^{-1}\text{cm}^{-1}$ and $60\text{mol}^{-1}\text{cm}^{-1}$ respectively, the low values of which are indicative of d - d transitions. The infra-red spectrum of the complex was identical to that of $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_2$, indicating no chemical or structural change in the

ligand due to electrolysis.³⁰⁵

The effective magnetic moment of the nickel atom in the complex was found to be 2.10 B.M. at room temperature indicating one unpaired electron which is consistent with a spin paired octahedral $d^7 (t_{2g}^6 e_g^1)$ configuration. Although the value of 2.10 is higher than the "spin only" magnetic moment of 1.73 B.M., it is very near to reported values for other nickel(III) complexes;^{145,198,203,229,306} the high value is attributed to a second order orbital contribution.

Tris(4,4'-dimethyl-2,2'-bipyridyl) nickel(III) perchlorate,
 $\{Ni(dimbipy)_3\}(ClO_4)_3$

The bright green needle shaped crystals were less soluble in acetonitrile than the corresponding bipyridyl complex, and some of the product precipitated out during electrolysis. The purified product, which again showed oxidising properties (c.f. section 4.5.1, page 90) appeared to be more stable than $\{Ni(bipy)_3\}(ClO_4)_3$ as it did not turn pink on exposure to the atmosphere even after a week. However, it was very hygroscopic and analytical data, presented below, indicated that up to two moles of water per mole of the complex could be taken up over a period of about 4 days, even when the sample was stored in a screw-tight bottle.

Element	C	H	N	Ni
% Calculated for	47.48	3.95	9.23	6.45
$\{Ni(dimbipy)_3\}(ClO_4)_3$				
% Found (next day)	47.50	3.98	9.20	6.38
(after 4 days)	45.97	4.55	8.88	6.26
% Calculated for	45.71	4.30	8.86	6.22
$\{Ni(dimbipy)_3\}(ClO_4)_3 \cdot 2H_2O$				

The analysis carried out the day after preparation is in excellent agreement with the composition $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_3$, while that carried out after four days corresponded closely to the composition $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. Although water was taken up by the complex, there did not appear to be any change in the chemical reactivity of the complex which retained its power to oxidise iodide to iodine.

The visible and near infra-red spectrum of this complex is presented in figure 73, page 189 and shows peak absorbances at 24150cm^{-1} and 16660cm^{-1} with corresponding molar extinction co-efficients of $125\text{mol}^{-1}\text{cm}^{-1}$ and $33\text{mol}^{-1}\text{cm}^{-1}$ respectively, the low values being indicative of d - d transitions.

The value of 1.95 B.M. determined for the effective magnetic moment of the complex is again consistent with a spin paired octahedral d^7 configuration.

Bis(2,2',2''-terpyridyl) nickel(III) perchlorate, $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_3$

The product consisted of hard dark grey coloured crystals. It gave a positive iodine test (c.f. section 4.5.1., page 90). Elemental analysis was carried out on two different batches prepared on two different dates and the results obtained for these are given below, the carbon, hydrogen and nitrogen data being obtained by two different analysts using the same instrument:

Element	C	H	N	Ni
% Calculated for the above formula	43.75	2.68	10.20	7.13
% Found (1st batch)	38.39	3.09	8.78	4.85
(2nd batch)	38.39	2.69	9.74	4.60

Agreement between the figures calculated for $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_3$ and those found are not good, although there is fair consistencey between the two sets of data for the different batches. Comparison between the experimental data and figures calculated for other formulae, such as $\{\text{Ni}(\text{terpy})_3\}(\text{ClO}_4)_3$ and $\{\text{Ni}_2(\text{terpy})_3\}(\text{ClO}_4)_6$ does not give any better overall correlation. If it is assumed that the nickel(III)-terpyridyl complex is much more stable than the nickel(III) complexes containing bipyridyl and dimethyl-bipyridyl ligands, then the low analytical figures for carbon, hydrogen and nitrogen might arise from incomplete combustion, the low nickel figures resulting from incomplete break-down of the complex during digestion or in the flame of atomiser of the atomic absorption spectrophotometer. It must be concluded, however, that the composition of the nickel(III)-terpyridyl complex is in some doubt.

The visible and near infra-red spectrum (figure 74, page 190) in acetonitrile displayed maximum absorbances at 24040cm^{-1} and 20240cm^{-1} with corresponding molar extinction co-efficients of $19\text{mol}^{-1}\text{cm}^{-1}$ and $114\text{mol}^{-1}\text{cm}^{-1}$ respectively.

The magnetic properties of this nickel(III) complex contrast with those of $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_3$ and $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_3$. The effective magnetic moment of the nickel atom in the nickel(III)-terpyridyl complex, assuming this to have the composition $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_3$, was found to be 4.90 B.M., the mean of two determinations (4.89 B.M. and 4.92 B.M.) at 20°C . This value is consistent with a spin free octahedral d^7 ($t_{2g}^5 e_g^2$) configuration with a large expected orbital contribution, the value being well within the range of magnetic moments reported for spin free octahedral

cobalt(II) complexes which have a similar configuration.

Tris(2,2'-bipyridyl) cobalt(III) perchlorate, $\{Co(bipy)_3\}(ClO_4)_3$

This complex was obtained in 80% yield as bright yellow crystals which analysed according to the composition $\{Co(bipy)_3\}(ClO_4)_3$ as confirmed by the following data:

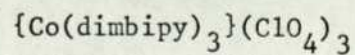
Element	C	H	N	Co
% Theoretical for the above formula	43.58	2.90	10.16	7.13
% Found (1st batch)	42.61	3.30	10.70	7.14
(2nd batch)	43.28	3.07	10.56	7.16

The agreement between the calculated figures and those determined for two different batches is good, with the possible exception of nitrogen figures; the high values for nitrogen content cannot readily be explained, except that it could be due to operative and/or instrumental error.

The spectrum in the visible and near infra-red region is presented in figure 75, page 191. Maximum absorbance occurs at 21840cm^{-1} the corresponding molar extinction co-efficients being $60\text{mol}^{-1}\text{cm}^{-1}$. The observation of this band is agreement with that found in aqueous solution by Martin and Waind,³⁰⁷ Csaszar²⁶⁸ and Maki³¹² who prepared the complex by the method described by Burstall and Nyholm.²⁷⁰

The complex was found to be diamagnetic at 292°K as expected for a spin paired octahedral d^6 configuration.

Tris(4,4'-dimethyl-2,2'-bipyridyl) cobalt(III) perchlorate,



The product obtained in about 80% yield was a brighter yellow

continued on page 192

Fig. 37 Relationship between concentration of the complex and forward peak current

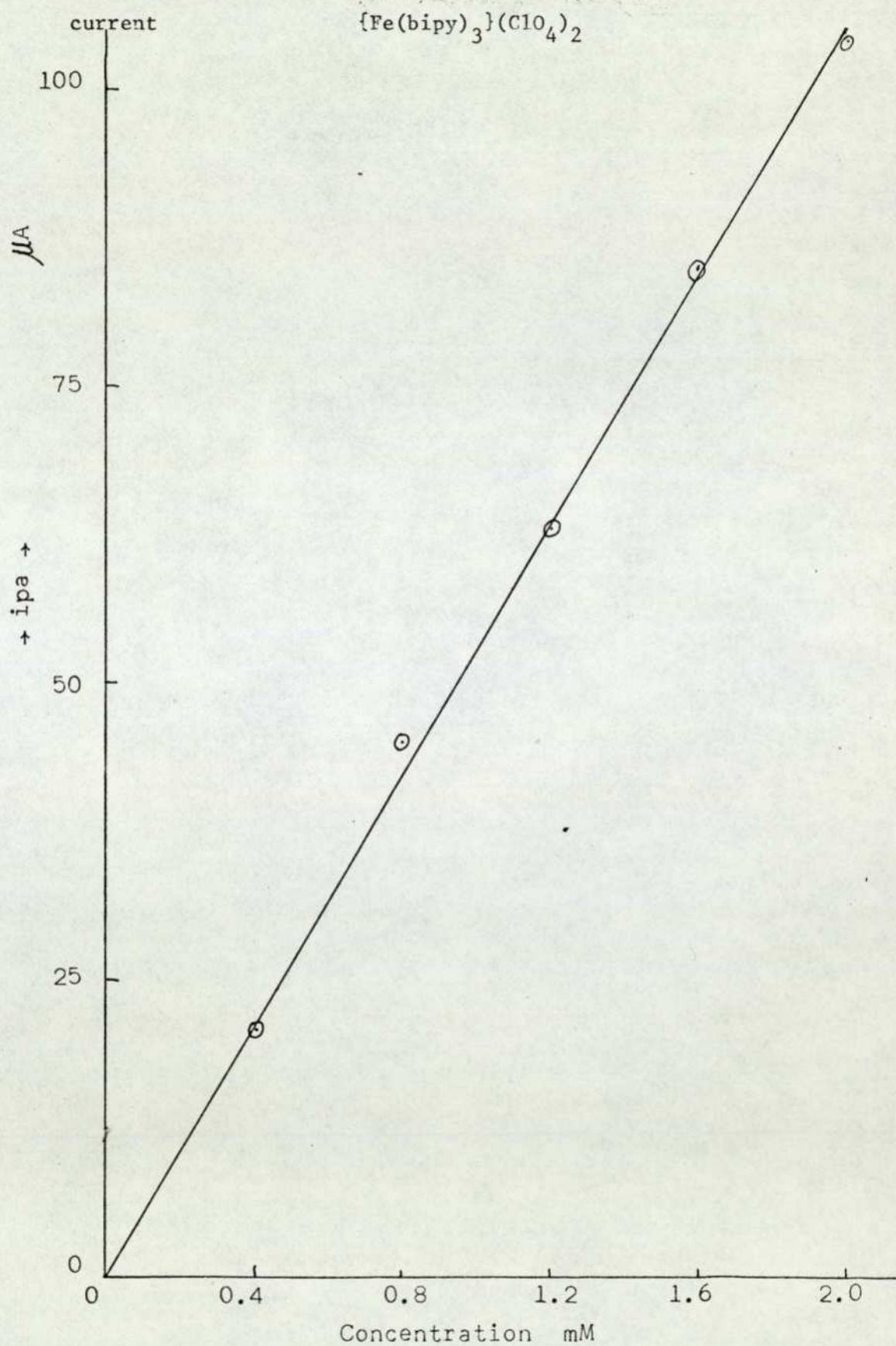
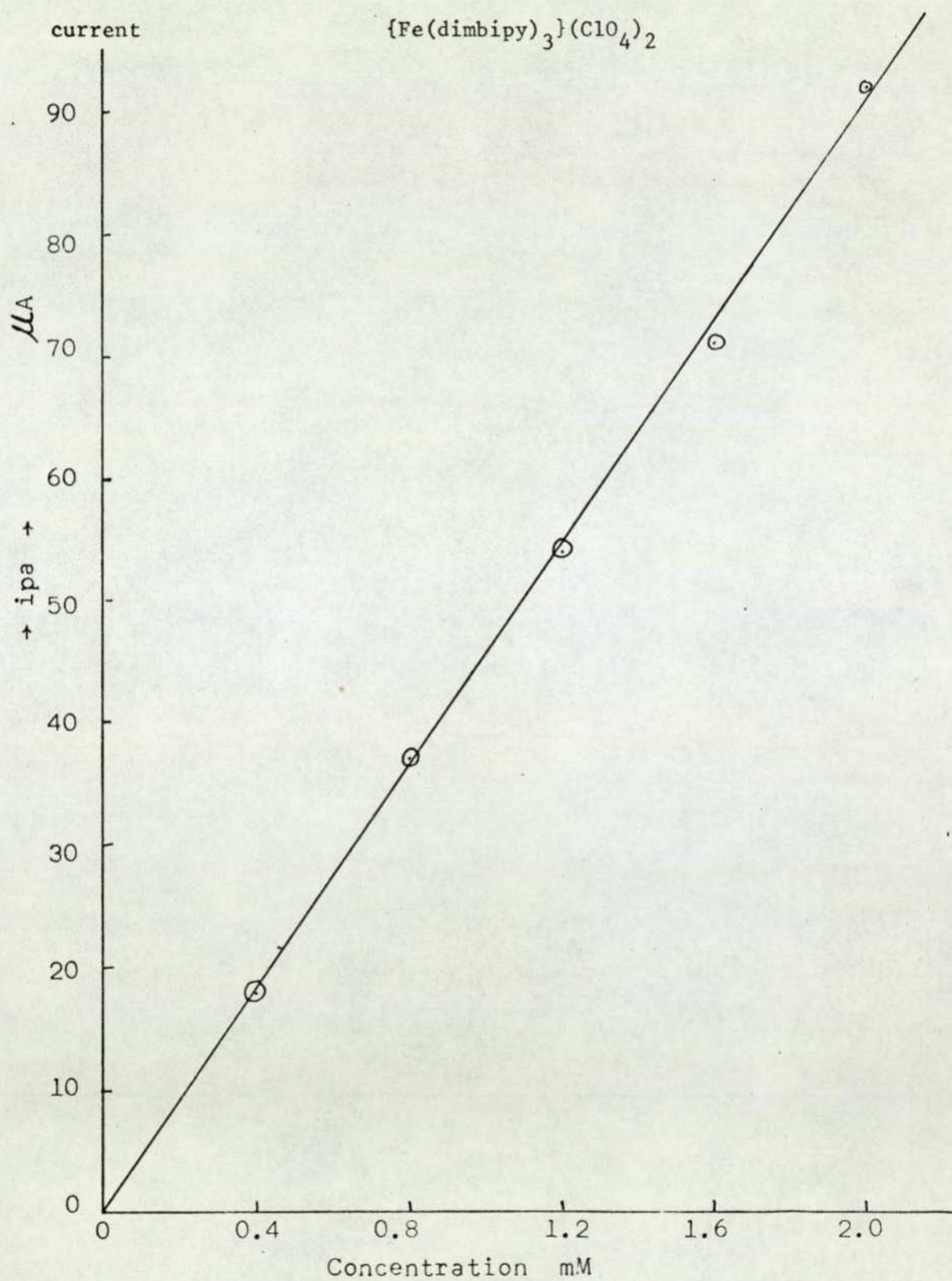


Fig. 38 Relationship between concentration of the complex and forward peak current



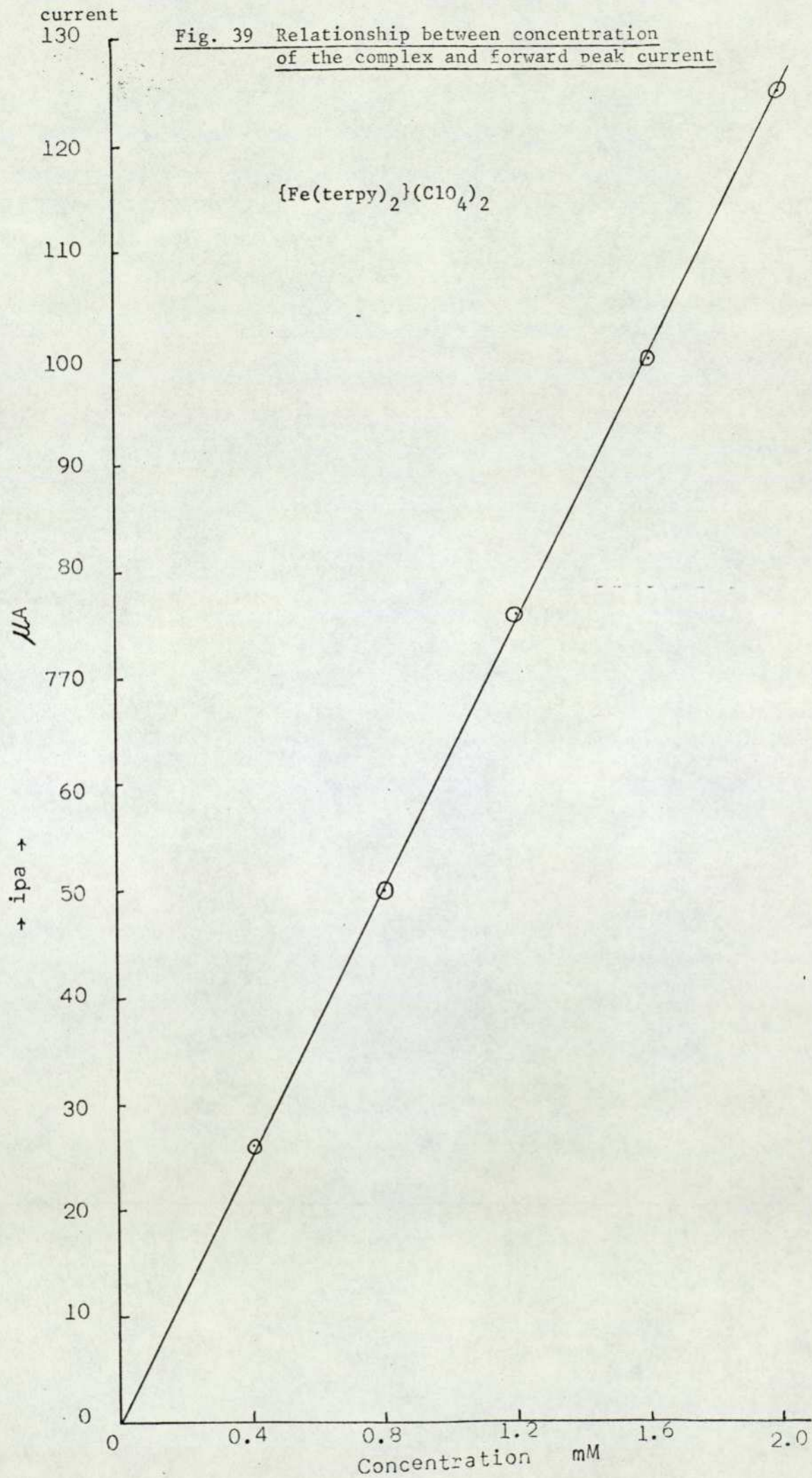


Fig. 40 Relationship between concentration of the complex and forward peak current

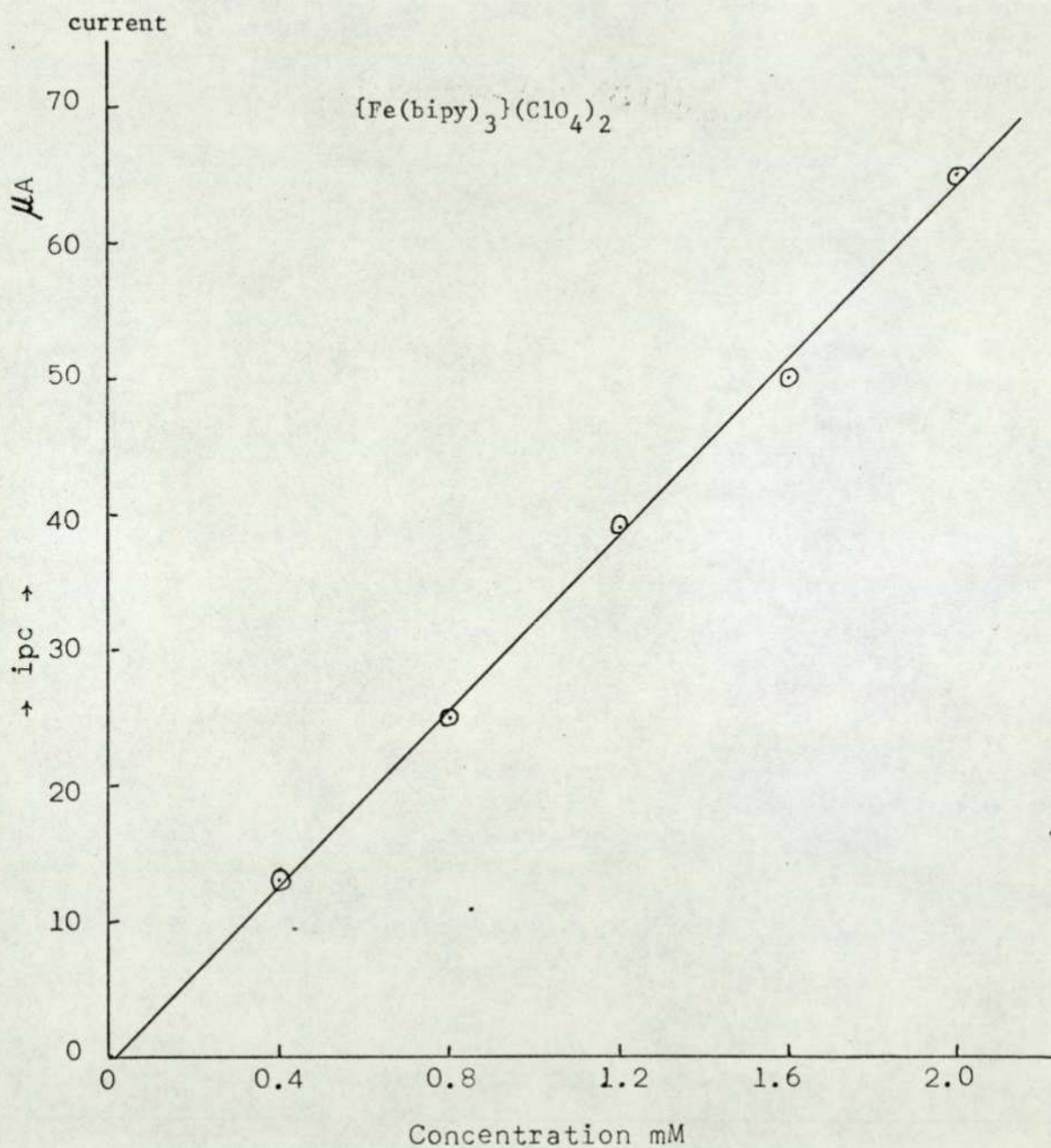


Fig. 41 Relationship between concentration of the complex and forward peak current

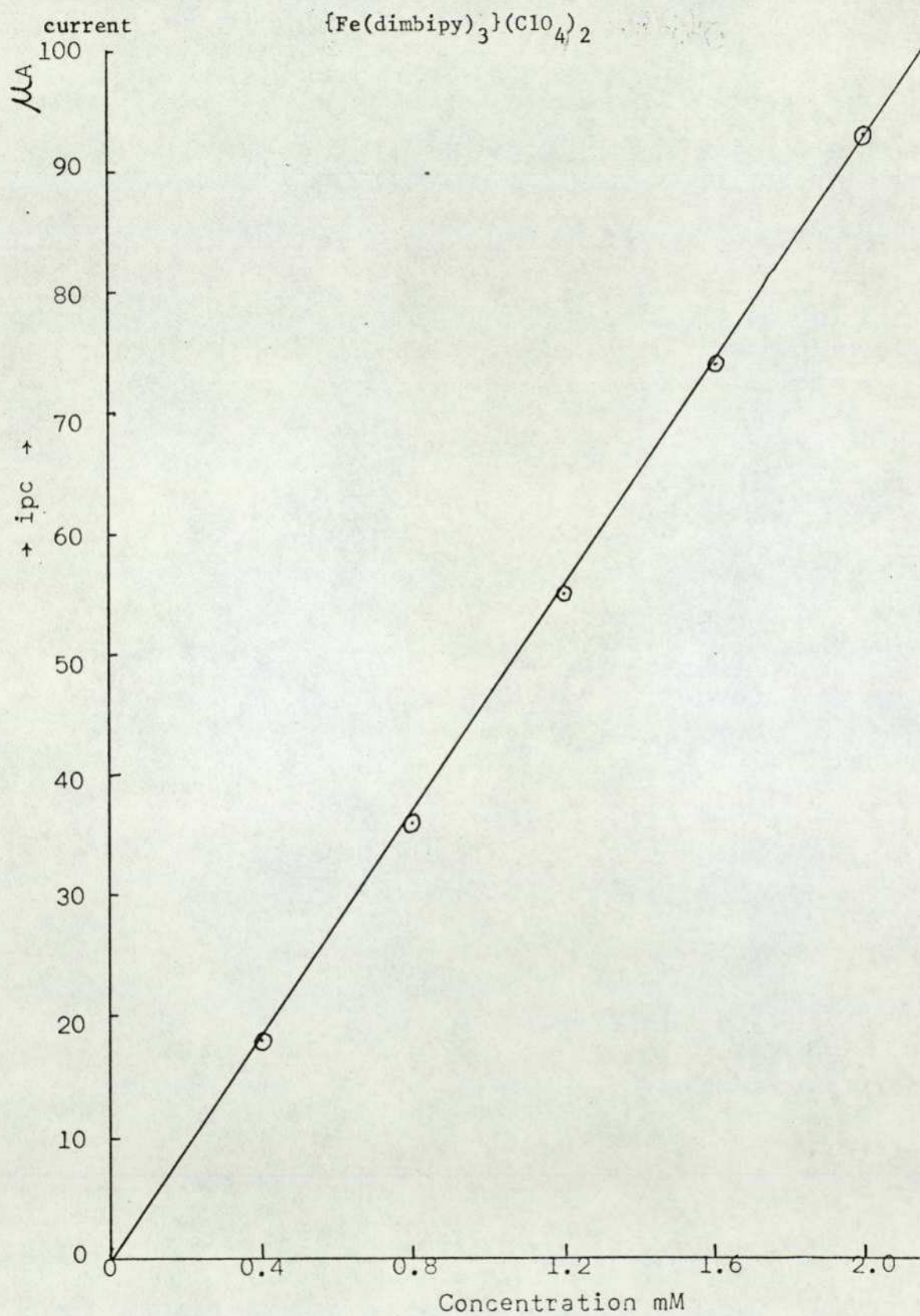


Fig. 42 Relationship between concentration of the complex and forward peak current

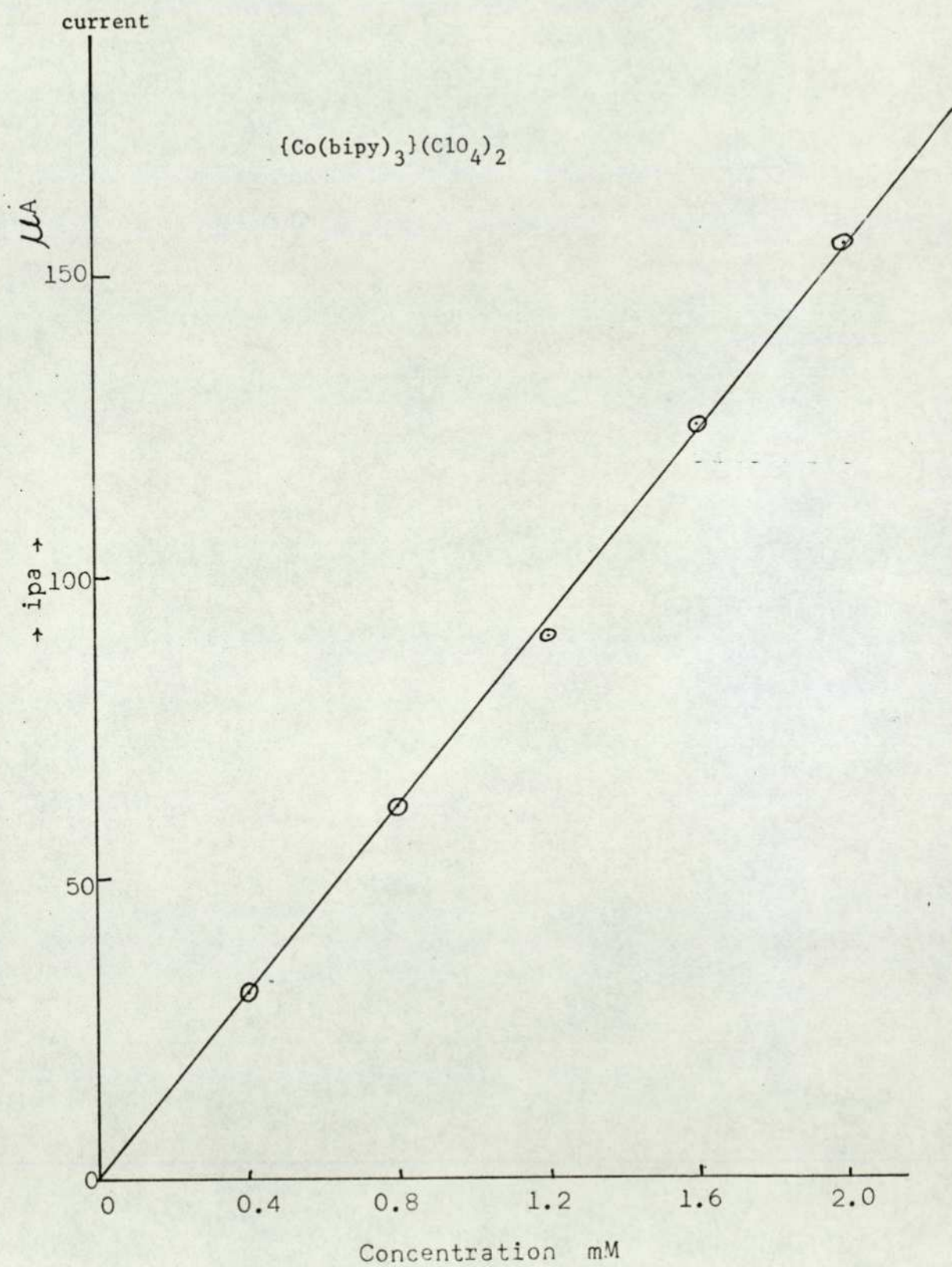


Fig. 43 Relationship between concentration of the complex and forward peak current

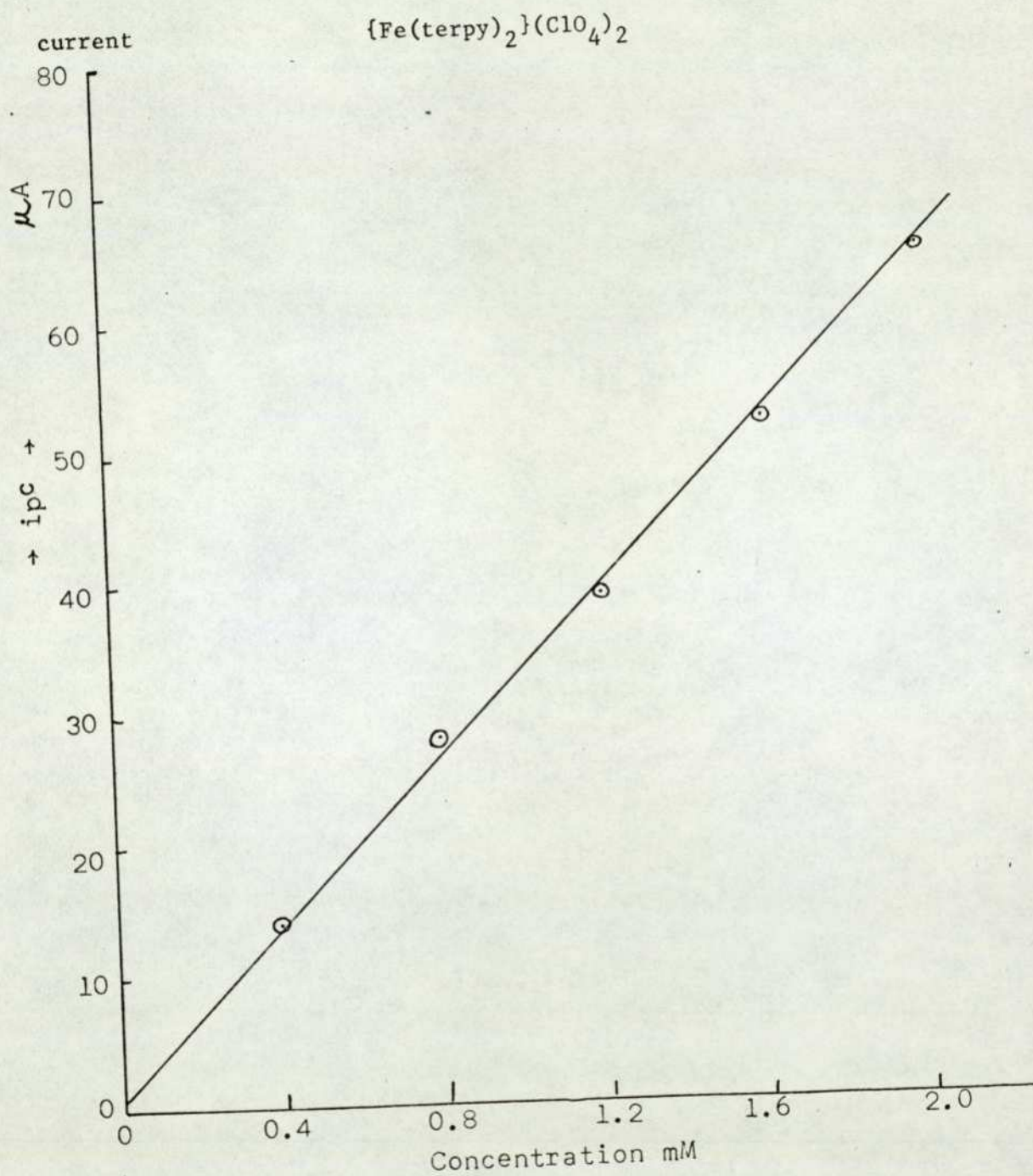
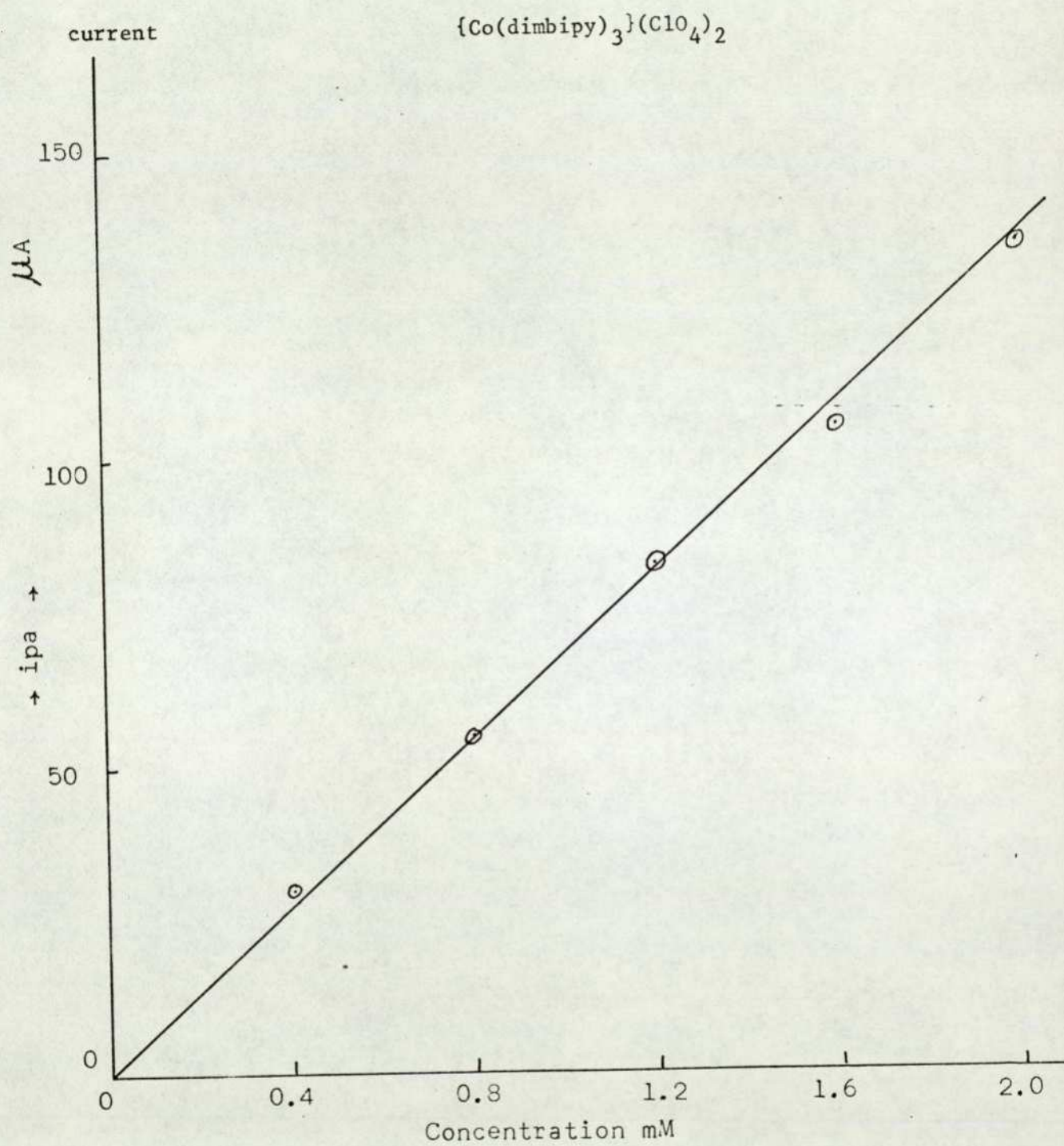


Fig. 44 Relationship between concentration of the complex and forward peak current



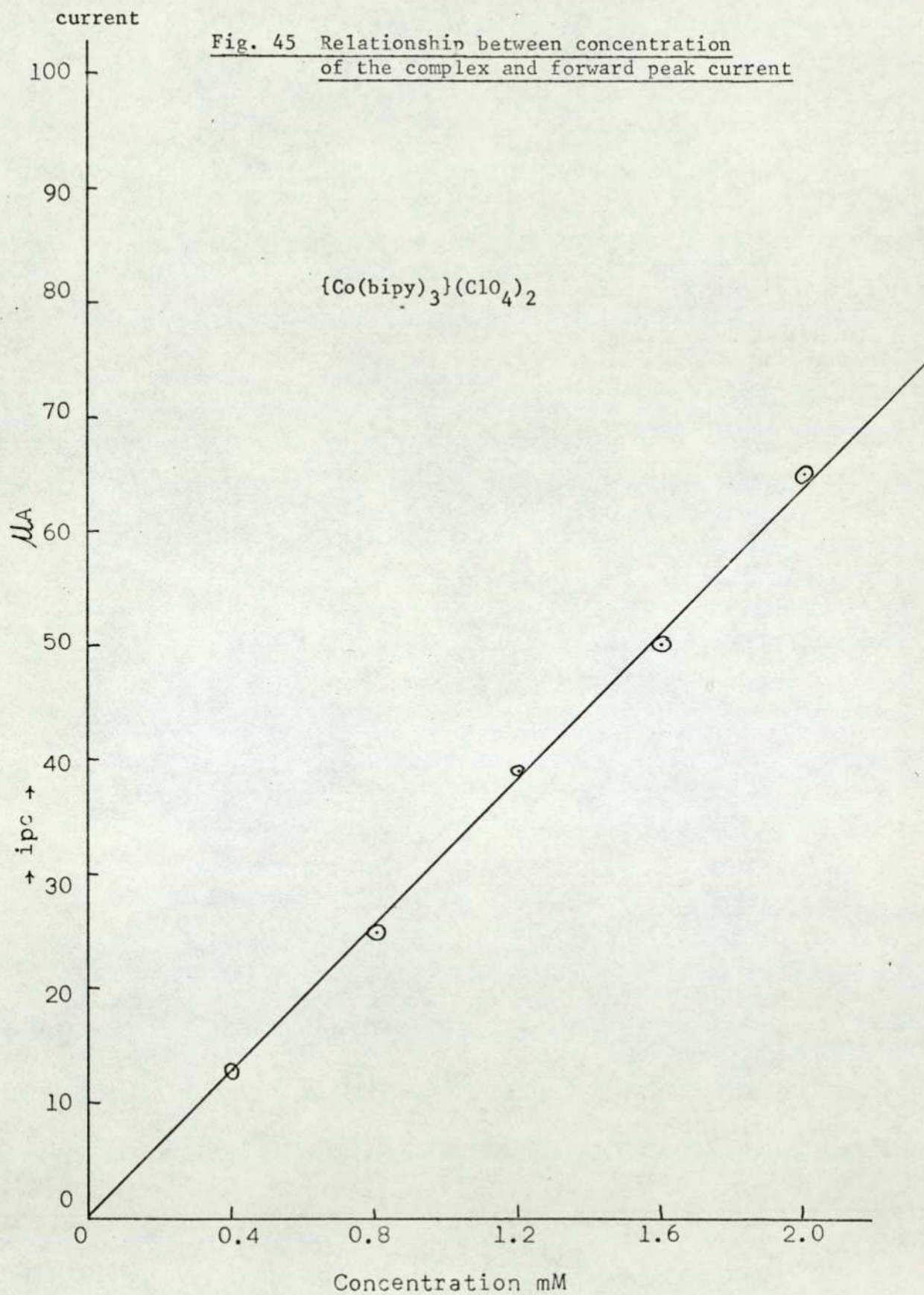


Fig. 46 Relationship between concentration of the complex and forward peak current

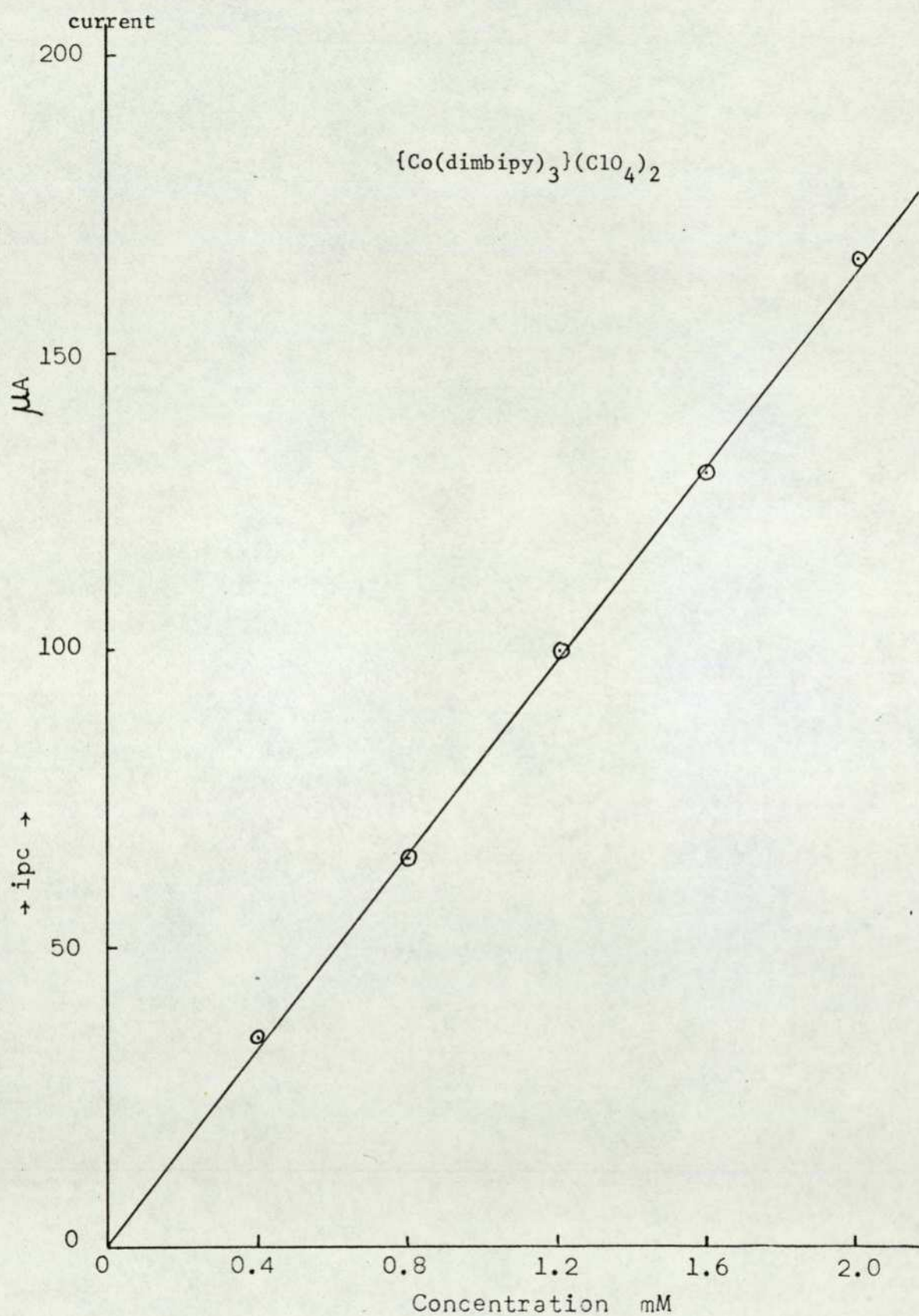
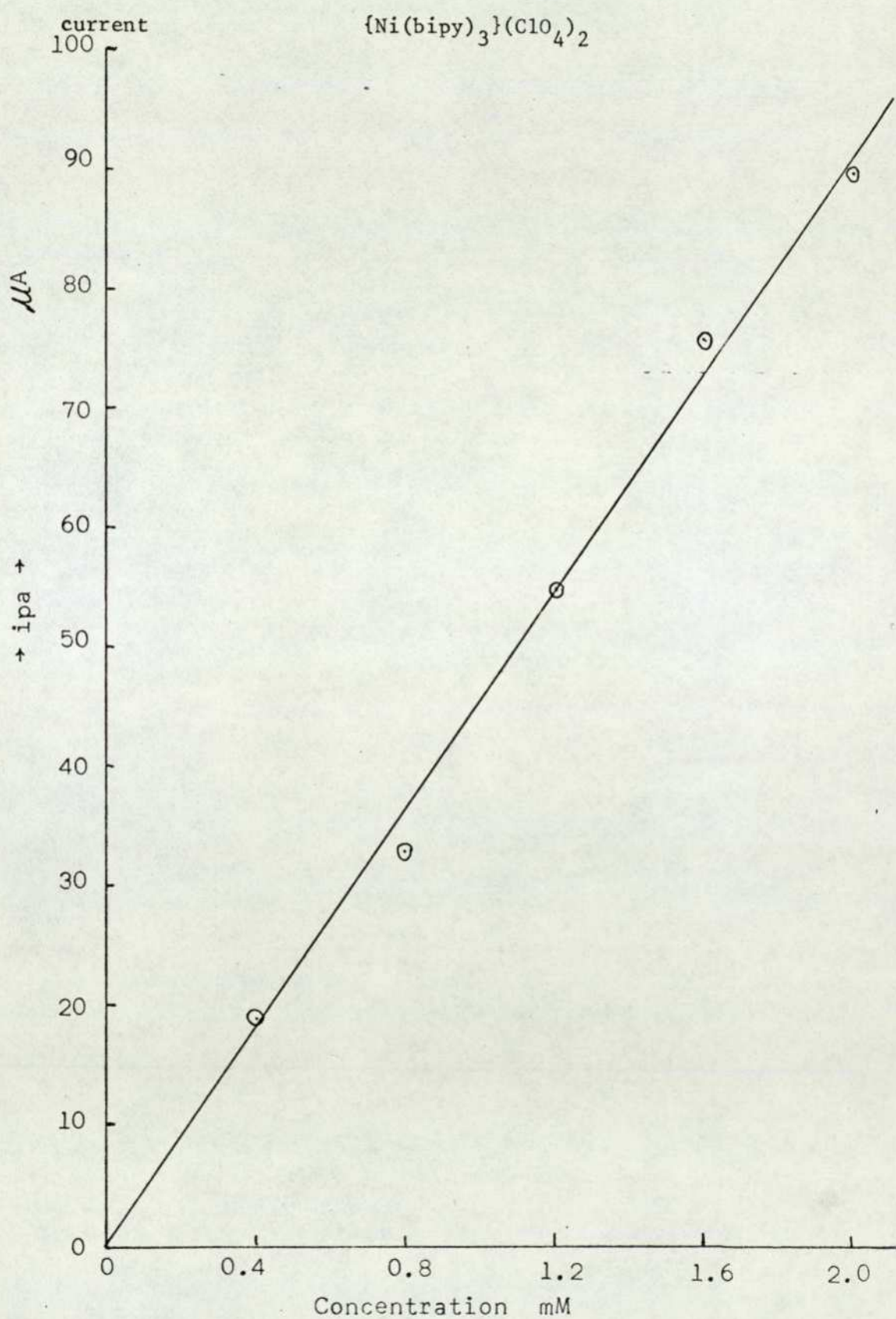


Fig. 47 Relationship between concentration of the complex and forward peak current



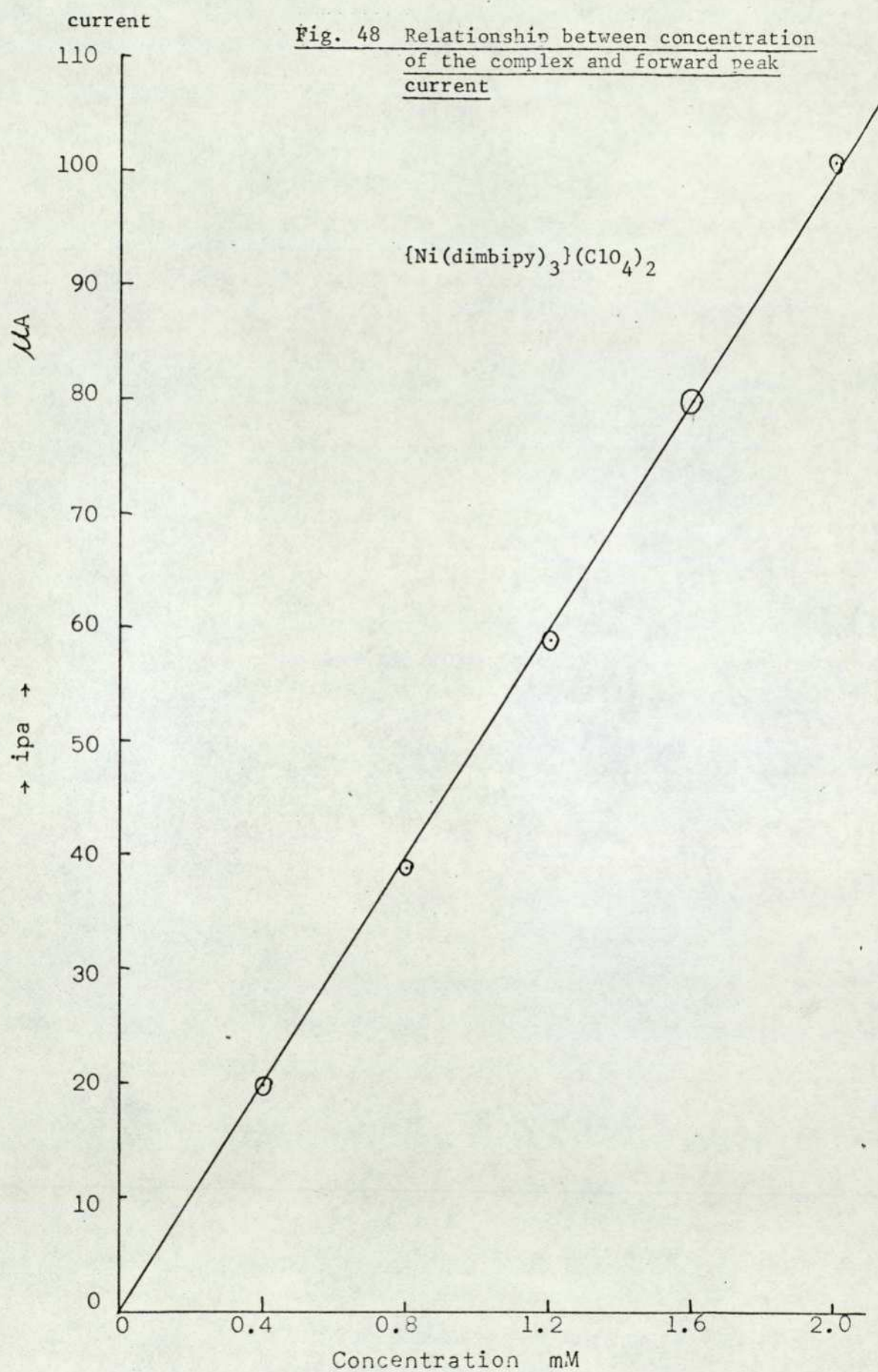


Fig. 49 Relationship between concentration
of the complex and forward peak current

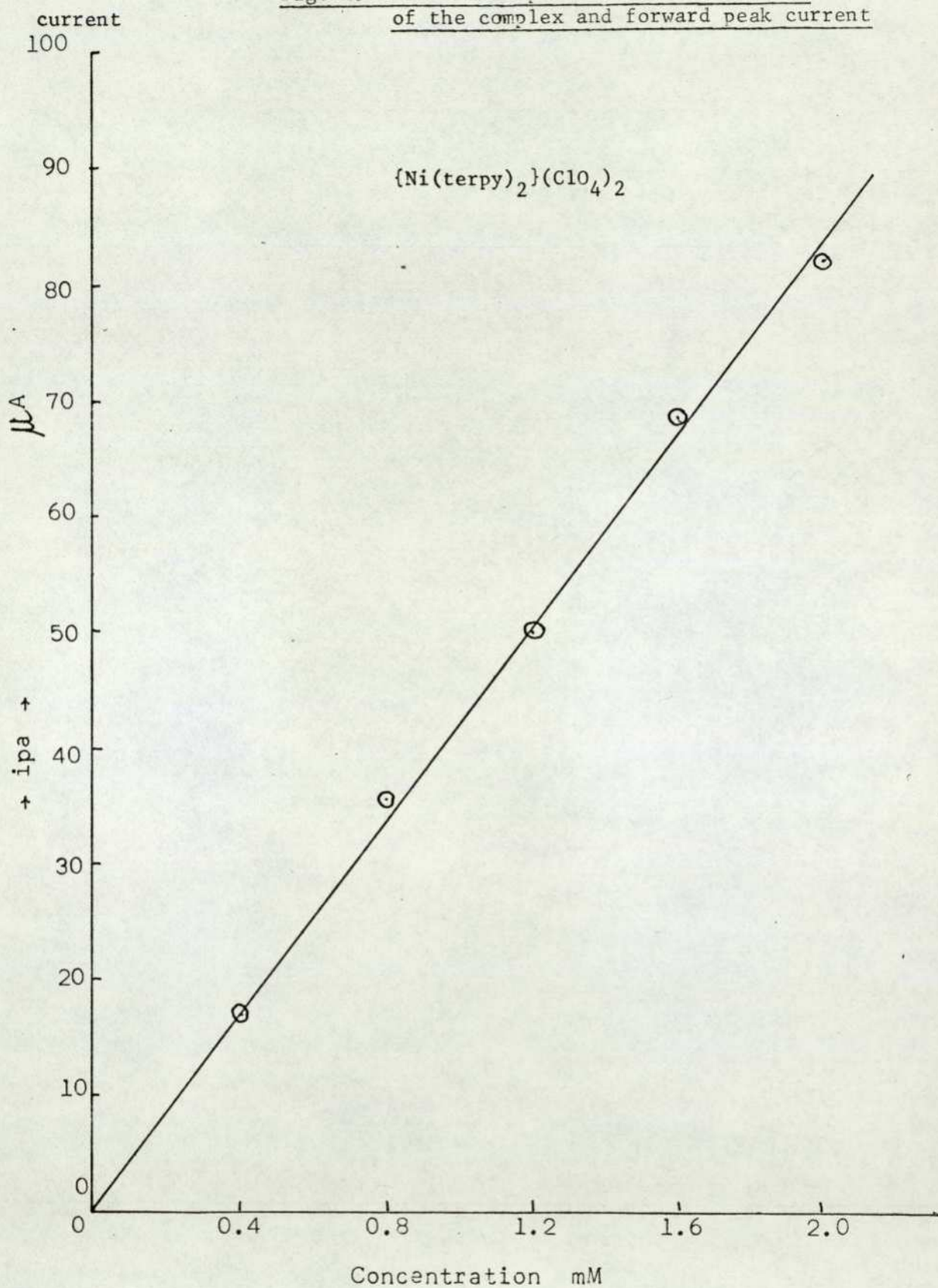
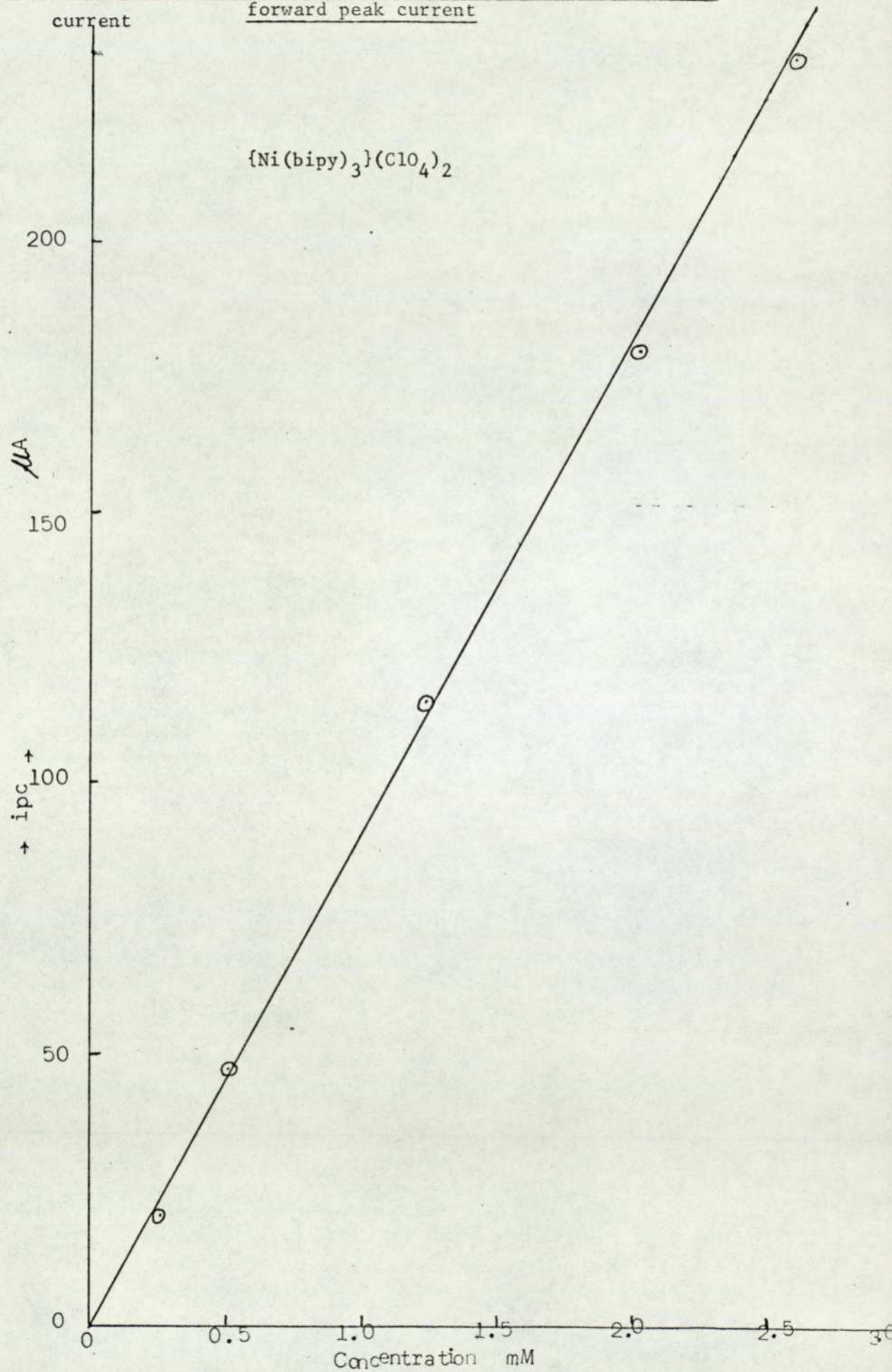
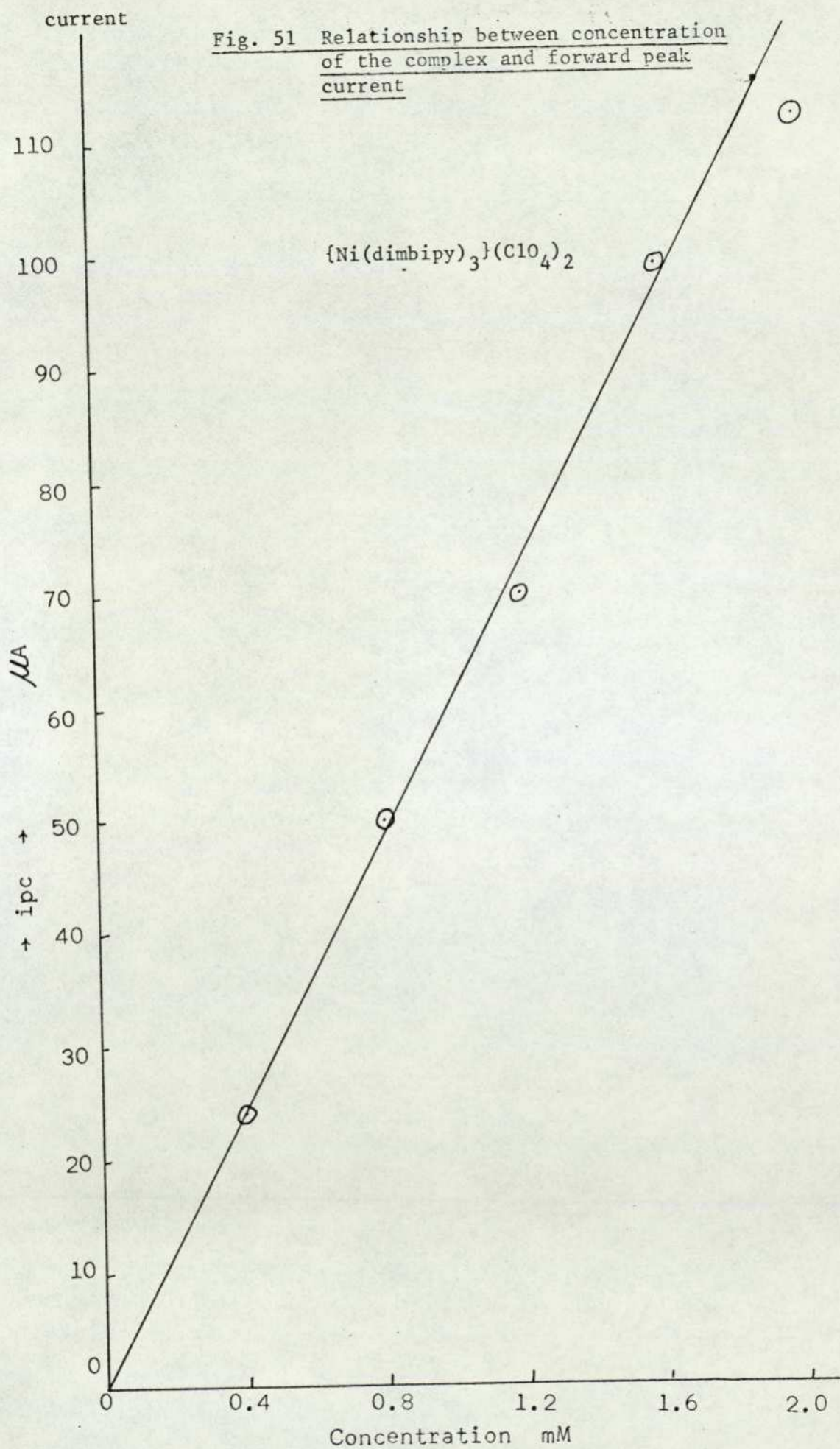
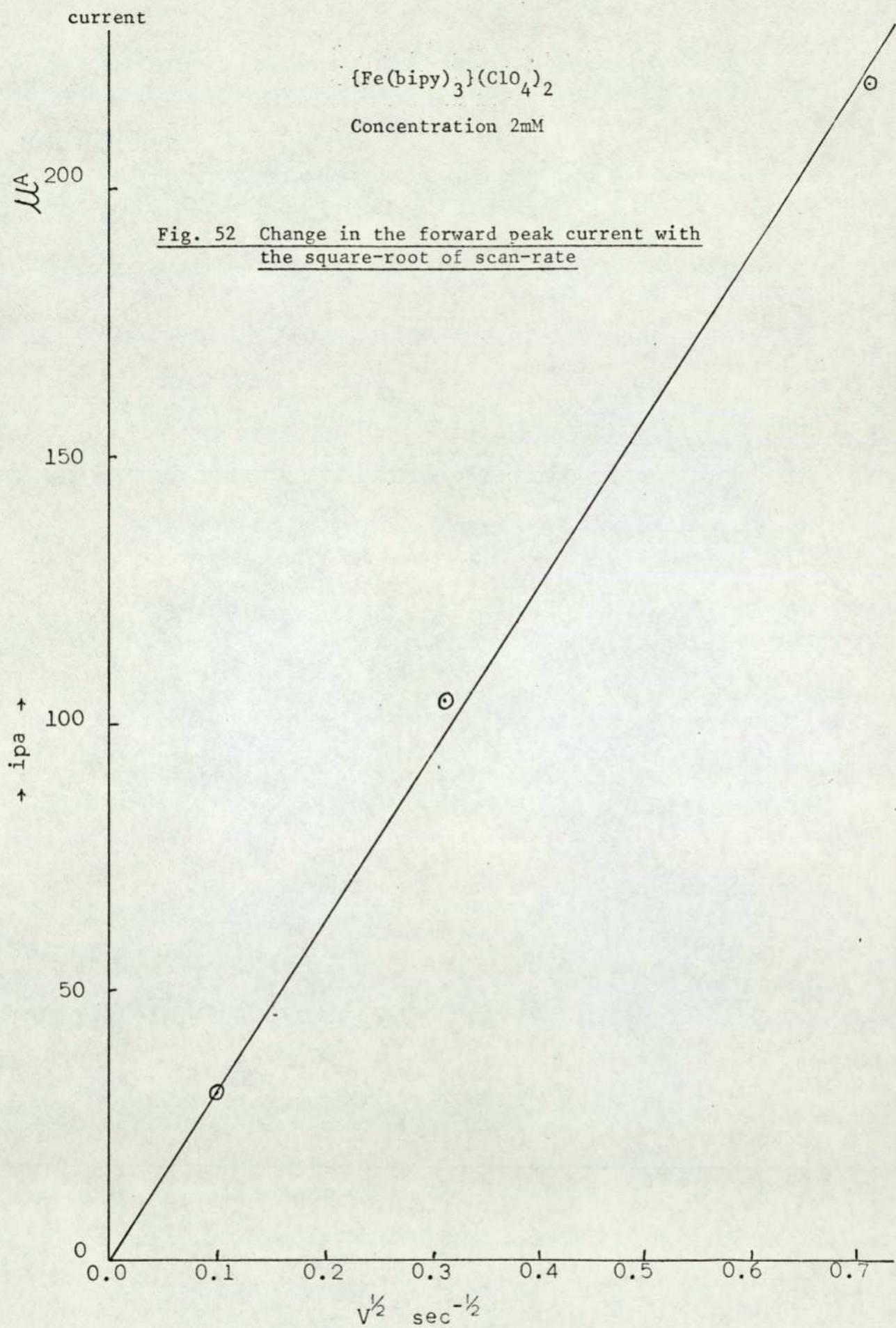
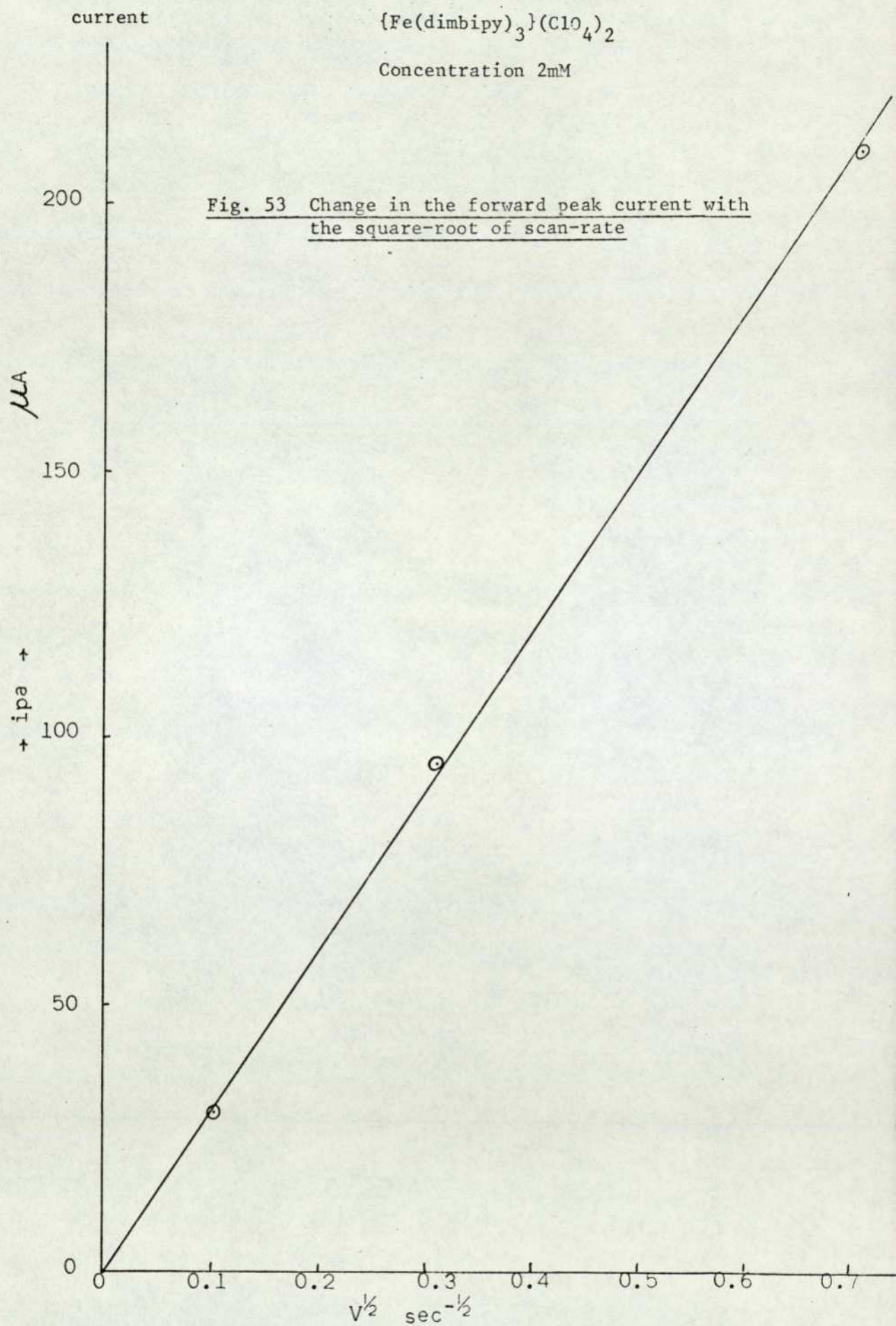


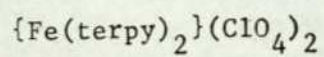
Fig. 50 Relationship between concentration of the complex and
forward peak current











Concentration 2mM

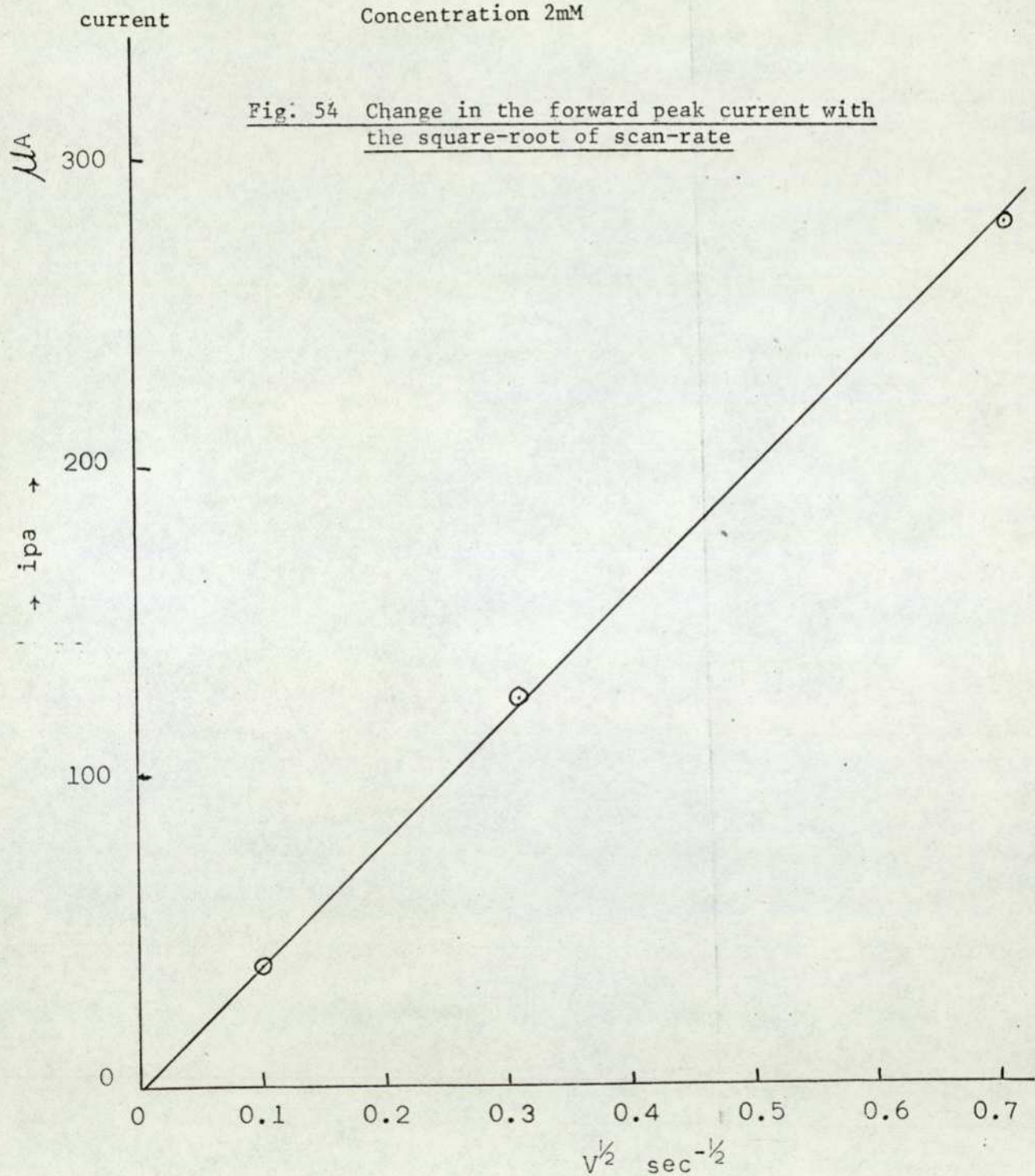


Fig. 55 Change in the forward peak current with the square-root of scan-rate

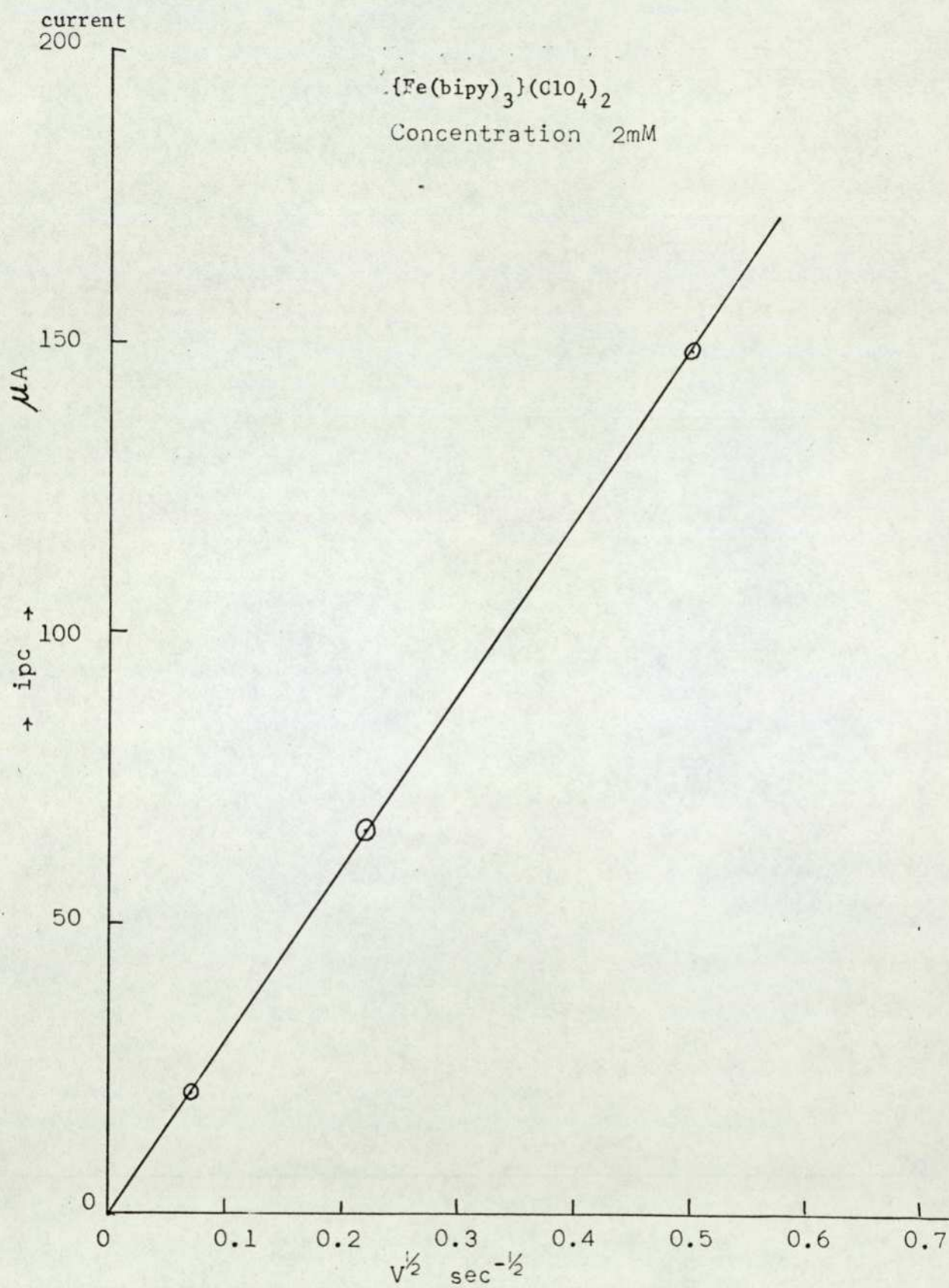


Fig. 56 Change in the forward peak current with the square-root of scan-rate

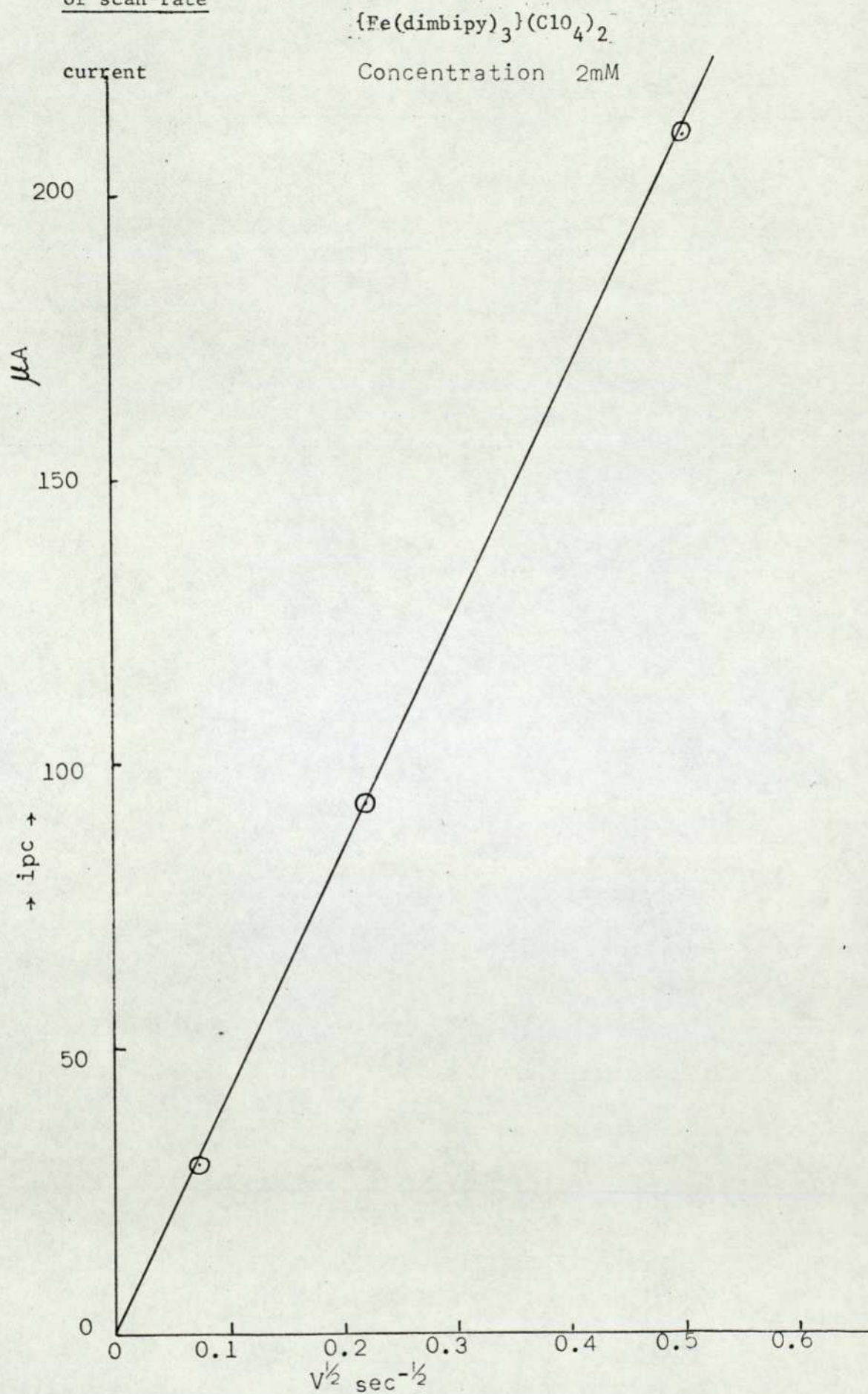
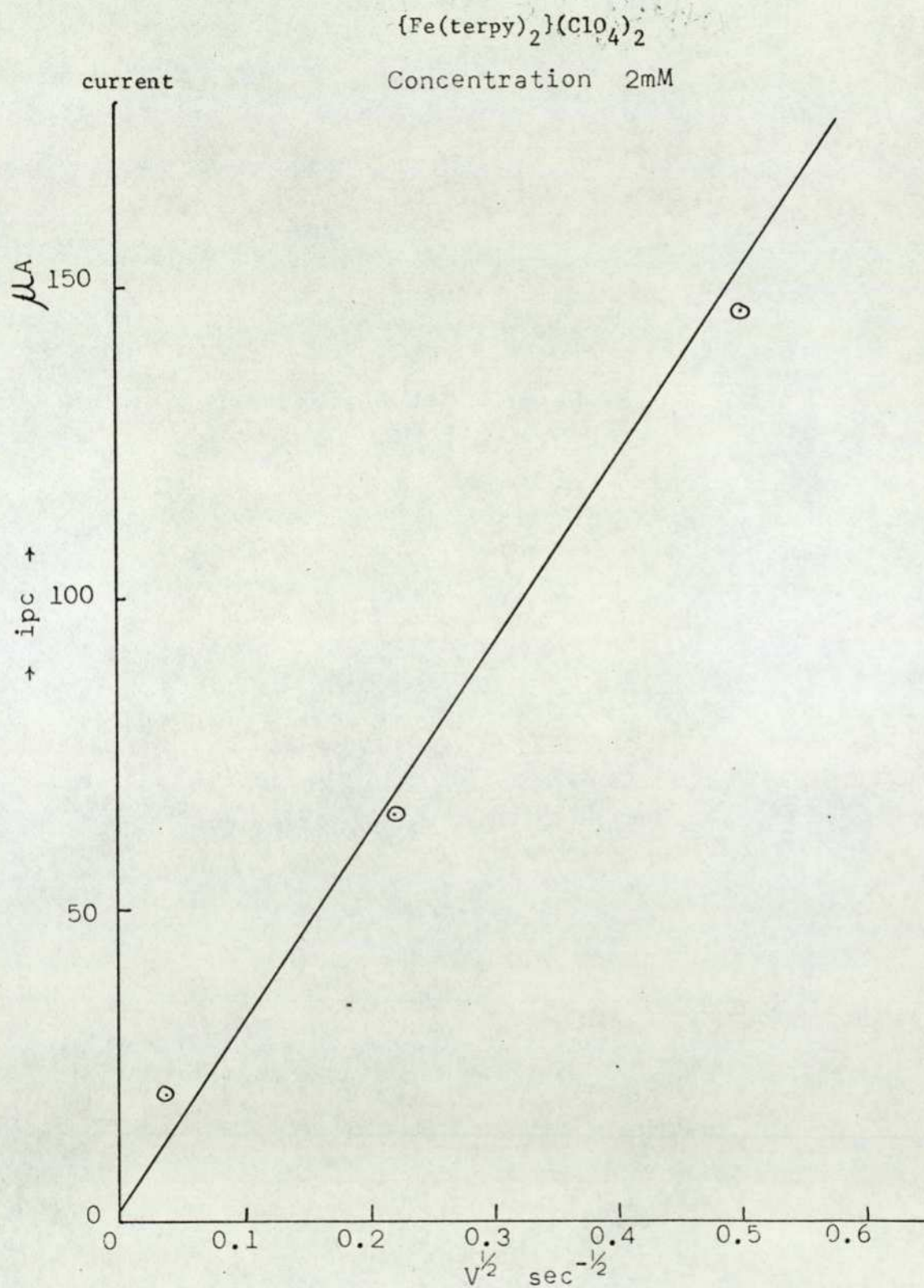
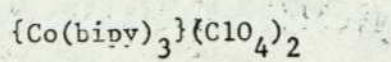


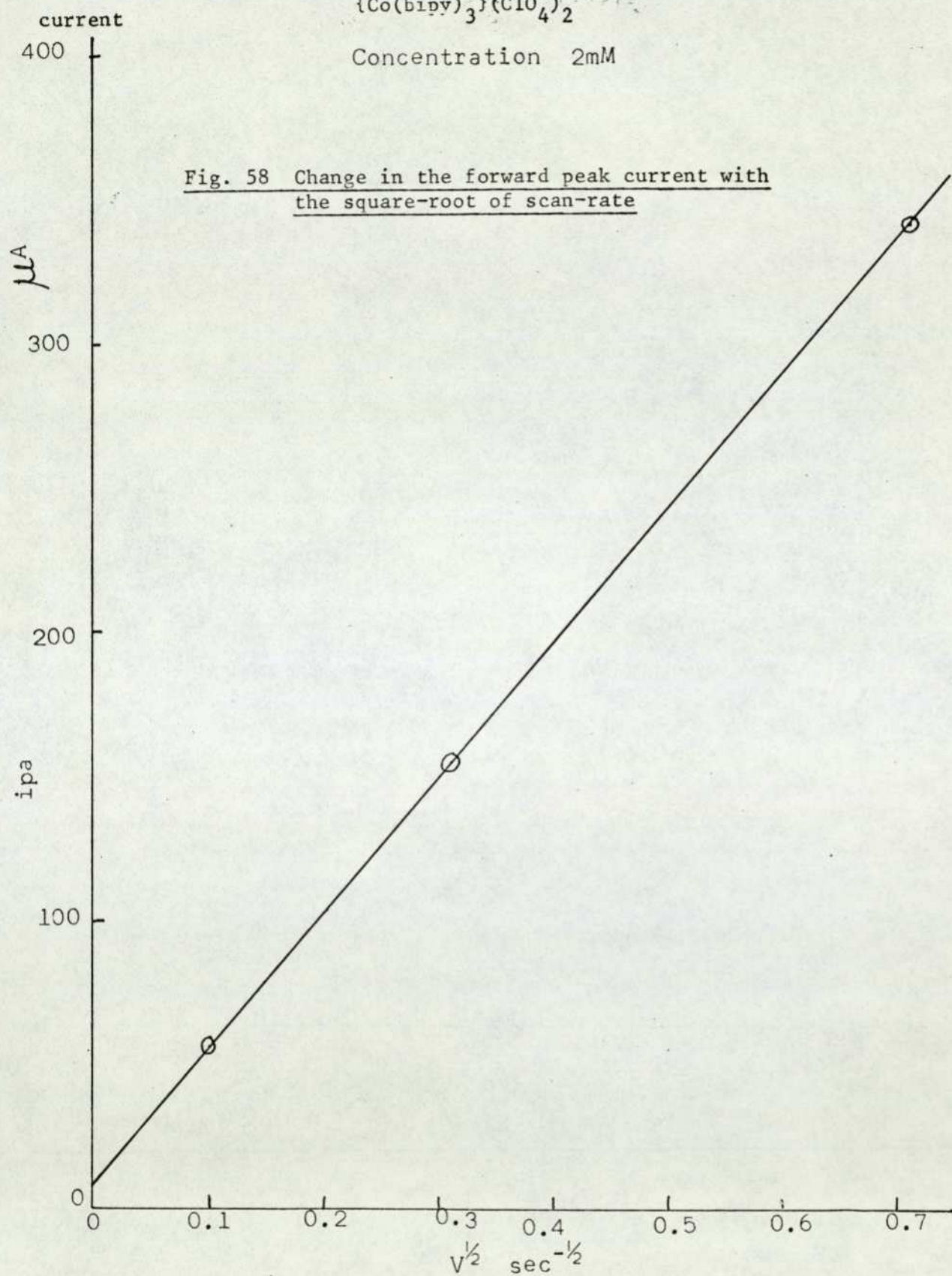
Fig. 57 Change in the forward peak current with the square-root of scan-rate

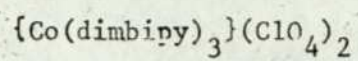




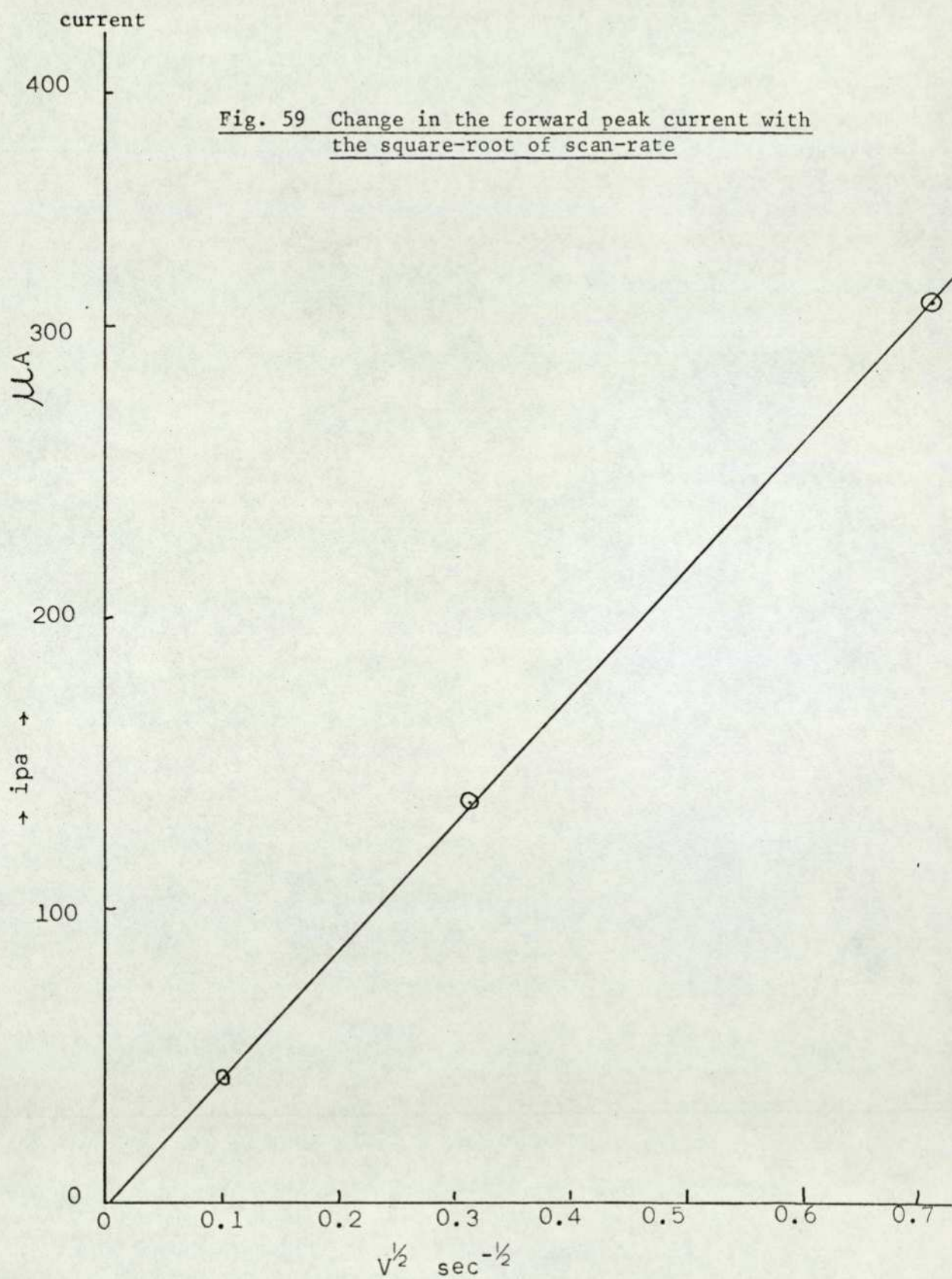
Concentration 2mM

Fig. 58 Change in the forward peak current with the square-root of scan-rate





Concentration 2mM



$\{\text{Co}(\text{terpy})_2\}(\text{ClO}_4)_2$

Concentration 2mM

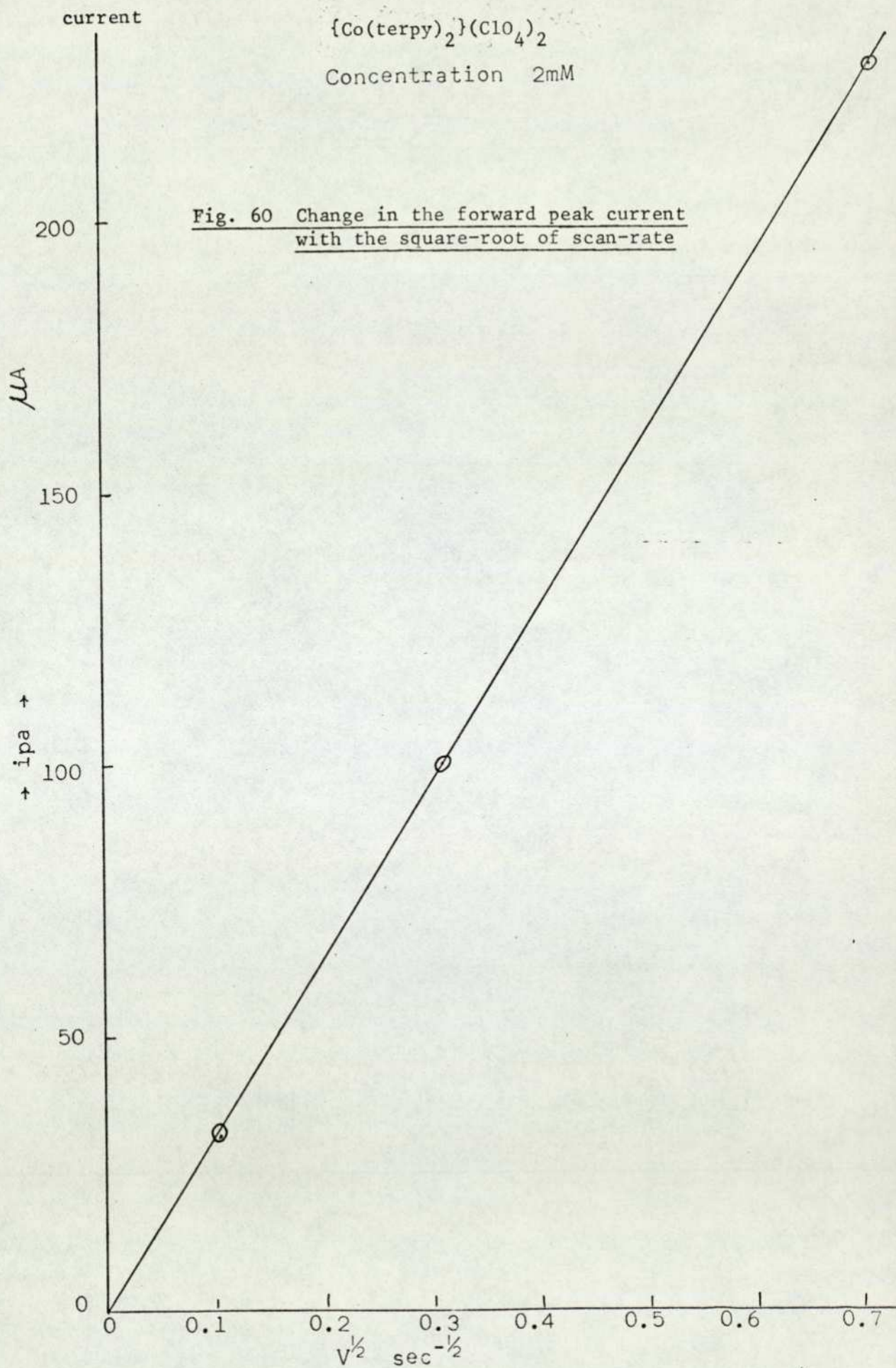
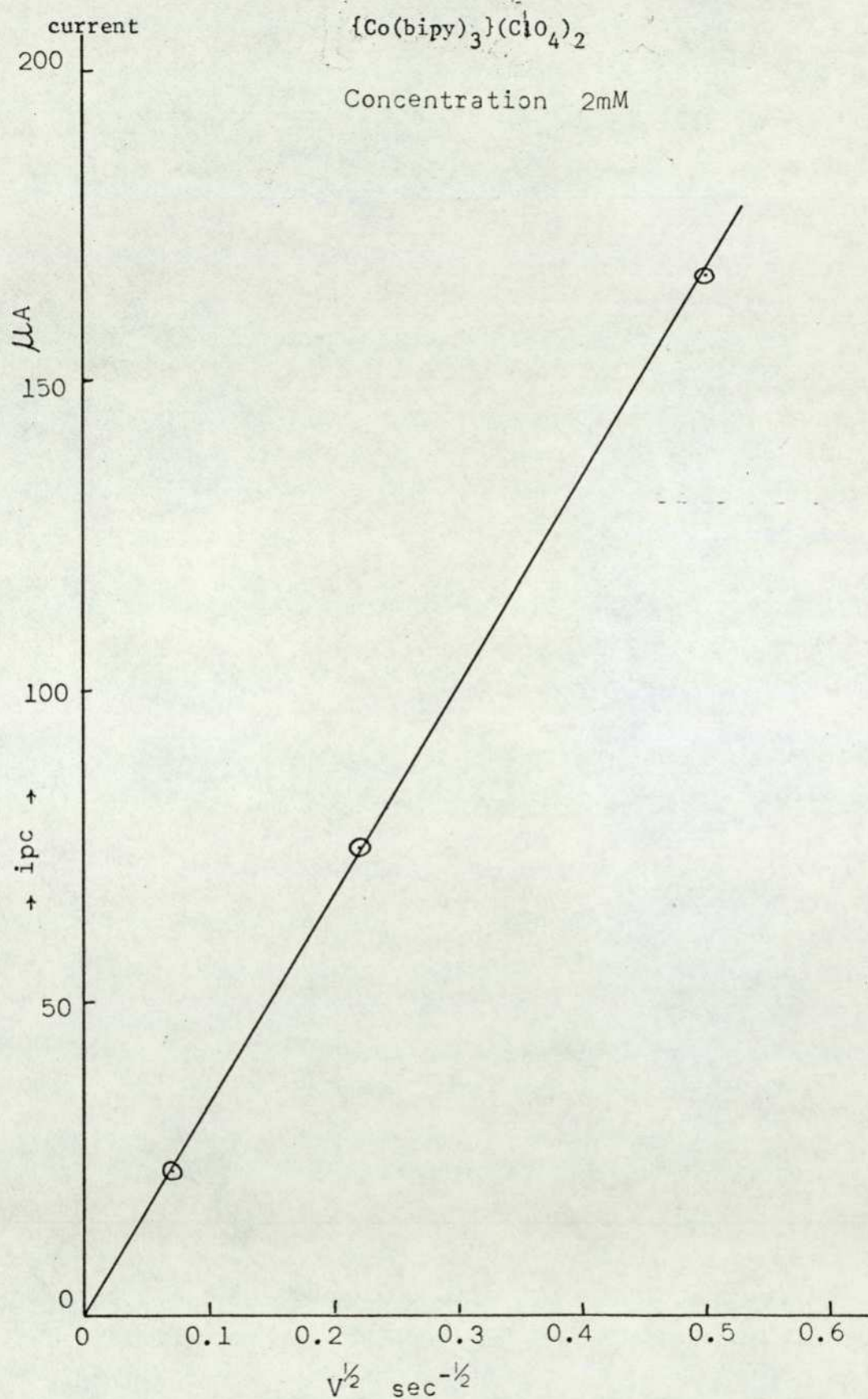
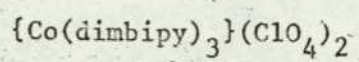
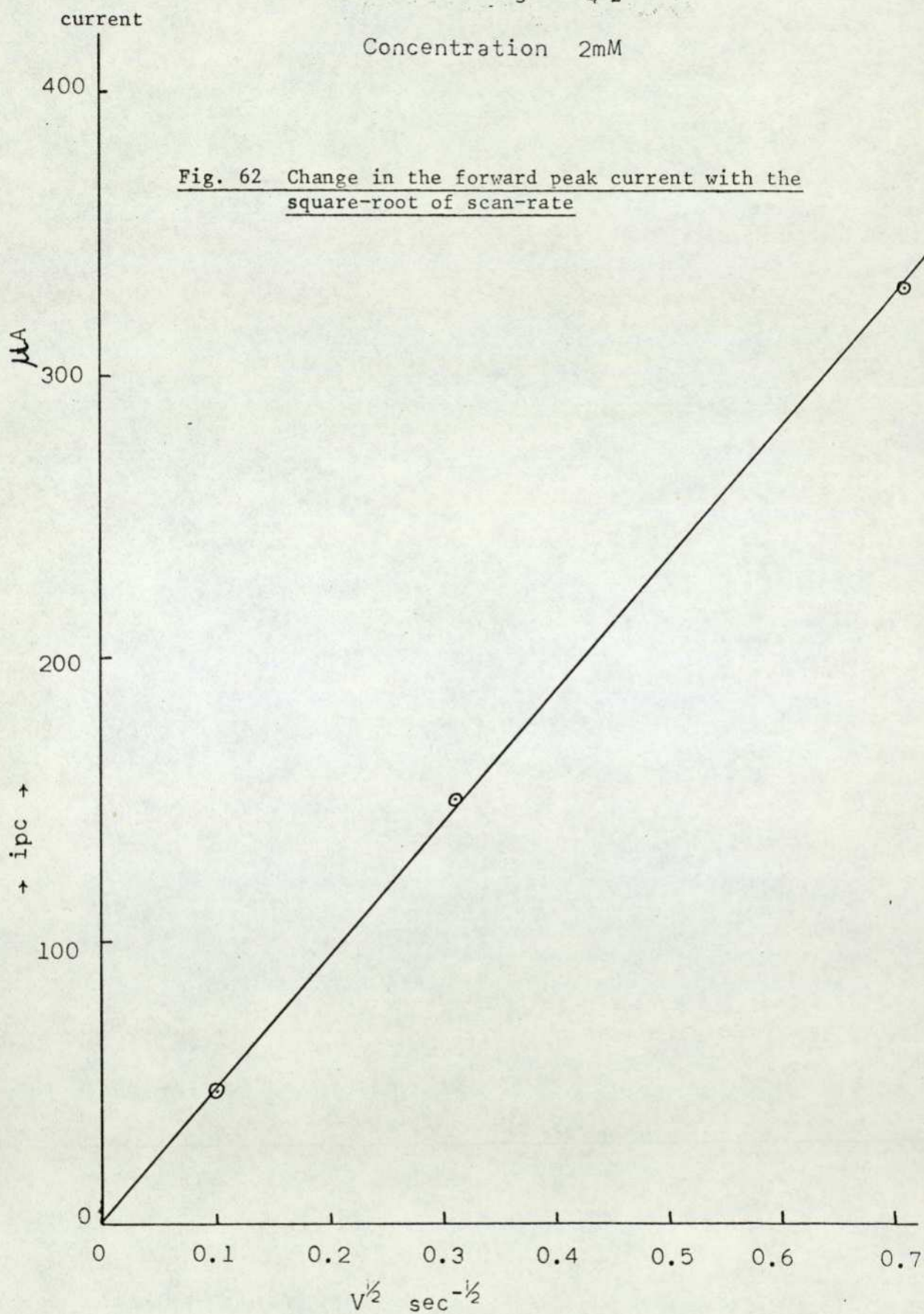


Fig. 61 Change in the forward peak current with the square-root of scan-rate





Concentration 2mM



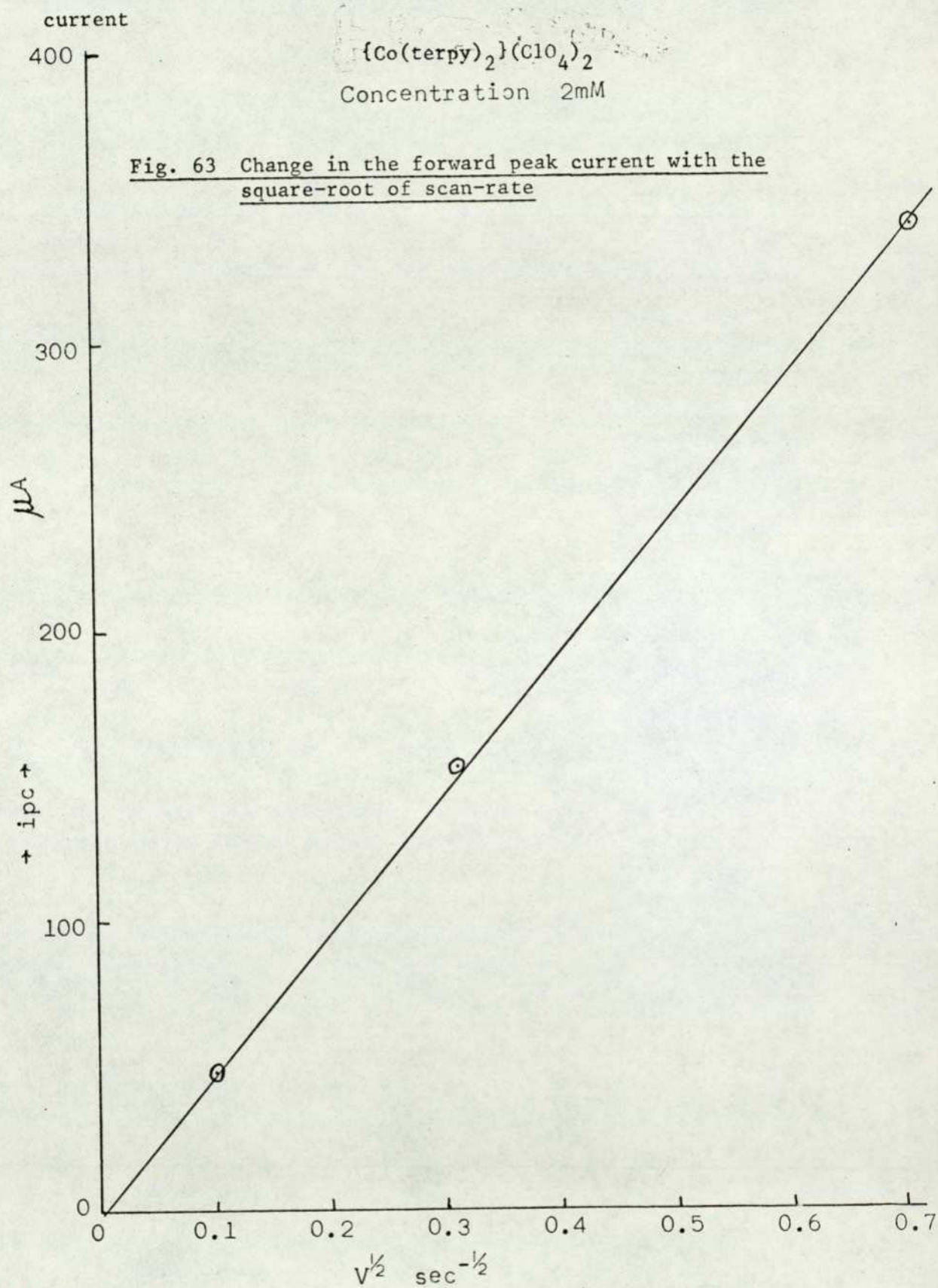


Fig. 64 Change in the forward peak current with the square-root of scan-rate

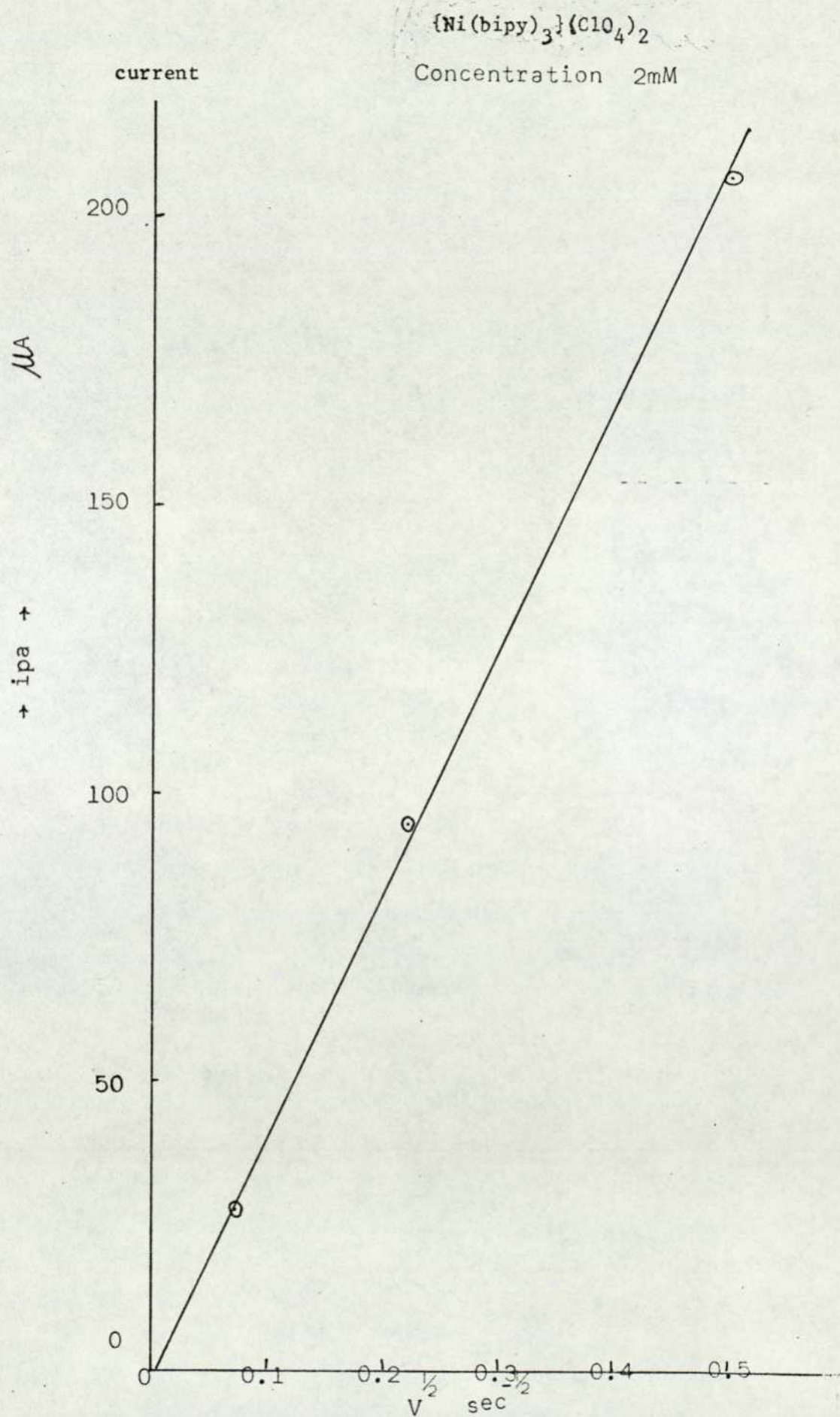
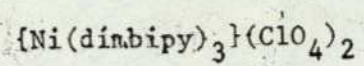


Fig. 65 Change in the forward peak current with the square-root of scan-rate



Concentration 2mM

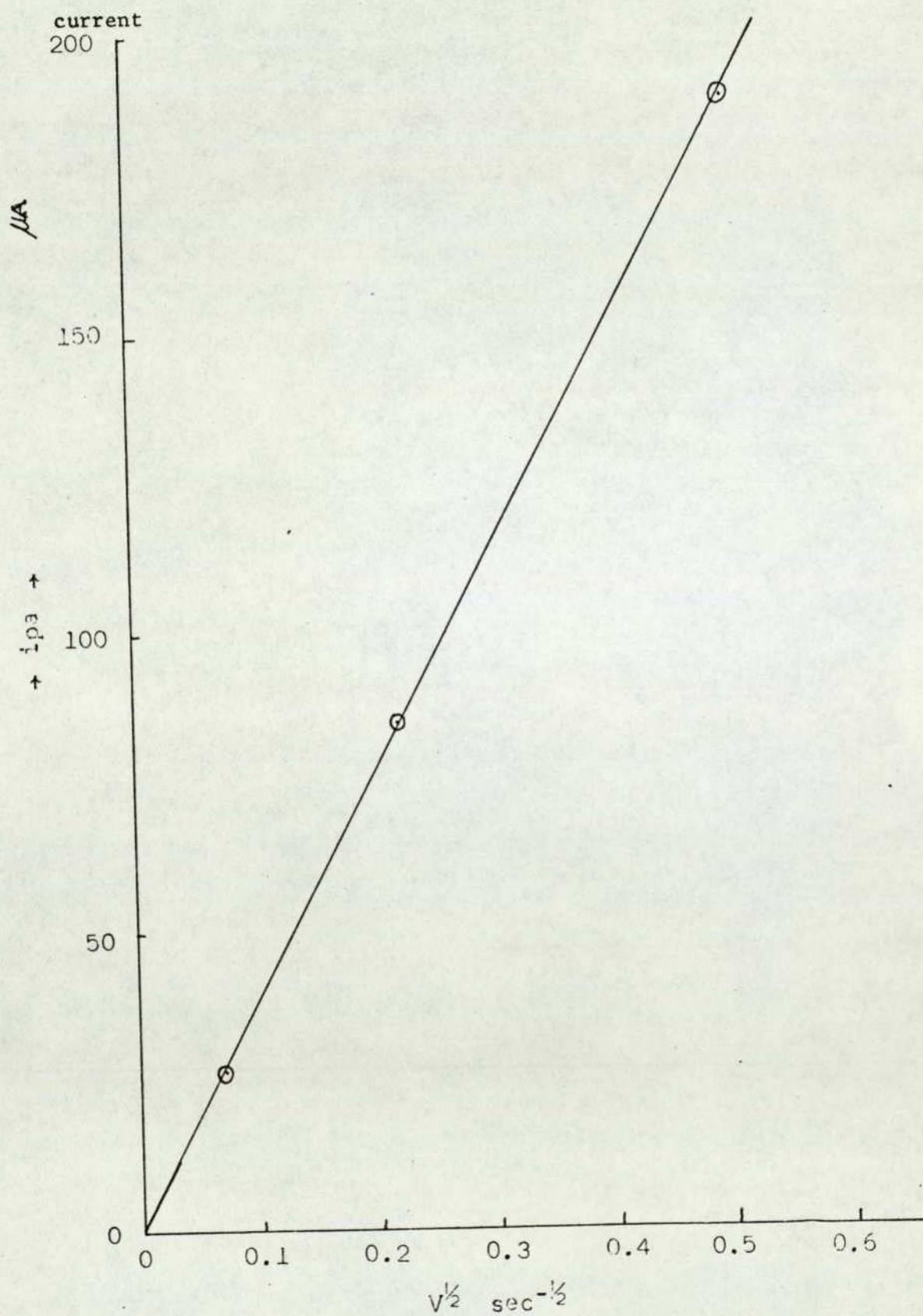


Fig. 66 Change in the forward peak current with the square-root of scan-rate

$\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_2$
Concentration 2mM

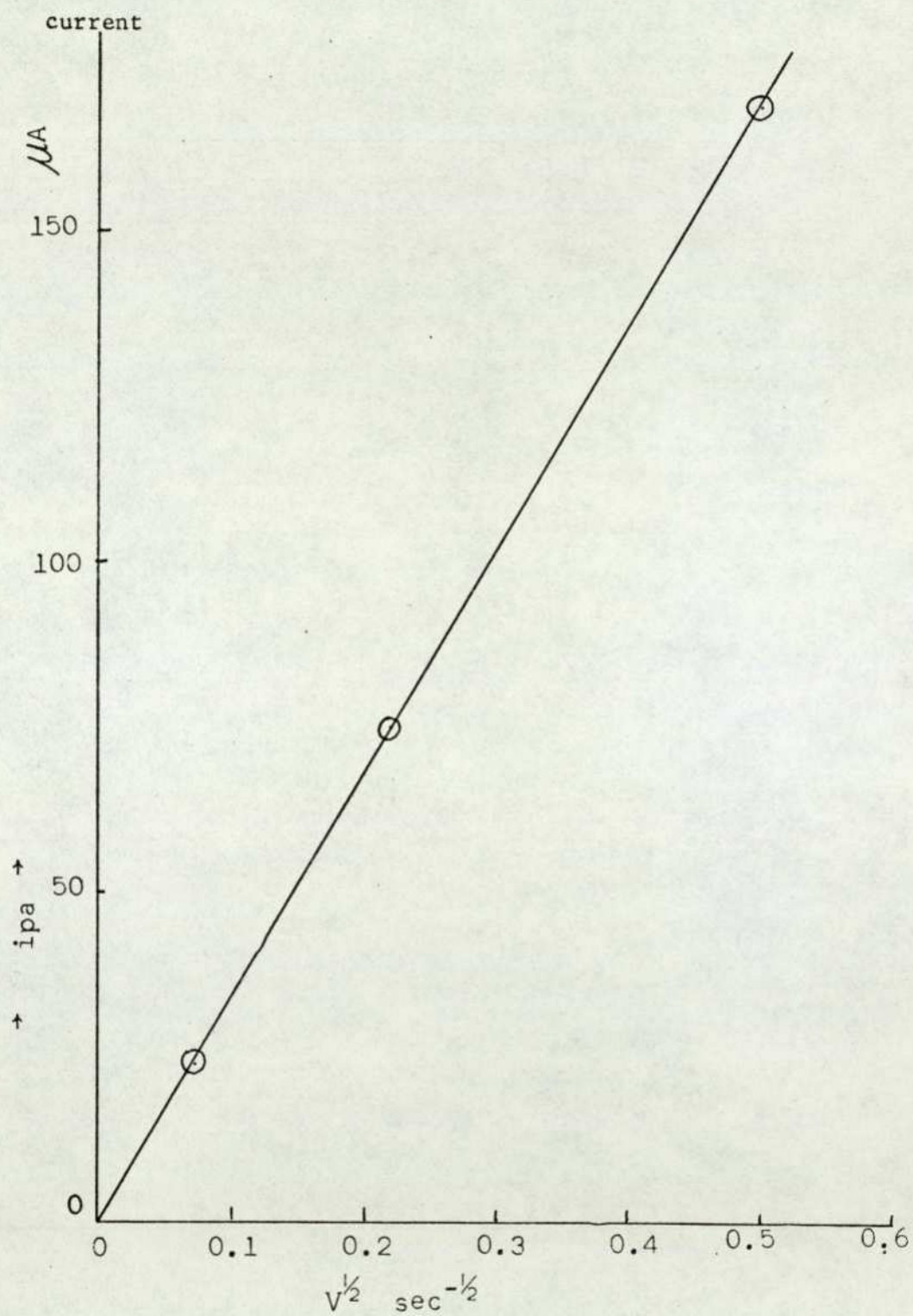
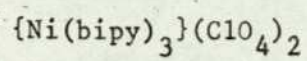


Fig. 67 Change in the forward peak current with the square-root of scan-rate



Concentration 2mM

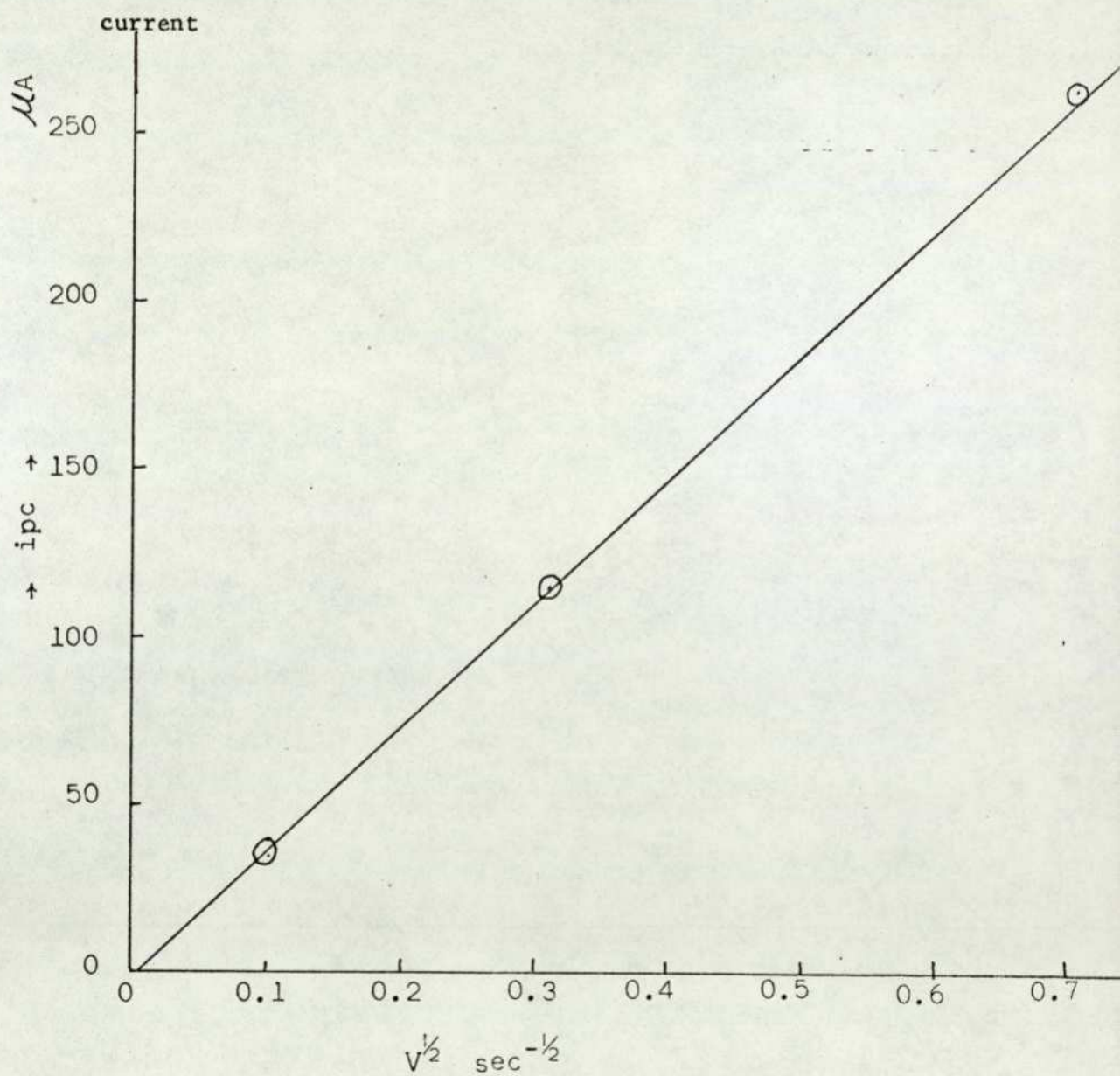
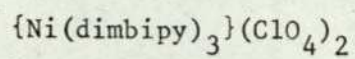


Fig. 68 Change in the forward peak current with the square-root of scan-rate



Concentration 2mM

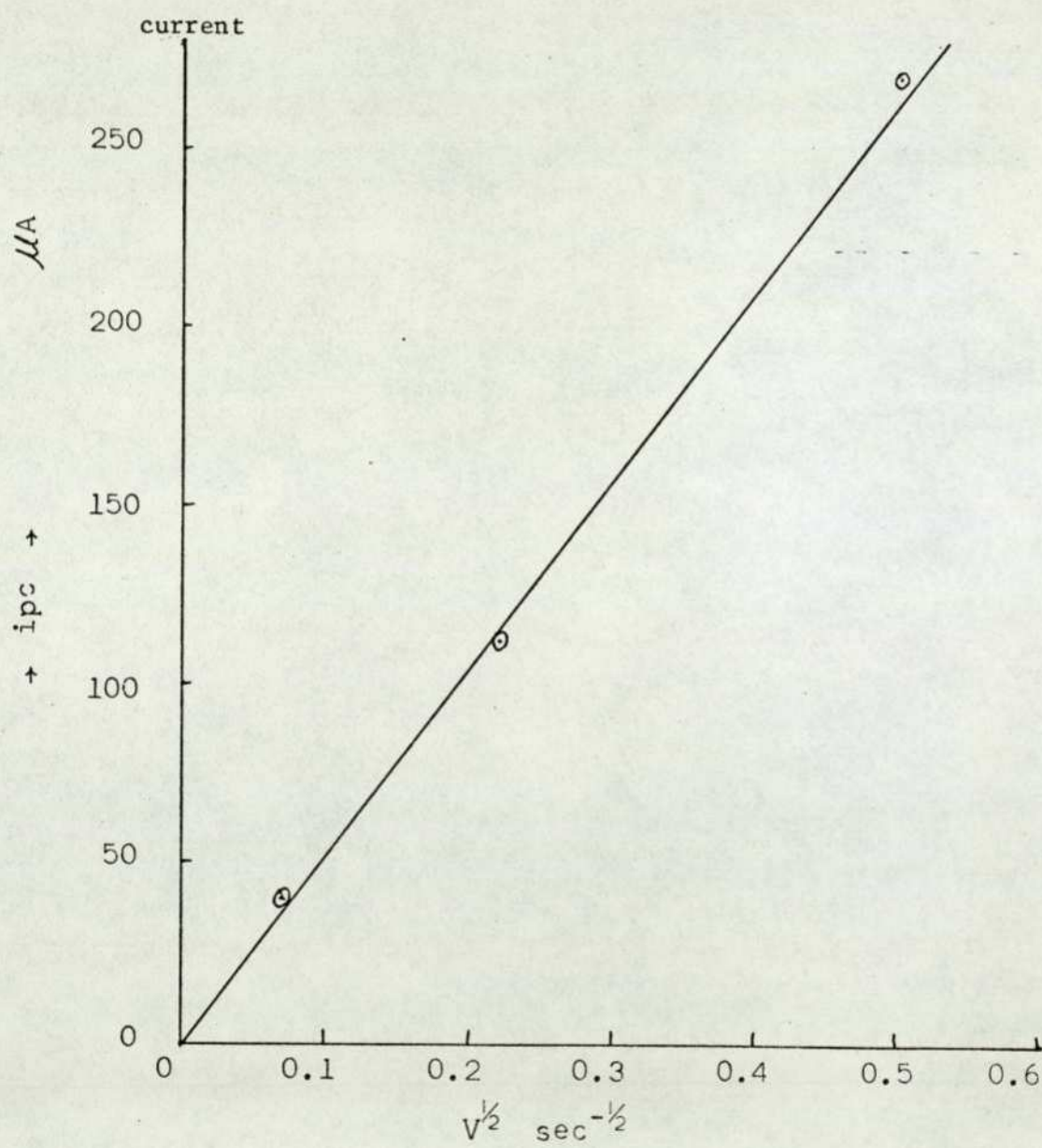


Fig. 69 Change in the forward peak current with the square-root of scan-rate

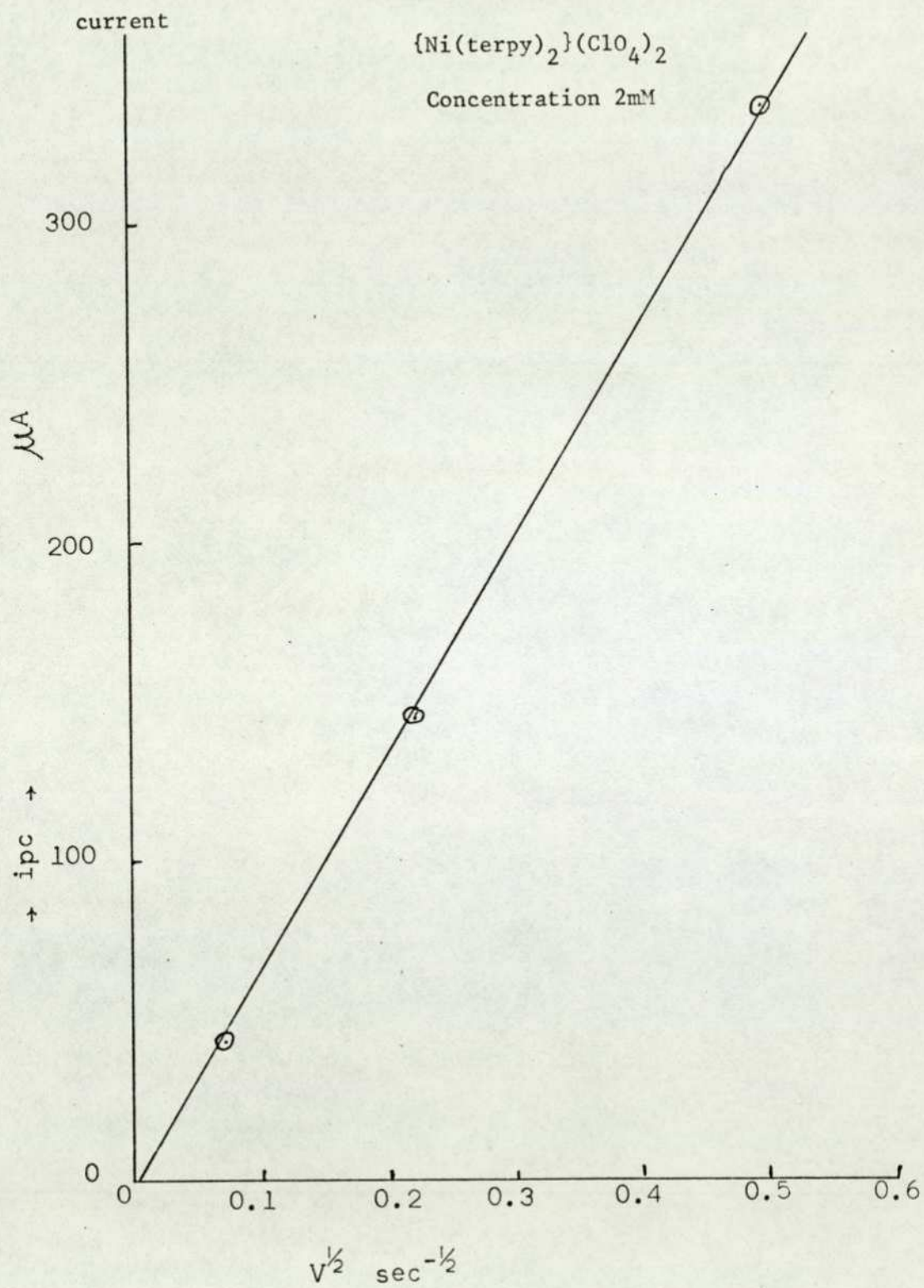


Fig. 70 Proportionality between $E_{\frac{1}{2}}$ for M^{3+}/M^{2+} complex couple and 3rd ionisation potential

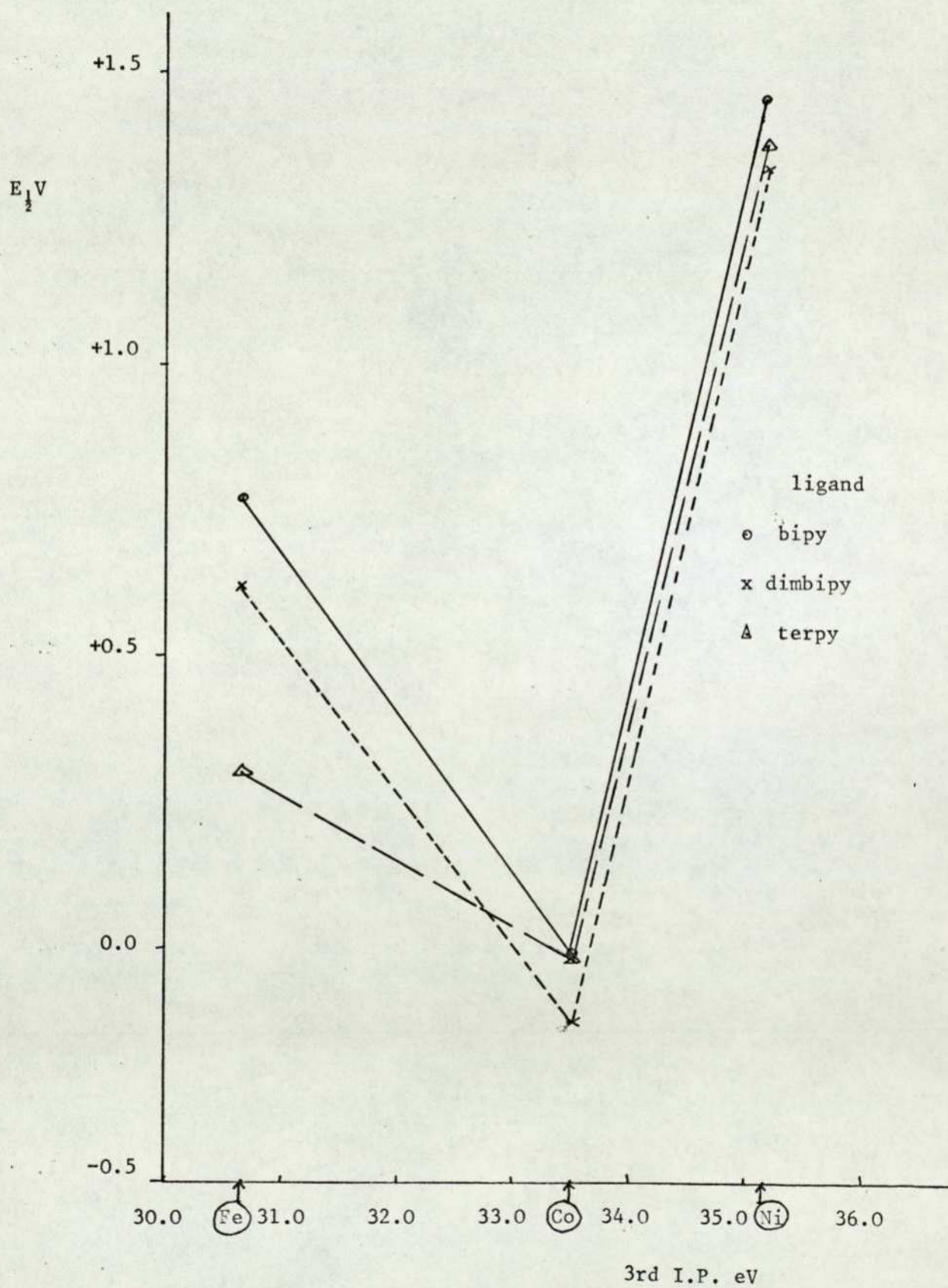


Fig. 71 Proportionality between $E_{\frac{1}{2}}$ for M^{2+}/M^{1+} complex couple and 2nd ionisation potential

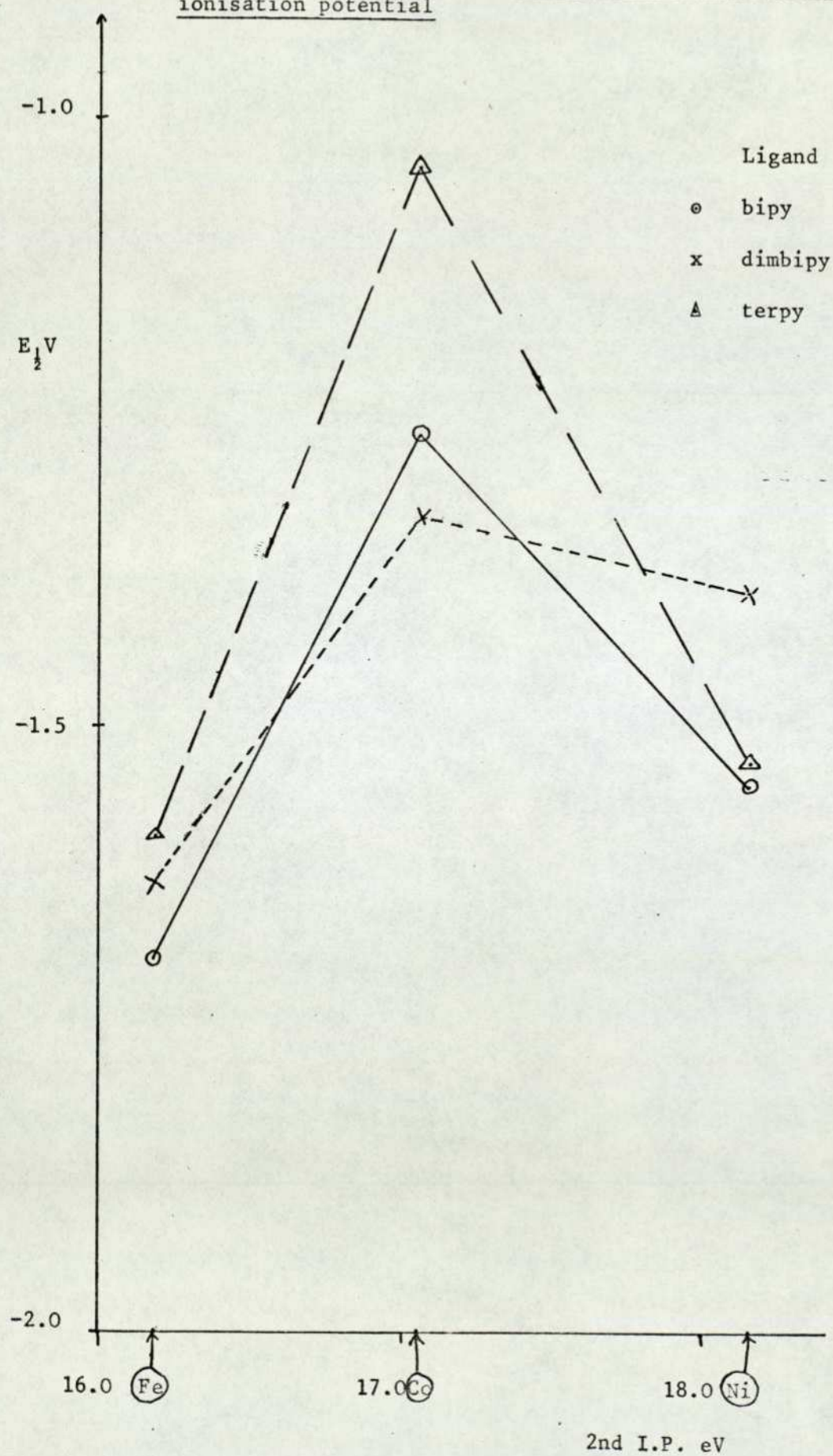


Fig. 72 Visible and near i.r. spectrum of
 $\text{Ni}(\text{bipy})_3(\text{ClO}_4)_3$

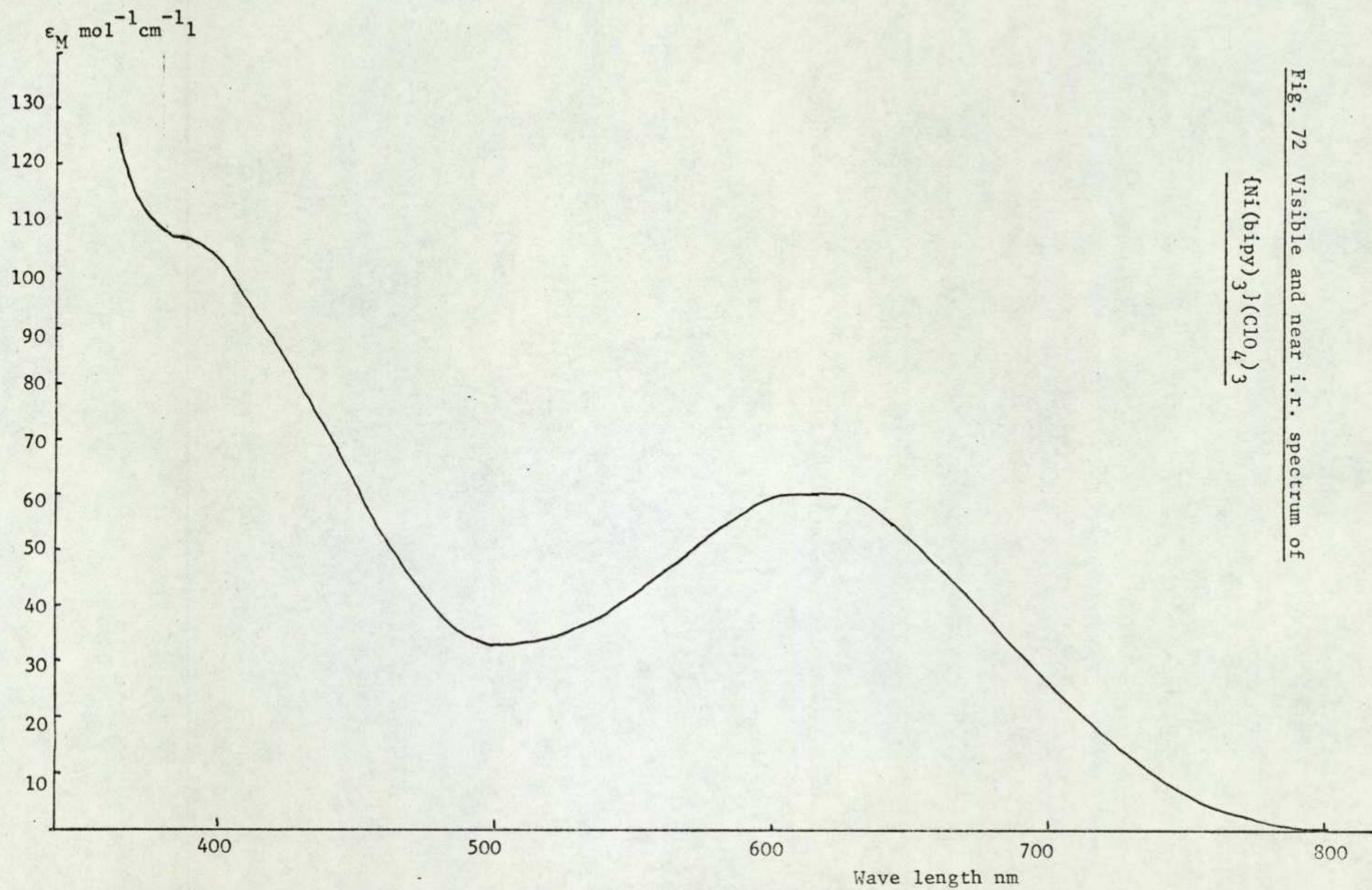


Fig. 73 Visible and near i.r. spectrum of
 $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_3$

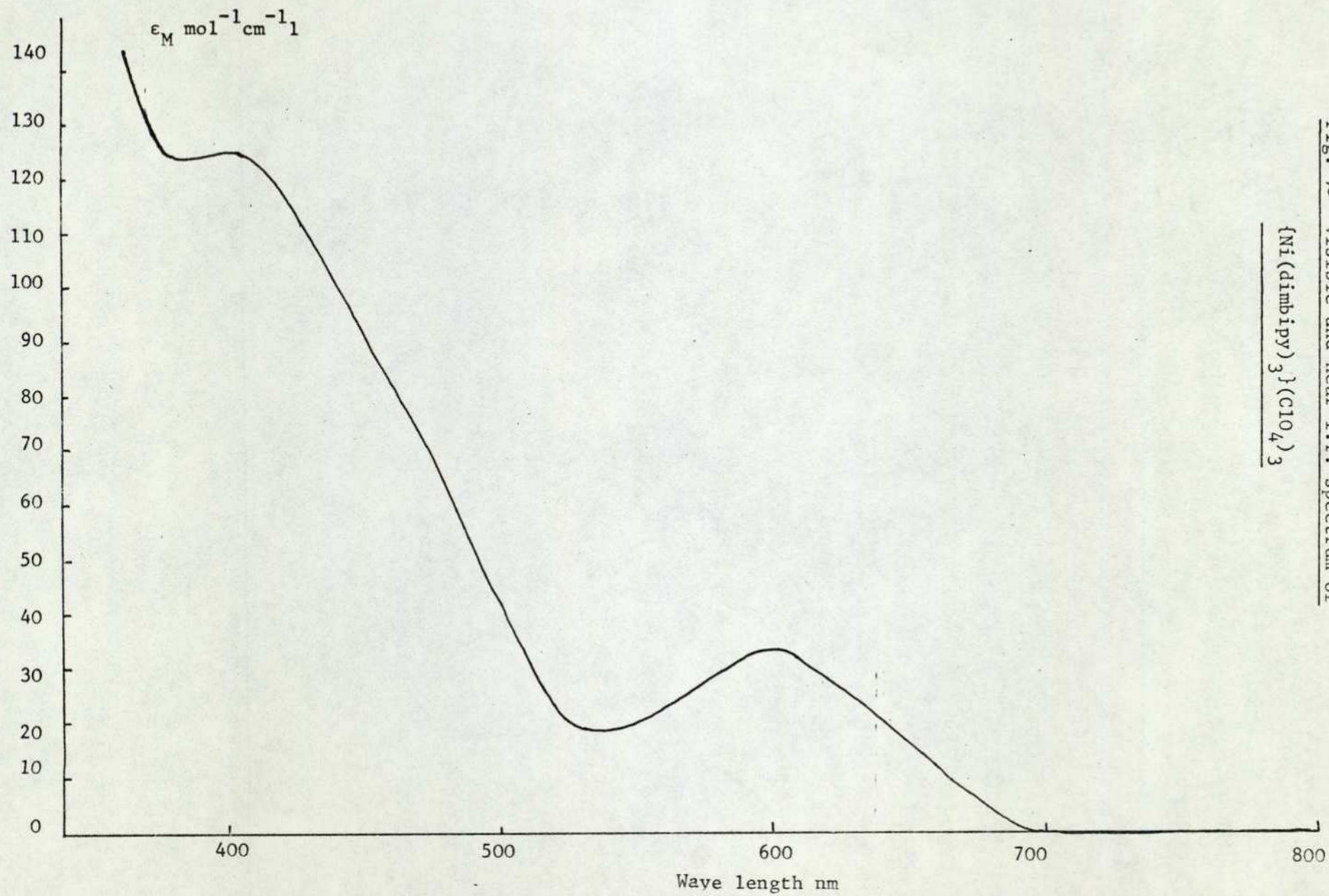
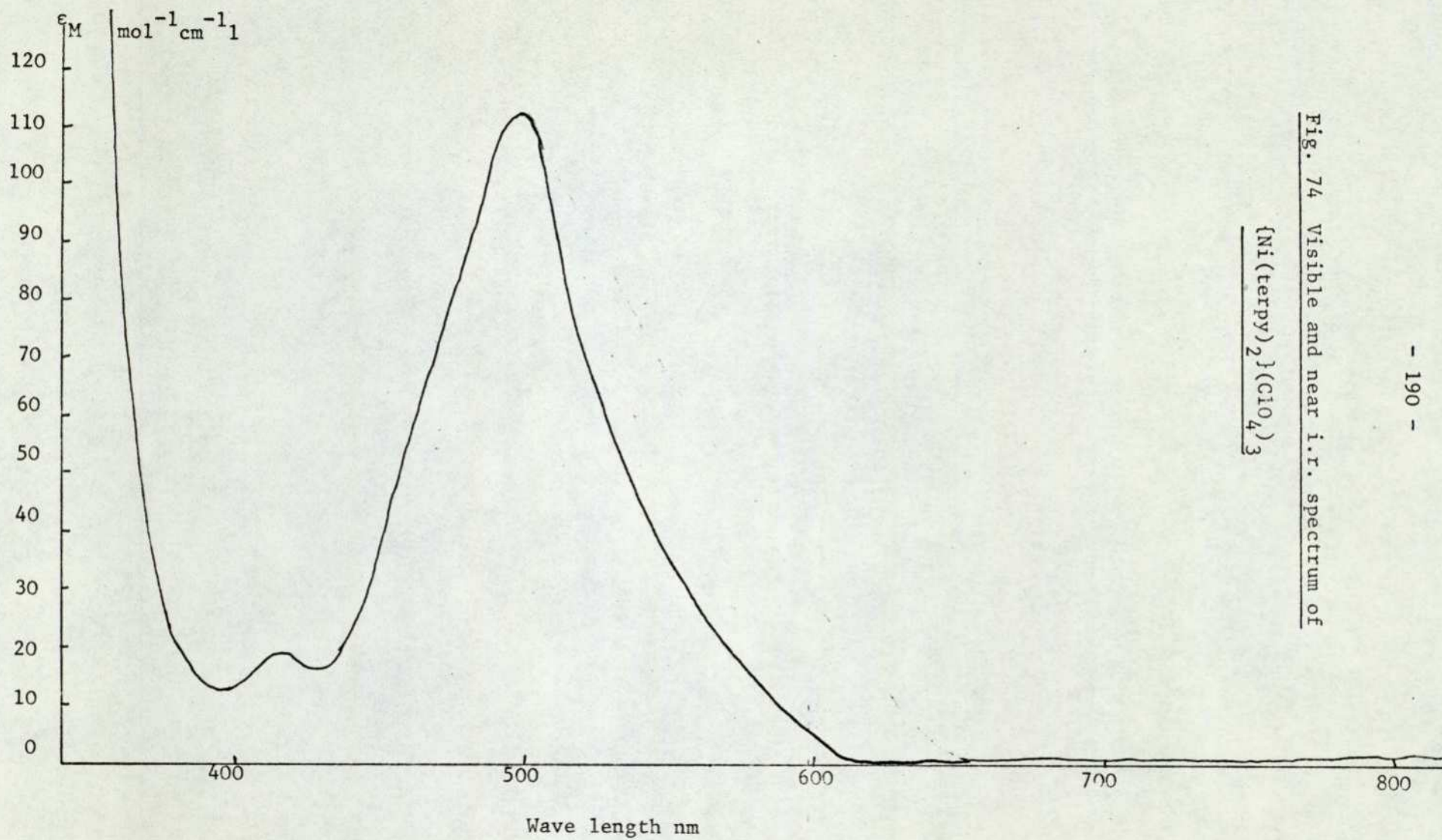
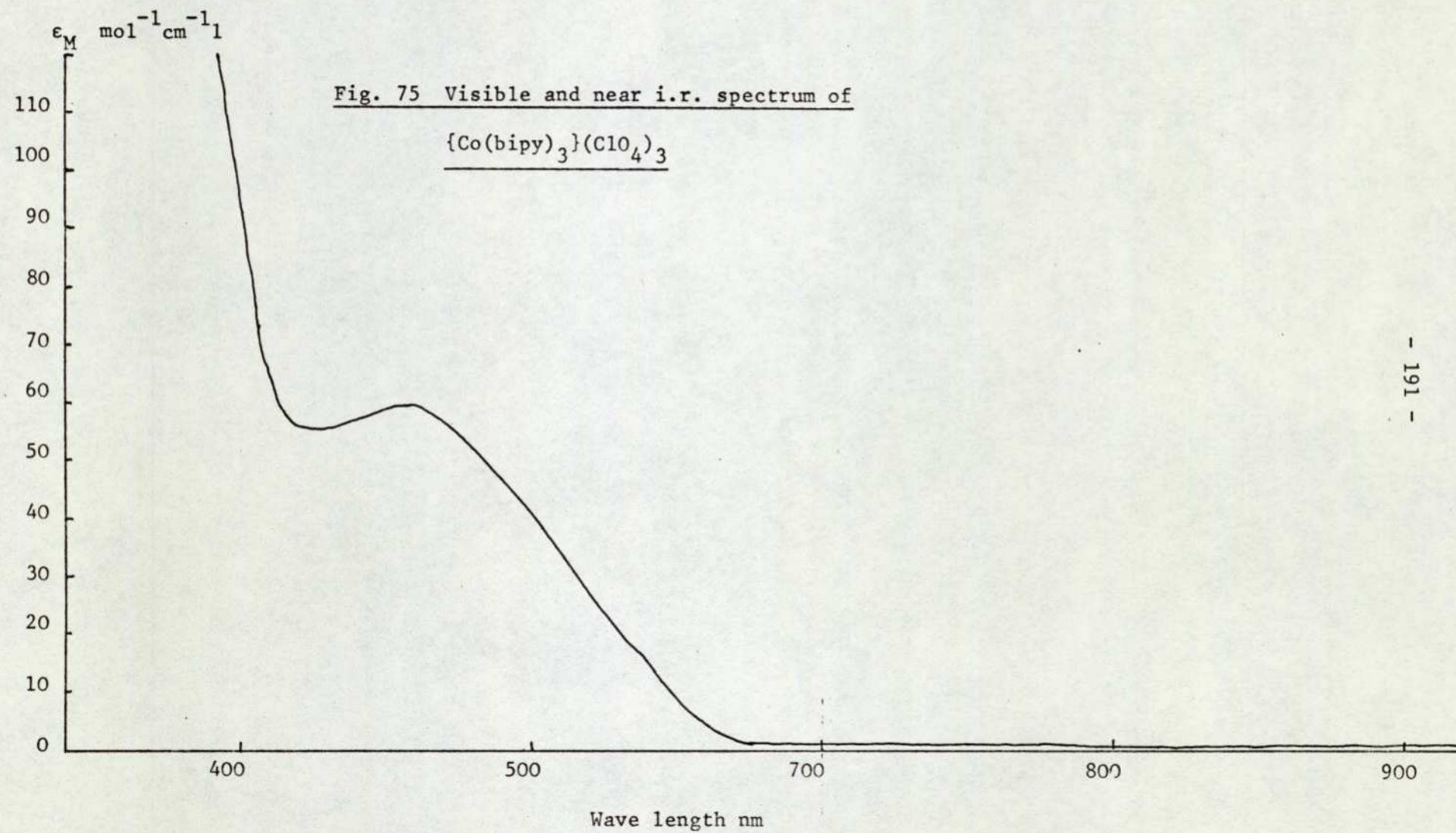


Fig. 74 Visible and near i.r. spectrum of
 $\text{Ni(terpy)}_2\text{(ClO}_4)_3$

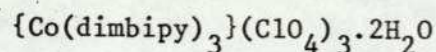




than the corresponding cobalt(III)-bipyridyl and cobalt(II)-dimethyl-bipyridyl complexes.

The results for elemental analysis are given below:

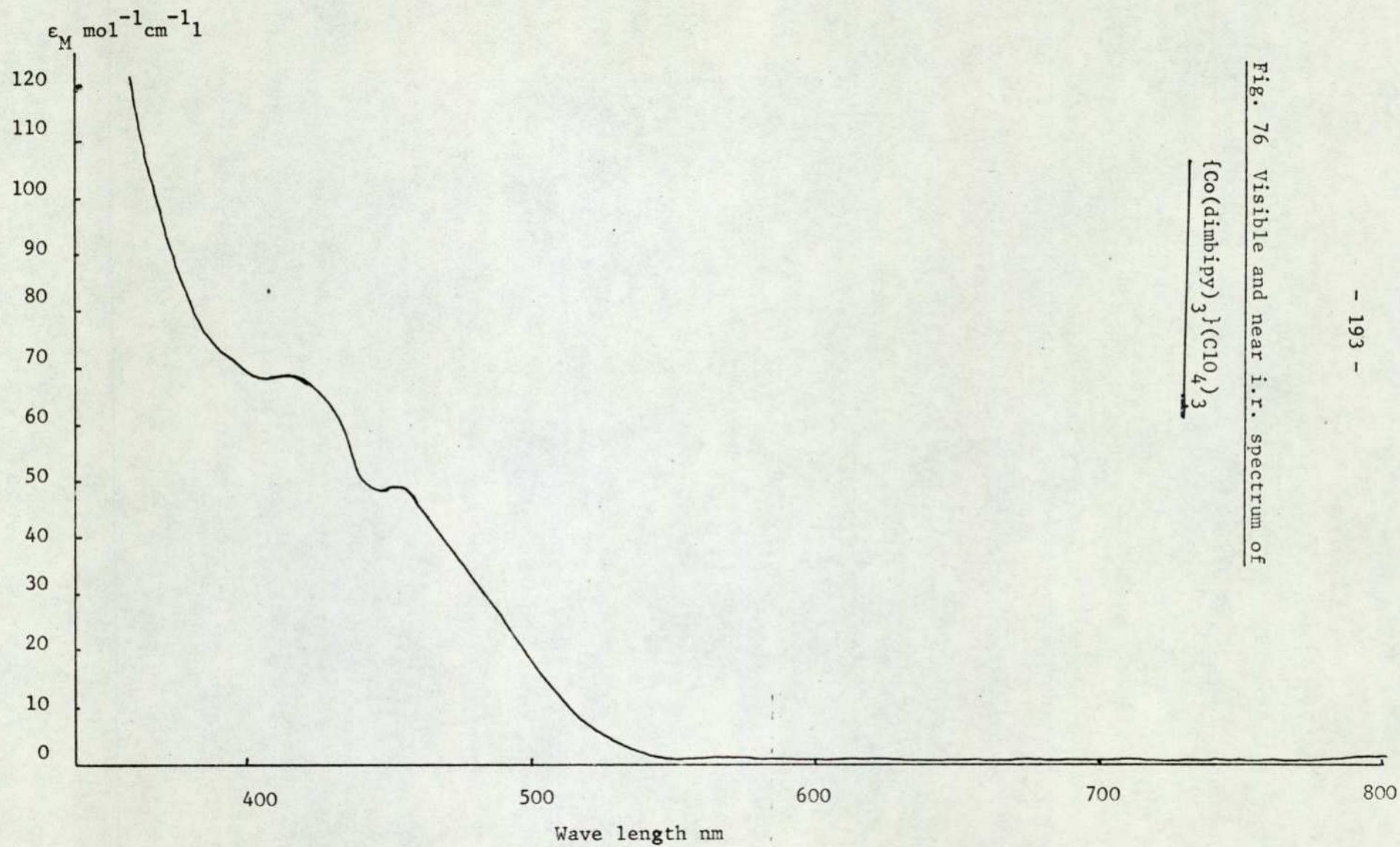
Element		C	H	N	Co
% Calculated for the above formula		47.47	3.95	9.23	6.45
% Found	1	46.98	4.08	9.47	6.45
	2	47.10	4.09	9.32	6.38
	3	45.49	4.48	9.41	6.40
	4	45.48	4.55	8.64	6.30
	5	45.61	4.66	8.60	6.35
% Calculated for formula		45.71	4.30	8.86	6.22



Analyses Nos. 1 and 2 were carried out the day after the preparation and show good agreement with the values calculated for the formula $\{\text{Co}(\text{dimbipy})_3\}(\text{ClO}_4)_3$. The strong affinity of the complex for water, which is similar to that exhibited by $\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_3$ is shown by the results of analyses Nos. 3, 4 and 5 which were carried out on samples of the same preparation after storing them for 4 days in screw-tight sample tubes kept outside the dry box. These data reveal a marked drop in the carbon content and a significant rise in the hydrogen content, giving figures which correspond closely to the formula $\{\text{Co}(\text{dimbipy})_3\}(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$.

The spectrum recorded in the visible and near infra-red region is presented in figure 76, page 193 for this complex in acetonitrile. Absorption peaks, which are probably due to d - d transitions are observed at 24630cm^{-1} ($\epsilon_M = 69.0\text{mol}^{-1}\text{cm}^{-1}$) and 22220cm^{-1} ($\epsilon_M = 48\text{mol}^{-1}\text{cm}^{-1}$).

Fig. 76 Visible and near i.r. spectrum of
 $\text{Co}(\text{dimbipy})_3\text{(ClO}_4)_3$



Again, the complex was found to be diamagnetic as expected for a spin-paired d^6 configuration.

Bis(2,2',2''-terpyridyl cobalt(III) perchlorate, $\{Co(terpy)_2\}(ClO_4)_3$

The yield of the orange crystalline powder was about 70% of the theoretical yield. Elemental analyses of two separate batches are given below:

Element	C	H	N	Co
% Calculated for formula $\{Co(terpy)_2\}(ClO_4)_3$	43.95	2.67	10.20	7.13
% Found (1st batch)	45.25	3.37	12.25	7.20
(2nd batch)	45.09	3.34	12.27	7.18

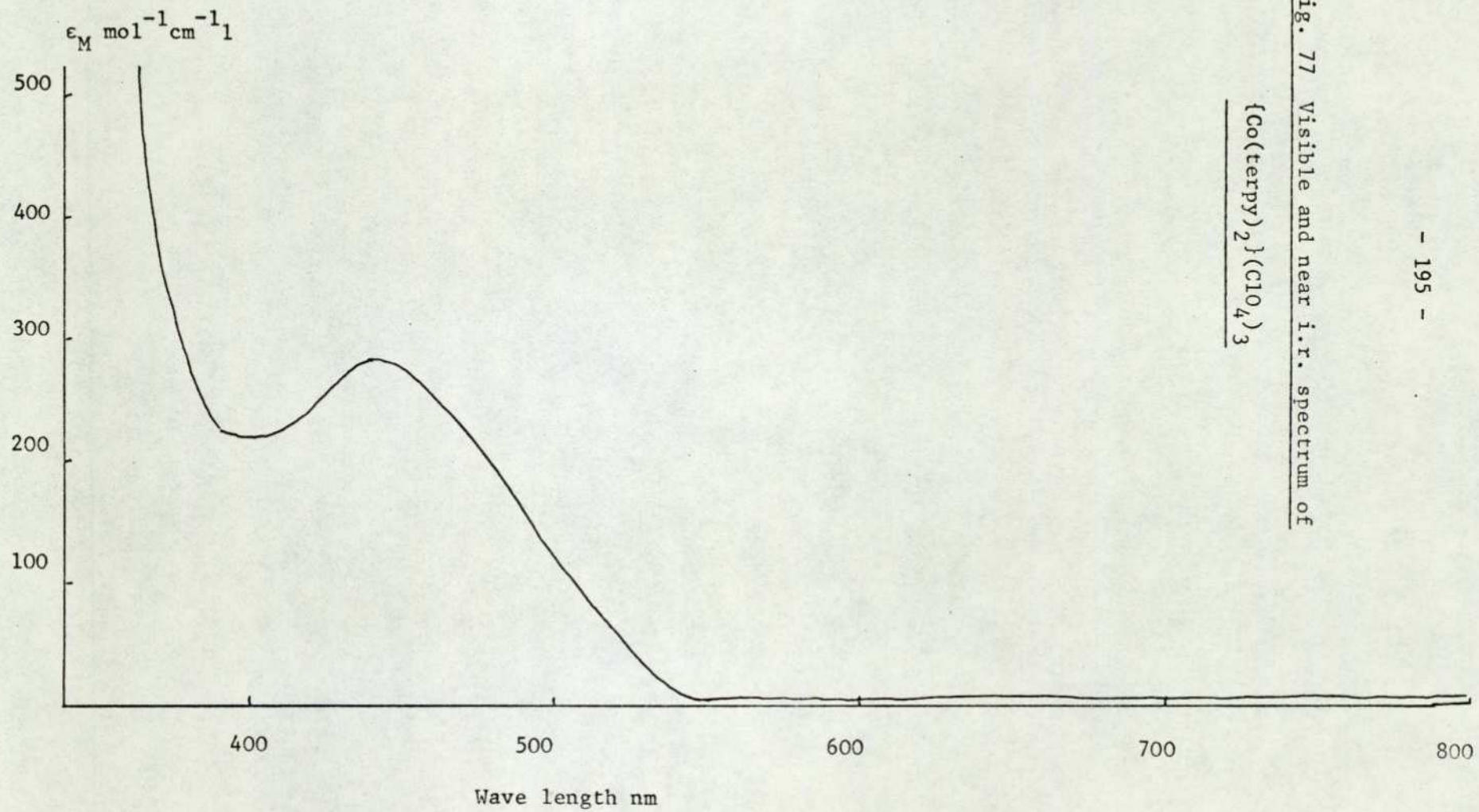
As for the nickel(III)-terpyridyl complex the analytical data are not in very good agreement with the expected composition of the complex. It is possible that the discrepancies could be due to the presence of some unoxidised cobalt(II) complex as a result of incomplete electrolysis. This can be the case even though electrolysis is continued until the current is only 0.01% of its initial value if, for example, the effective area of the working electrode is reduced by adsorption of the product.

The visible and near infra-red spectrum of the complex is shown in figure 77, page 195. Absorption band observed at 22570cm^{-1} ($\epsilon_M = 280\text{mol}^{-1}\text{cm}^{-1}$) is in agreement with that found in aqueous solution by Maki³¹² for the $\{Co(terpy)_2\}Cl_3$ complex.

As in the case of $\{Co(bipy)_3\}(ClO_4)_3$ and $\{Co(dimbipy)_3\}(ClO_4)_3$ the cobalt(III)-terpyridyl complex exhibited diamagnetic behaviour at 293°K indicating a spin paired d^6 configuration.

It is of interest to note that, while the cobalt(II) complexes

Fig. 77 Visible and near i.r. spectrum of
 $\{\text{Co}(\text{terpy})_2\}(\text{ClO}_4)_3$



$\{\text{Co}(\text{terpy})_2\}(\text{ClO}_4)_2$ and $\{\text{Co}(\text{terpy})\}(\text{ClO}_4)_2$ have been reported²⁷¹ the corresponding cobalt(III) complexes do not appear to have been prepared.

Tris(2,2'-bipyridyl) iron(III) perchlorate, $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_3$

The blue crystalline product, obtained in about 70% of the theoretical yield, gave the following elemental analysis:

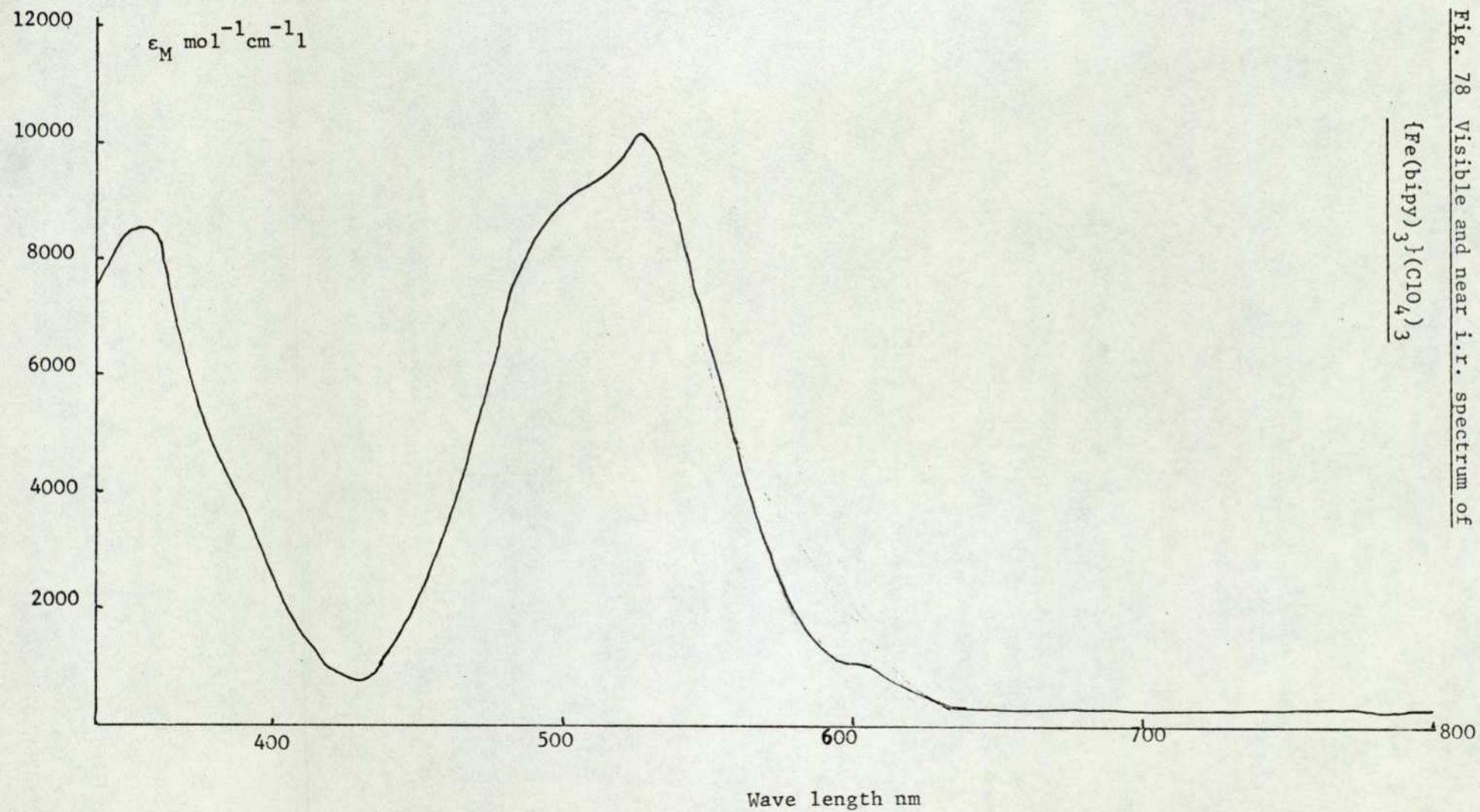
Element	C	H	N	Fe
% Calculated for the formula $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_3$	43.74	2.91	10.21	6.77
% Found	43.70	3.14	10.05	6.80

These results are in excellent agreement with the expected composition of the product, $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_3$.

The visible and near infra-red spectrum of the product in acetonitrile is presented in figure 78, page 197. Strong absorption maxima were observed at 28170cm^{-1} , 20620cm^{-1} (shoulder), 19150cm^{-1} and 16700cm^{-1} (shoulder), having molar extinction co-efficients of 8500, 9000, $10200\text{mol}^{-1}\text{cm}^{-1}$ and $670\text{mol}^{-1}\text{cm}^{-1}$ respectively, in agreement with the published data of Fergusson and Harris.²⁶⁴

The effective magnetic moment of $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_3$ determined as 2.18 B.M. at 293°K is in agreement with the value of 2.36 B.M. reported by Burstall and Nyholm²⁷⁰ for the trihydrated complex, $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, and is consistent with a spin paired d^5 (t_{2g}^5) configuration. Figgis³⁰⁸ who studied the magnetic properties of the trihydrate over a range of temperature, suggests that the moment in excess of the spin only value for one unpaired electron (1.73 B.M.) could be due to a small degree of delocalisation of the t_{2g} electrons on to the ligands; a first order

Fig. 78 Visible and near i.r. spectrum of
 $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)_3$



orbital contribution is also to be expected.

Tris(4,4'-dimethyl-2,2'-bipyridyl) iron(III) perchlorate,
 $\{Fe(dimbipy)_3\}(ClO_4)_3$

The analysis of the blue crystalline product obtained in 70% of the theoretical yield was as follows:

Element	C	H	N	Fe
% Calculated for the formula $\{Fe(dimbipy)_3\}(ClO_4)_3$	47.63	3.97	9.26	6.15
% Found	47.70	4.08	9.26	6.00

The experimental data are in good agreement with the figures calculated for the composition $\{Fe(dimbipy)_3\}(ClO_4)_3$.

The visible and near infra-red spectrum is presented in figure 79, page 199. The absorption bands at $28170cm^{-1}$, $20410cm^{-1}$ (shoulder), $18870cm^{-1}$ and $16400cm^{-1}$, having molar extinction co-efficients 8000, 10000, $11000mol^{-1}cm^{-1}$ and $700mol^{-1}cm^{-1}$ respectively are similar to those observed in $\{Fe(bipy)_3\}(ClO_4)_3$ and may be similarly assigned (c.f. page 196).

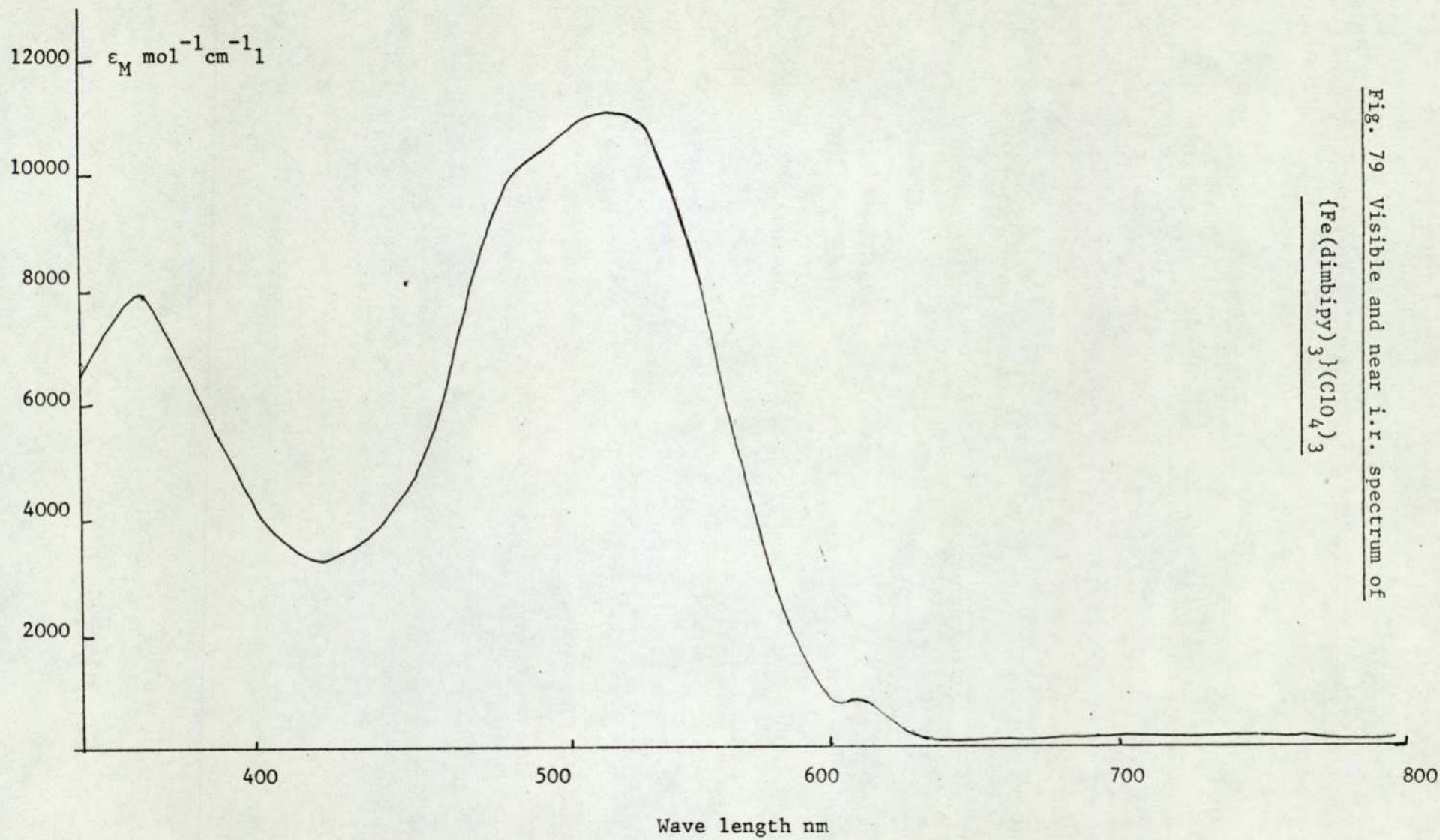
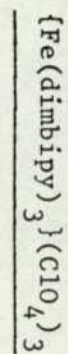
The magnetic susceptibility determinations gave an effective magnetic moment of 2.36 B.M. at $294^{\circ}K$, similar to that of the corresponding bipyridyl complex. Again, an octahedral spin paired configuration (t_{2g}^5) is indicated.

Bis(2,2',2''-terpyridyl) iron(III) perchlorate, $\{Fe(terpy)_2\}(ClO_4)_3$

The blue-grey coloured product was obtained in 85% yield. Below are given the elemental analysis data which show good agreement between observed and calculated figures:

Element	C	H	N	Fe
% Theoretical for above formula	43.87	2.68	10.23	6.8
% Found	44.01	2.90	10.17	6.8

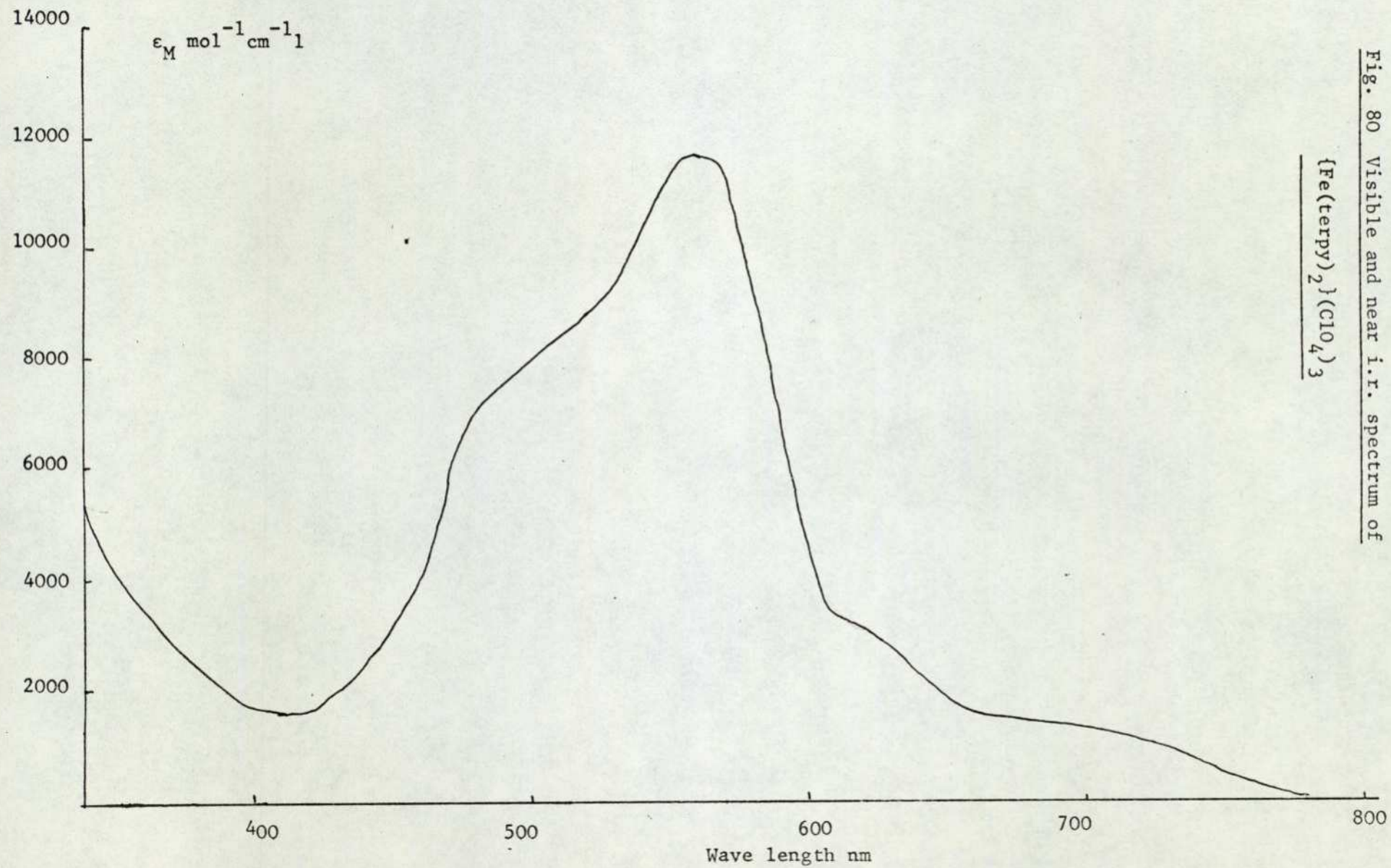
Fig. 79 Visible and near i.r. spectrum of



The visible and near infra-red spectrum of the product in acetonitrile solution is presented in figure 80, page 201. Absorbance maxima, indicative of charge transfer transitions, were observed at 19610cm^{-1} ($\epsilon_M = 3500\text{mol}^{-1}\text{cm}^{-1}\text{l}$), 18180cm^{-1} ($\epsilon_M = 5800\text{mol}^{-1}\text{cm}^{-1}\text{l}$), 16130cm^{-1} ($\epsilon_M = 1600\text{mol}^{-1}\text{cm}^{-1}\text{l}$) and 14290cm^{-1} ($\epsilon_M = 700\text{mol}^{-1}\text{cm}^{-1}\text{l}$).

The magnetic susceptibility determined at 20°C gave an effective magnetic moment of 2.12 B.M. This is consistent with a spin paired d^5 configuration.

Fig. 80 Visible and near i.r. spectrum of
 $\{\text{Fe}(\text{terpy})_2\}(\text{ClO}_4)_3$



5.4.2. Preparation of polypyridyl complexes of iron(I), cobalt(I) and nickel(I) perchlorates by electro-reduction of corresponding metal(II) complexes

Iron(I), cobalt(I) and nickel(I) polypyridyl complexes are rare and very few have been reported. Unfortunately, these complexes are extremely unstable, very soluble in acetonitrile and are readily reoxidised to the corresponding metal(II) complexes by the presence of traces of molecular oxygen; consequently, the preparation, isolation and handling of these complexes was much more difficult than for metal(III) complexes. In all cases, attempts to isolate the product from the supporting electrolyte by Method A (c.f. page 87) failed due to the extremely high solubility of the complexes. In the case of bipyridyl complexes, the technique of omitting tetra-n-butylammonium perchlorate from the cell solutions and using the metal(II) complex perchlorate as its own supporting electrolyte was adopted and this was followed by the isolation procedure Method B, on page 88. This was successful in the case of nickel(I) and cobalt(I) bipyridyl complexes. Unfortunately, the method could not be attempted for the dimethyl-bipyridyl and terpyridyl complexes due to the prohibitive cost of these ligands which were required in much larger quantities than in the normal procedure.

A summary of the electrochemical preparations carried out by the method described in section 4.3.3., page 86 is given in Table XIII, page 203. The controlled cathode potential used in each electrolysis was the same as that of the corresponding coulometric experiment (c.f. Table XI, pages 143,144). Magnetic susceptibility data are included for those cases where a solid product was obtained. As in the discussion of metal(III) polypyridyl complexes, a more detailed consideration of the

Table XIII

Metal(I) complex (expected composition)		Weight of metal(II) complex taken g	Cathodic potential V	Method of isolation	% Yield theoretical	Nature of product	Effective magnetic moment B.M.
(i)	{Fe(bipy) ₃ }(ClO ₄)	2.0	-1.70	-	-	Blue-violet	-
(ii)	{Fe(dimbipy) ₃ }(ClO ₄)	1.0	-1.65	-	-	Blue-violet	-
(iii)	{Fe(terpy) ₂ }(ClO ₄)	1.0	-1.65	-	-	Blue-violet	-
(iv)	{Co(bipy) ₂ }(ClO ₄)	3.0	-1.29	B	70	Blue	2.94
(v)	{Co(dimbipy) ₂ }(ClO ₄)	1.0	-1.50	-	-	Blue	-
(vi)	{Co(terpy) ₂ }(ClO ₄)	1.0	-1.52	-	-	Blue	-
(vii)	{Ni(bipy) ₂ }(ClO ₄)	3.0	-1.55	B	70	Blue	1.99
(viii)	{Ni(dimbipy) ₂ }(ClO ₄)	1.0	-1.43	-	-	Blue	-
(ix)	{Ni(terpy) ₂ }(ClO ₄)	1.0	-1.52	-	-	Blue	-

electronic spectra is reserved until later (c.f. section 5.5.).

The properties and analytical data (where available) for each of the preparations are now given.

Bis(bipyridyl) nickel(I) perchlorate, $\{\text{Ni}(\text{bipy})_2\}(\text{ClO}_4)$

The solid product, obtained in 70% of the theoretical yield, exhibited the property of reducing acidified potassium dichromate solution using the test described in section 4.5.2., page 90. The following analytical data were obtained for two samples of the same preparation. Calculated figures are also given for various empirical formulae:

Element		C	H	N	Ni
% Found	(1)	47.02	3.67	11.75	13.8
	(2)	47.17	3.88	11.95	13.6
% Calculated for the formula		57.41	3.82	13.40	9.4
$\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)$					
% Calculated for the formula		49.58	3.30	11.56	12.6
$\{\text{Ni}(\text{bipy})_2\}(\text{ClO}_4)$					
% Calculated for the formula		38.20	2.54	8.91	13.6
$\{\text{Ni}(\text{bipy})\}(\text{ClO}_4)$					

The two sets of experimental data are in good agreement and correspond reasonably well to the figures calculated on the basis of $\{\text{Ni}(\text{bipy})_2\}(\text{ClO}_4)$. Although the carbon and nickel are lower than the calculated values, the agreement is considered to be satisfactory in view of the difficulties of preparing and handling the product; the high hydrogen figure might be due to the hygroscopic nature of the complex. The instability of the complex was demonstrated by the fact that, even when stored in a stoppered tube under commercial oxygen-free

nitrogen, the blue solid turned pink over a period of 36 hours, presumably due to the formation of the corresponding nickel(II) complex.

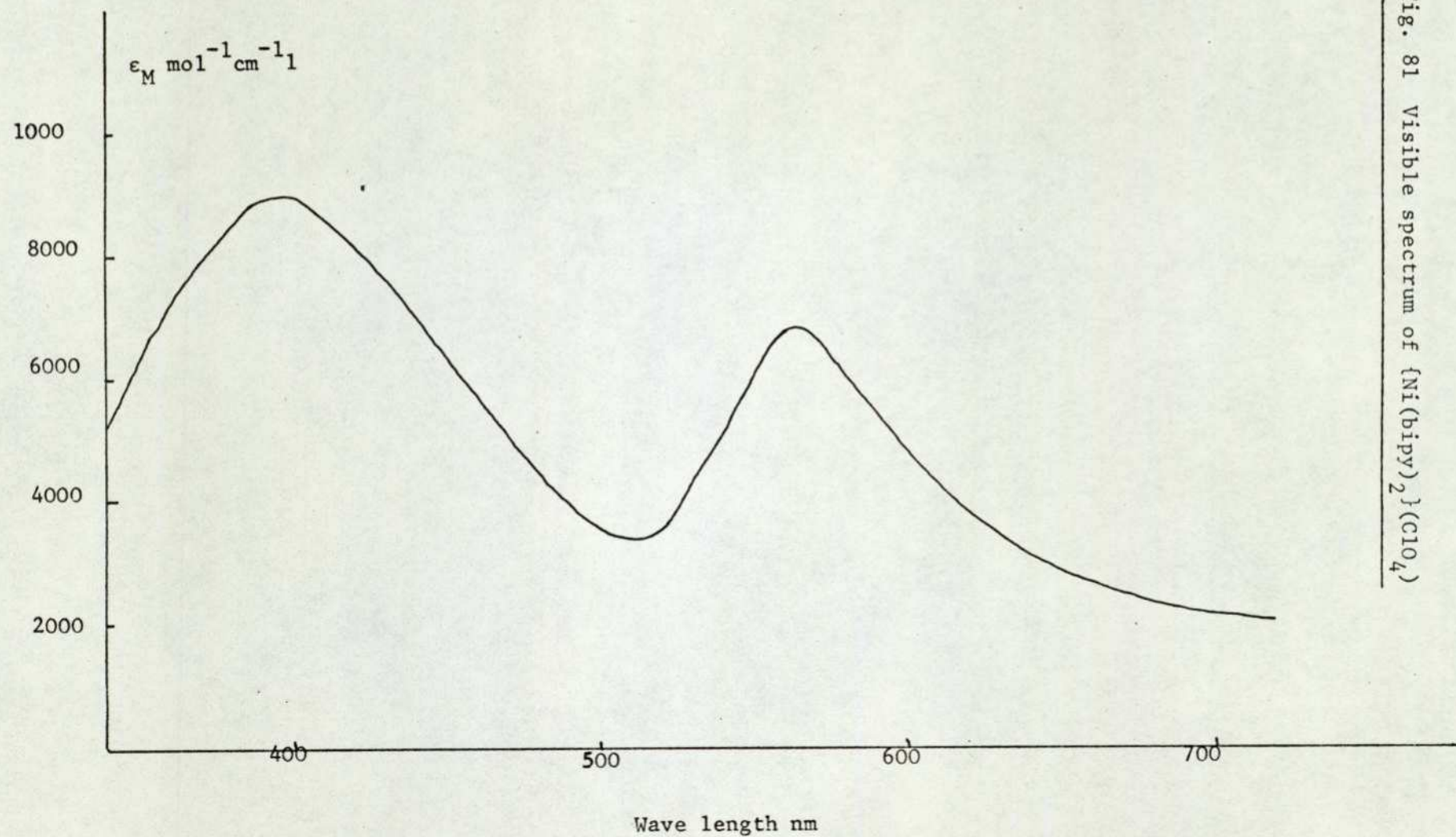
The visible and near infra-red spectrum of the complex in acetonitrile determined immediately after preparation is shown in figure 81, page 206. Maximum absorbances occur at 25000cm^{-1} and 17540cm^{-1} with corresponding molar extinction co-efficients of $9000\text{mol}^{-1}\text{cm}^{-1}$ and $6880\text{mol}^{-1}\text{cm}^{-1}$ respectively. The high intensity of these bands, which are possibly due to charge transfer transitions, makes observation of any d - d transitions in the same region of the spectrum impossible.

The effective magnetic moment of the complex, determined soon after its preparation was found to be 1.99 B.M. at 291°K indicating the presence of one unpaired electron ($\mu_s = 1.73$ B.M.) which is consistent with a d^9 configuration. This value is within the range of values (1.73-2.31 B.M.) observed for other mononuclear nickel(I) complexes.^{139,140,142,144,145,310-311} The value of the magnetic moment does not give support to any particular stereochemical arrangement. Several possibilities exist including square planar, tetragonal or octahedral (involving the co-ordination of the anion as a bridging group in a polymeric chain system), and distorted tetrahedral (as found in four co-ordinated halide complexes of copper(II)) all of which would be expected to give moments in excess of the spin only value due to a first order orbital contribution or spin-orbit coupling effects.³⁰⁹

Attempted preparation of bis(4,4'-dimethyl-2,2'-bipyridyl nickel(I) perchlorate, $\{\text{Ni}(\text{dimbipy})_2\}(\text{ClO}_4)$

Attempts to isolate the pure product from the deep blue solution formed by electrochemical reduction were unsuccessful. By

Fig. 81 Visible spectrum of $\{\text{Ni}(\text{bipy})_2\}(\text{ClO}_4)_4$



analogy with the corresponding nickel(I)-bipyridyl complex, this complex would be expected to have the composition $\{\text{Ni}(\text{dimbipy})_2\}(\text{ClO}_4)$. The reducing power of the product in solution was demonstrated by its ability to reduce the dichromate ion in the test described on page 90. The visible and near infra-red spectrum of a solution of the product taken directly from the electrolytic cell is shown in figure 82, page 208. Intense bands were observed at 23420cm^{-1} ($\epsilon_M = 9800\text{mol}^{-1}\text{cm}^{-1}$) and 16260cm^{-1} ($\epsilon_M = 5440\text{mol}^{-1}\text{cm}^{-1}$) which are characteristic of charge transfer transitions.

Attempted preparation of bis(2,2',2''-terpyridyl) nickel(I) perchlorate
 $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)$

As in the case of the previous preparations, the product, which gave a deep blue solution in acetonitrile, could not be isolated without contamination of supporting electrolyte. Its reducing properties were indicated by a positive dichromate test (c.f. section 4.5.2., page 90).

The visible and near infra-red spectrum of a freshly prepared cathode solution, presented in figure 83, page 209, showed absorbance maxima at 21980cm^{-1} and 15410cm^{-1} . The high intensities of the bands having molar extinction co-efficients of $13000\text{mol}^{-1}\text{cm}^{-1}$ and $6800\text{mol}^{-1}\text{cm}^{-1}$ respectively, indicate charge transfer transitions.

Bis(2,2'-bipyridyl cobalt(I) perchlorate, $\{\text{Co}(\text{bipy})_2\}(\text{ClO}_4)$

The product was successfully prepared in the absence of tetra-n-butylammonium perchlorate as supporting electrolyte and isolated by Method B on page 88. It gave a positive dichromate reduction test (c.f. section 4.5.2., page 90). The results of the elemental analysis

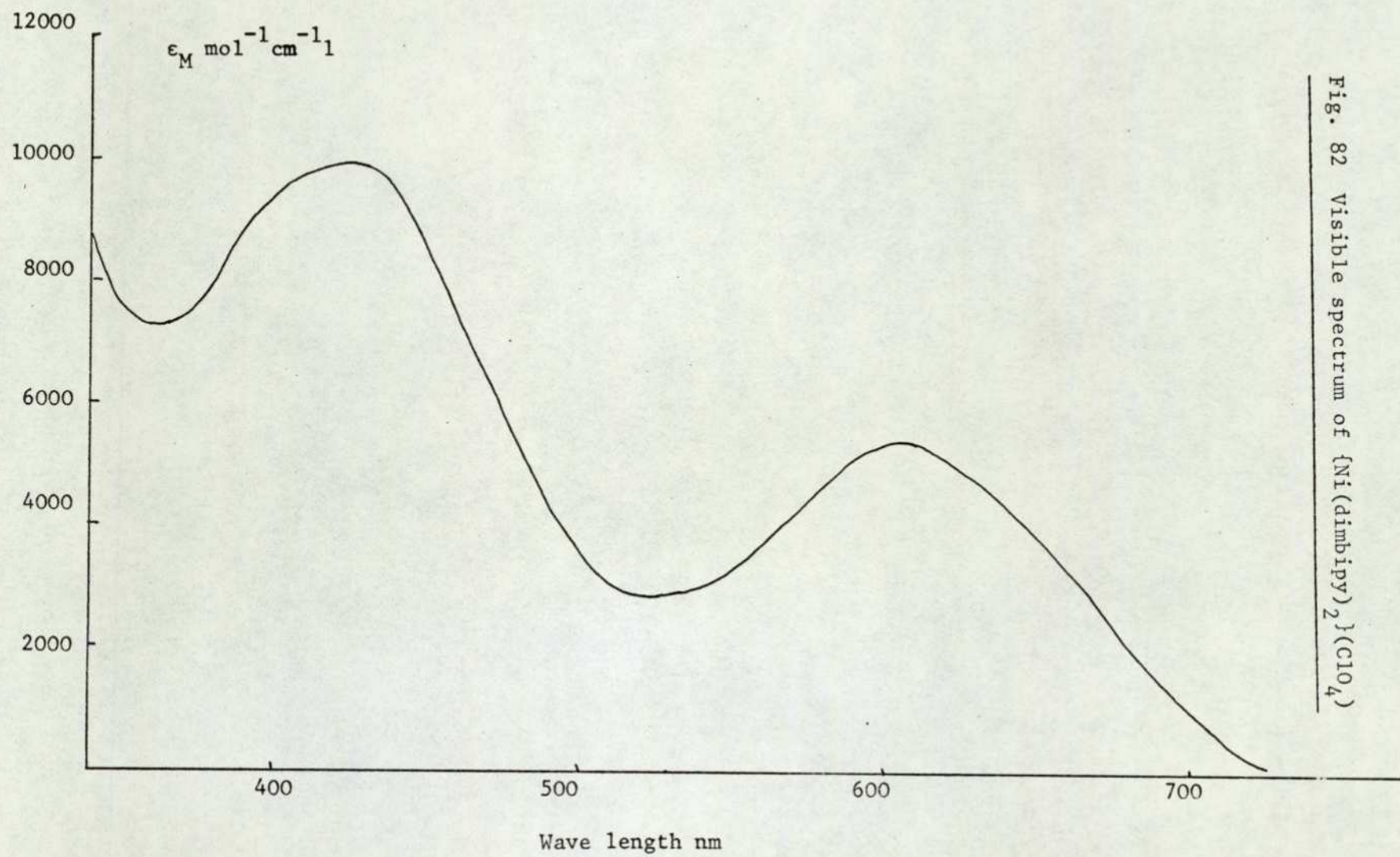


Fig. 82 Visible spectrum of $[\text{Ni}(\text{dimipy})_2](\text{ClO}_4)$

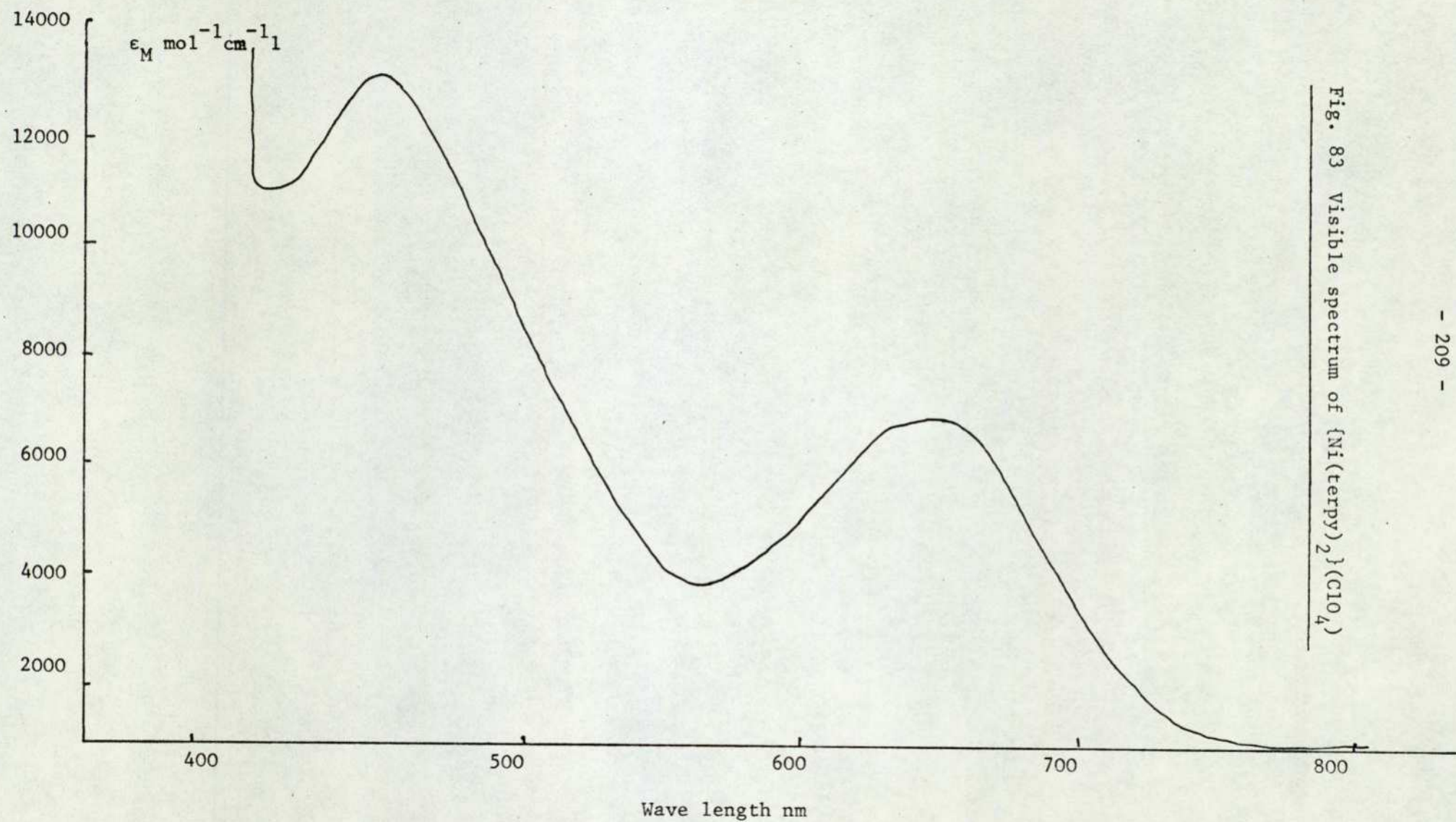


Fig. 83 Visible spectrum of $[\text{Ni}(\text{terpy})_2](\text{ClO}_4)_2$

of the product are given below:

Element	C	H	N	Co
% Found	50.04	3.45	11.85	11.9
% Calculated for formula $\{\text{Co}(\text{bipy})_3\}(\text{ClO}_4)$	57.50	3.83	13.41	9.4
% Calculated for formula $\{\text{Co}(\text{bipy})_2\}(\text{ClO}_4)$	49.58	3.30	11.50	12.6

Previous reported preparations of the cobalt(I)-bipyridyl perchlorate complexes have been in disagreement as to whether two or three ligand molecules are present in the complex.¹⁰⁰⁻¹⁰³ The present data are in good agreement with the composition $\{\text{Co}(\text{bipy})_2\}(\text{ClO}_4)$ in support of the complex described by Vlcek,¹⁰¹ only small discrepancies being found between the experimental and calculated figures. The composition $\{\text{Co}(\text{bipy})_3\}(\text{ClO}_4)$ can be ruled out for the product obtained.

The visible and near infra-red spectrum (figure 84, page 211) showed charge transfer bands at 25600cm^{-1} ($\epsilon_M = 6500\text{mol}^{-1}\text{cm}^{-1}$) and 16640cm^{-1} ($\epsilon_M = 7800\text{mol}^{-1}\text{cm}^{-1}$) which are in agreement with the reported data of Waing and Martin¹⁰² and Csarszar.²⁶⁸

The extreme sensitivity of the complex to molecular oxygen made handling difficult, a colour change to green thence to brown being observed during the packing of a Gouy tube inside the nitrogen filled glove box. This meant that too much significance could not be placed on the magnetic susceptibility determination, which gave an effective magnetic moment of 2.94 B.M. at 291°K .

The experimental value of effective magnetic moment corresponds fairly closely to the spin only value of 2.83 B.M. for two unpaired

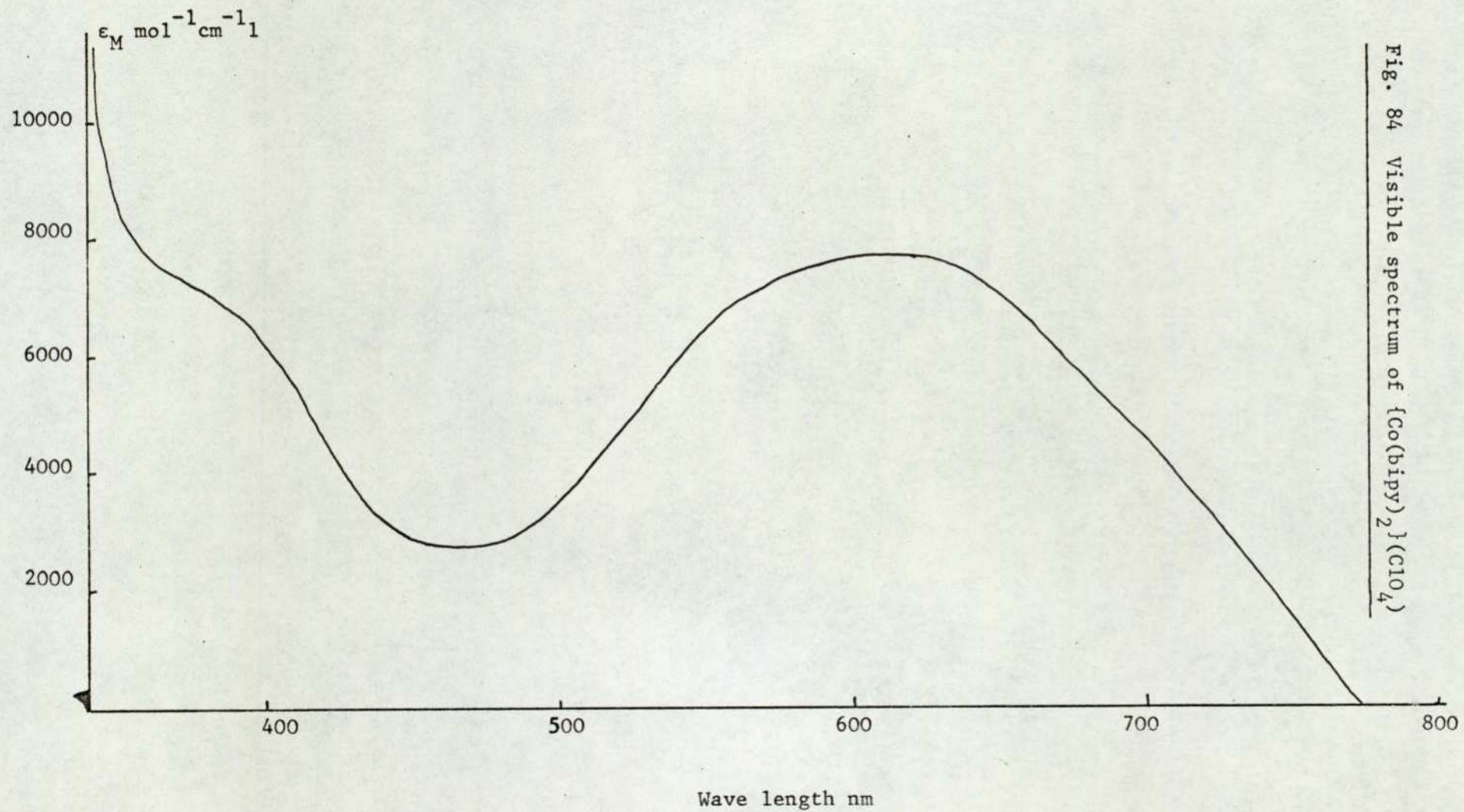


Fig. 84 Visible spectrum of $[\text{Co}(\text{bipy})_2](\text{ClO}_4)_2$

electrons and would seem to rule out a tetrahedral structure for the four co-ordinate complex for which a large first order orbital contribution would be expected. The square planar configuration is not considered, since all known d^8 square planar complexes are spin paired. A possible environment for the cobalt(I) might be tetragonal or octahedral with the anion molecules acting as bridging groups in trans positions in a polymeric chain. In view of the doubt of the reliability of the present data, however, speculation as to the structure of the complex is not very meaningful.

Attempted preparation and isolation of bis(4,4'-dimethyl-2,2'-bipyridyl) cobalt(I) perchlorate, $\{Co(dimbipy)_2\}(ClO_4)_2$

The method of using the starting material, $\{Co(bipy)_3\}(ClO_4)_2$, as its own supporting electrolyte was not tried because of the expense involved. Electro-reduction of the cobalt(II) complex in the presence of tetra-n-butylammonium perchlorate supporting electrolyte gave dark blue solutions from which the cobalt(I) complex could not be isolated by Method A (page 87) and the investigation of the product was carried out directly on the cathode compartment solution. Attempts to isolate the product by stripping off the solvent under reduced pressure gave a blue viscous mass.

The solution containing the product had the power to reduce the dichromate ion (c.f. section 4.5.2., page 90). The visible and near infra-red spectrum of the product (figure 85, page 213) showed intense absorption bands at 23810cm^{-1} ($\epsilon_M = 11000\text{mol}^{-1}\text{cm}^{-1}$) and 16440cm^{-1} ($\epsilon_M = 8000\text{mol}^{-1}\text{cm}^{-1}$). The composition of the complex, by comparison with cobalt(I)-bipyridyl is expected to be $\{Co(dimbipy)_2\}(ClO_4)_2$.

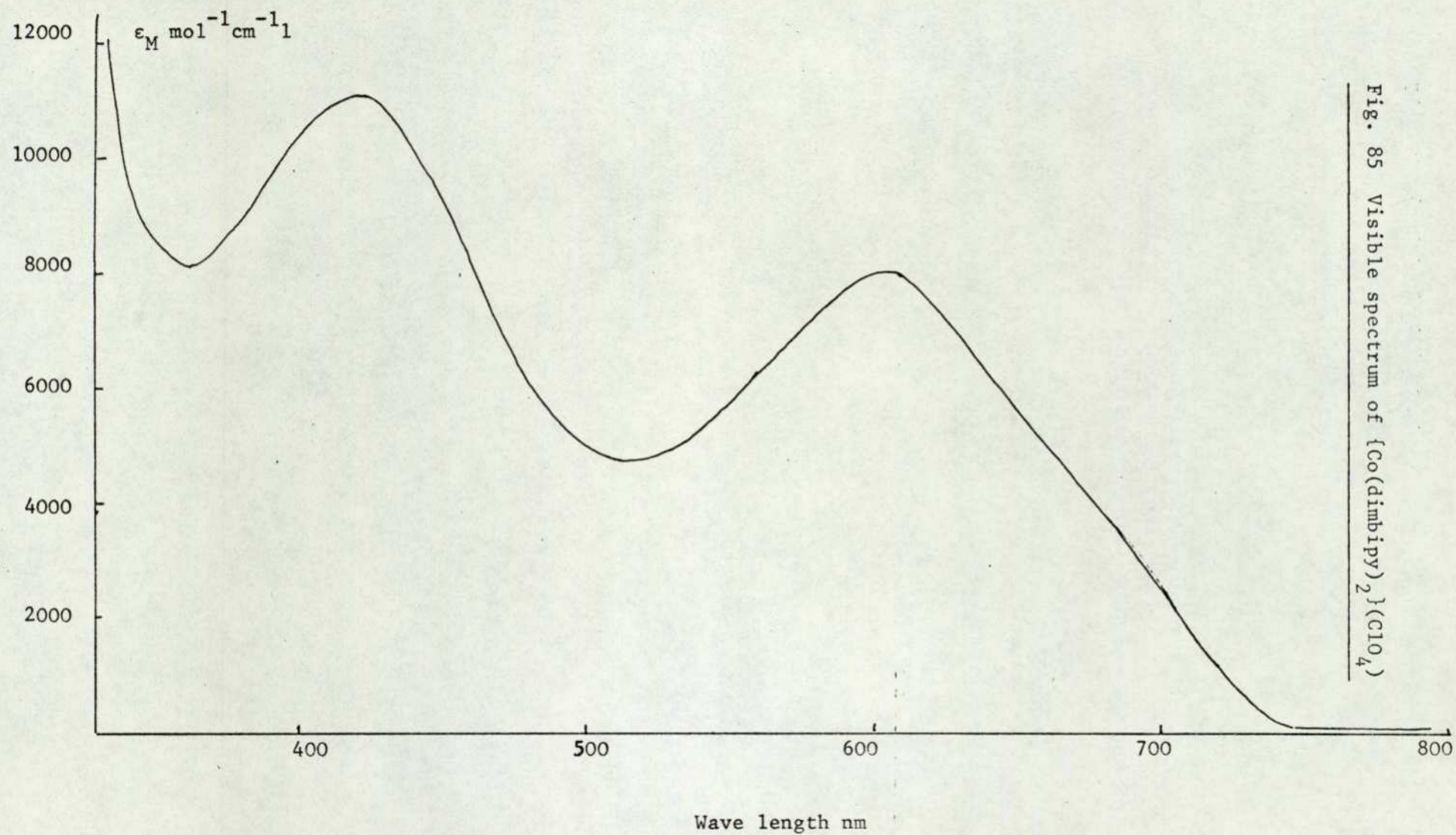


Fig. 85 Visible spectrum of $\{\text{Co}(\text{dimbipy})_2\}(\text{ClO}_4)$

Attempted preparation and isolation of a 2,2',2''-terpyridyl complex of cobalt(I) perchlorate

Similar difficulties were encountered as in the previous preparations.

The intense blue coloured solution which formed on the electro-reduction of $\{\text{Co}(\text{terpy})_2\}(\text{ClO}_4)_2$ with tetra-n-butylammonium perchlorate as supporting electrolyte exhibited reducing properties, and gave a visible and near infra-red spectrum (figure 86, page 215) having intense absorption bands at 23200cm^{-1} ($\epsilon_M = 8500\text{mol}^{-1}\text{cm}^{-1}$), 19420cm^{-1} ($\epsilon_M = 6200\text{mol}^{-1}\text{cm}^{-1}$) and 18110cm^{-1} ($\epsilon_M = 5800\text{mol}^{-1}\text{cm}^{-1}$), again indicative of charge transfer transitions.

Attempted preparation and isolation of a 2,2'-bipyridyl complex of iron(I) perchlorate

Electro-reduction was carried out in the absence of tetra-n-butylammonium perchlorate as in the preparation of $\{\text{Ni}(\text{bipy})_2\}(\text{ClO}_4)$ and $\{\text{Co}(\text{bipy})_2\}(\text{ClO}_4)$. This was followed by Method B (page 88) for isolation of the product. Unfortunately, the dark blue-violet solutions were so unstable that they reverted to the red colour of the starting material before the isolation procedure could be completed even though the usual care and precautions were taken. The product could only be collected as a blue viscous mass by stripping off the solvent. Examination of the product was limited to tests carried out on the cathode compartment solution immediately after electrolysis. The dichromate reduction test (c.f. section 4.5.2., page 90) was positive. Intense absorption bands were observed in the visible spectrum region (figure 87, page 216) at 25510cm^{-1} ($\epsilon_M = 9000\text{mol}^{-1}\text{cm}^{-1}$), 20410cm^{-1} ($\epsilon_M = 6300\text{mol}^{-1}\text{cm}^{-1}$), 19140cm^{-1} (shoulder, $\epsilon_M = 7100\text{mol}^{-1}\text{cm}^{-1}$) and 16530cm^{-1} ($\epsilon_M = 4600\text{mol}^{-1}\text{cm}^{-1}$).

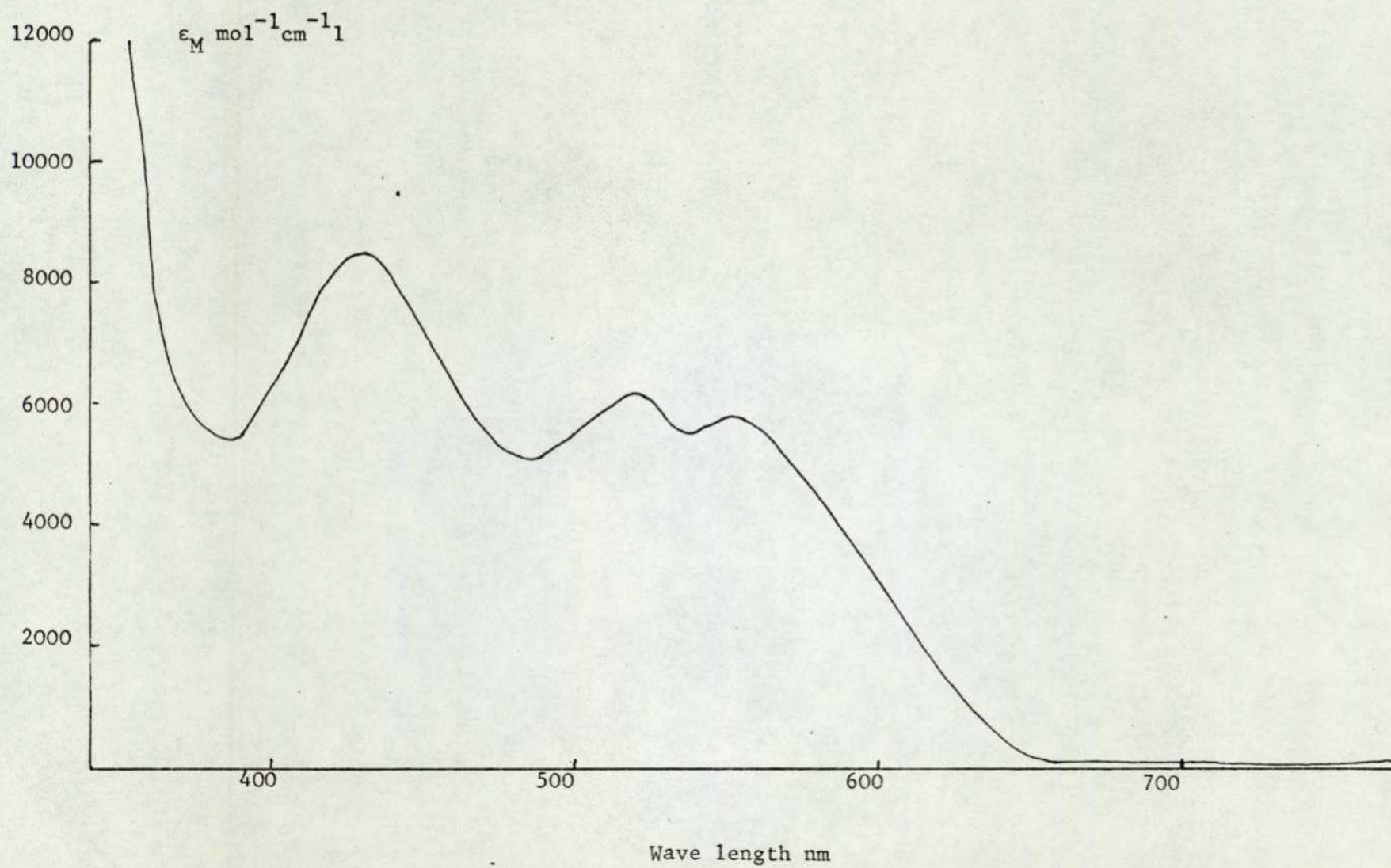
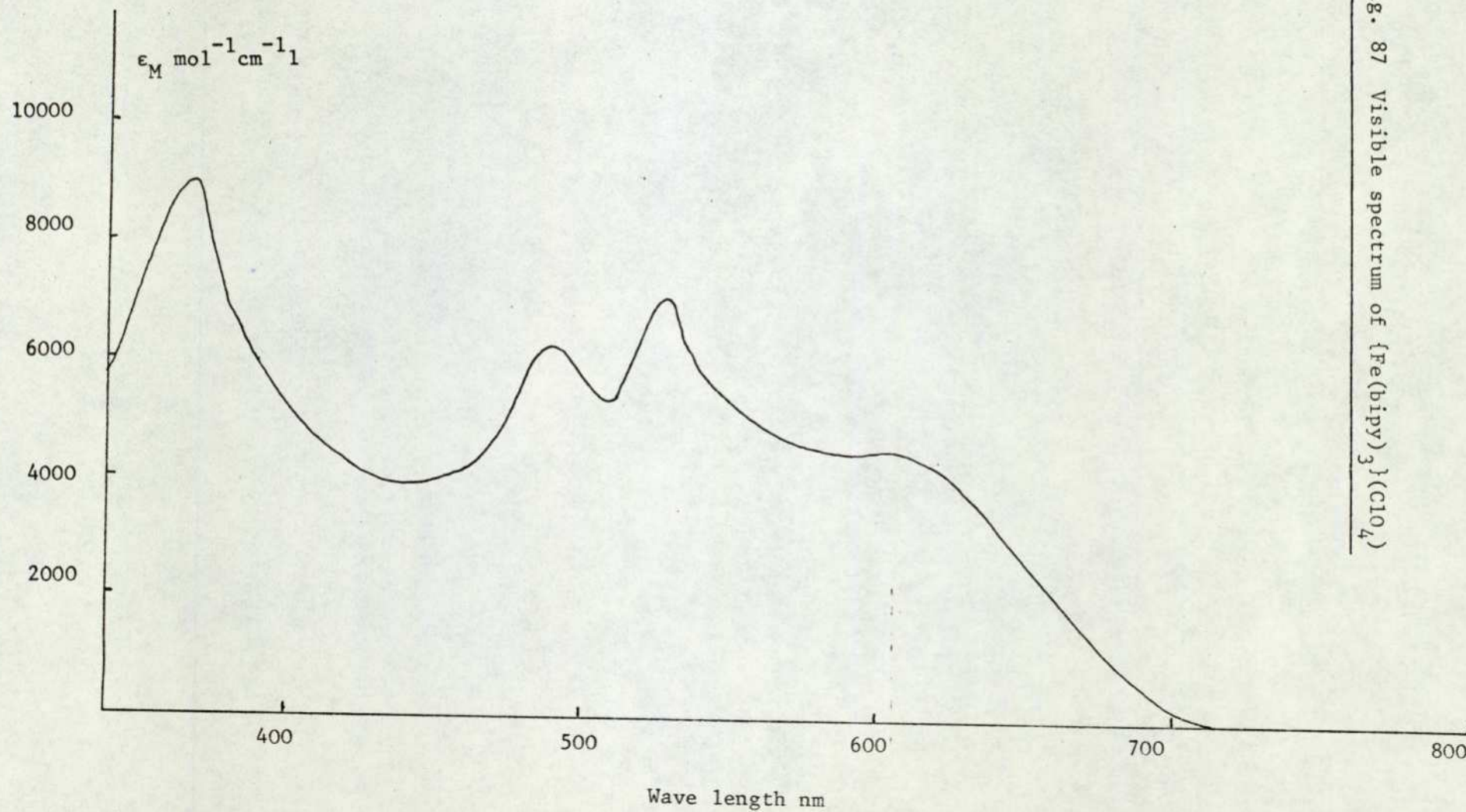


Fig. 86 Visible spectrum of $\{\text{Co}(\text{terpy})_2\}(\text{ClO}_4)_2$

Fig. 87 Visible spectrum of $\{\text{Fe}(\text{bipy})_3\}(\text{ClO}_4)$



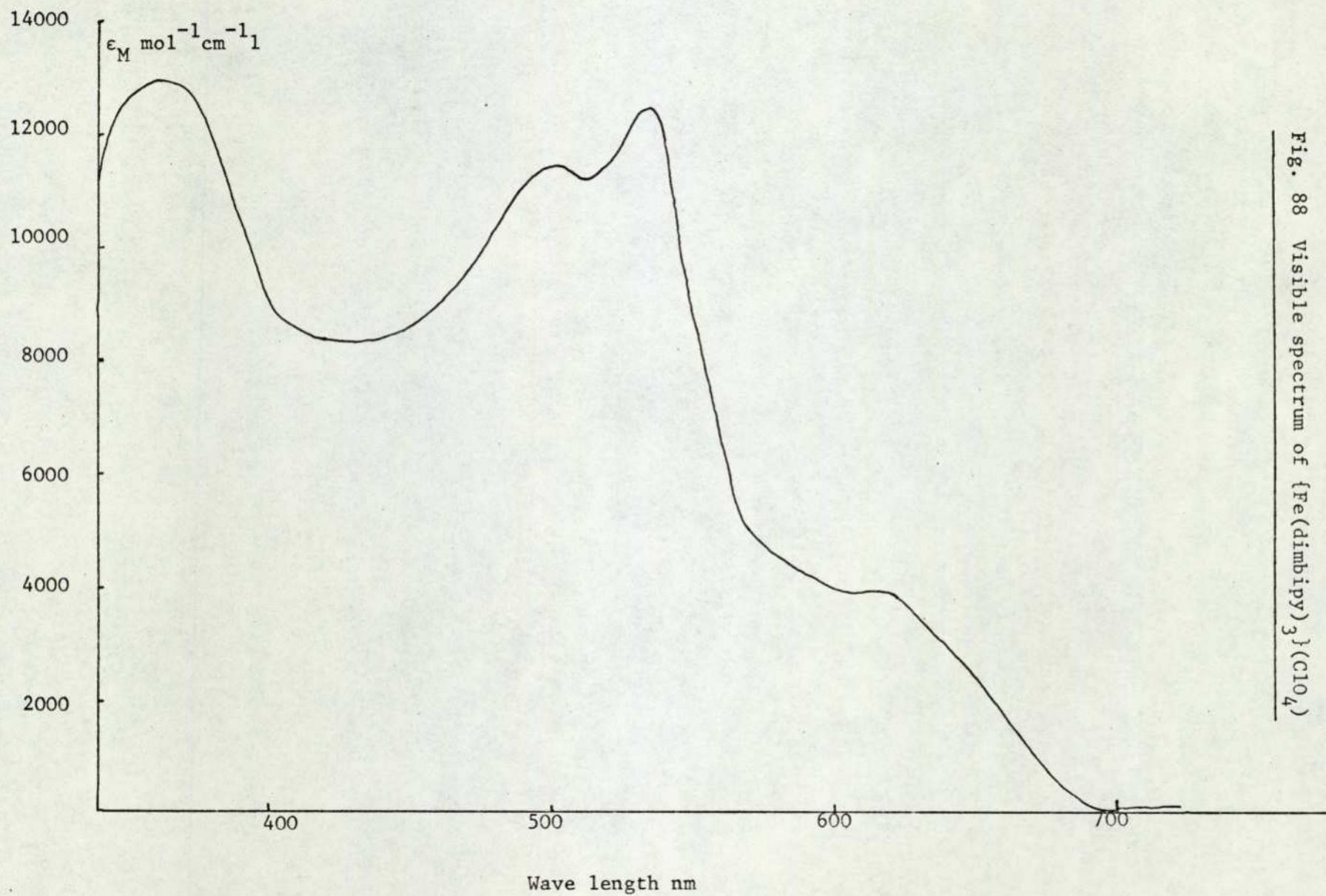
Attempted preparation and isolation of 4,4'-dimethyl-2,2'-bipyridyl
and 2,2',2''-terpyridyl complexes of iron(I) perchlorate

Isolation of the products was not possible and in both attempted preparations, tests were carried out on the cathode compartment solutions obtained on electrochemical reduction of the corresponding metal(II) complexes in the presence of tetra-n-butylammonium perchlorate supporting electrolyte. Both product solutions were similar in colour to the iron(I)-bipyridyl complex and both gave positive dichromate tests (c.f. section 4.5.2., page 90).

The visible and near infra-red spectrum (figure 88, page 218) of the dimethylbipyridyl-iron(I) complex gave intense bands at 27470cm^{-1} ($\epsilon_M = 13000\text{mol}^{-1}\text{cm}^{-1}\text{l}$), 19870cm^{-1} ($\epsilon_M = 11500\text{mol}^{-1}\text{cm}^{-1}\text{l}$), 18690cm^{-1} ($\epsilon_M = 12500\text{mol}^{-1}\text{cm}^{-1}\text{l}$) and 16400cm^{-1} ($\epsilon_M = 3900\text{mol}^{-1}\text{cm}^{-1}\text{l}$) typical of charge transfer transitions.

The spectrum of the iron(I)-terpyridyl complex, presented in figure 89, page 219, showed intense bands at 23530cm^{-1} ($\epsilon_M = 7000\text{mol}^{-1}\text{cm}^{-1}\text{l}$), 18870cm^{-1} ($\epsilon_M = 9800\text{mol}^{-1}\text{cm}^{-1}\text{l}$) and 18180cm^{-1} ($\epsilon_M = 10750\text{mol}^{-1}\text{cm}^{-1}\text{l}$).

Fig. 88 Visible spectrum of $\{\text{Fe}(\text{dimbipy})_3\}(\text{ClO}_4)$



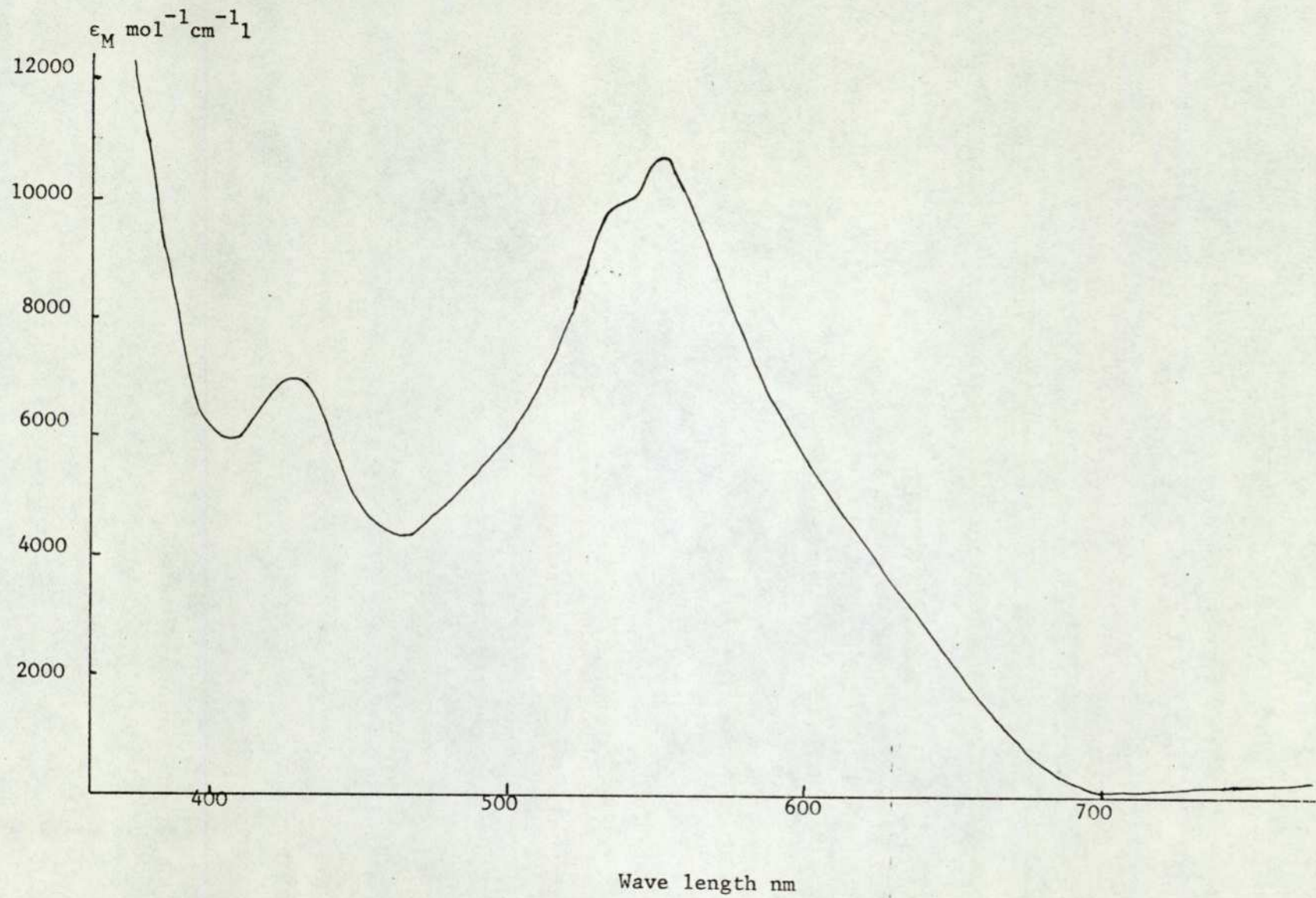


Fig. 89 Visible spectrum of {Fe(terpy)₂}(ClO₄)₂

5.4.3. Discussion

A major success of the electrochemical technique has been in the preparation of polypyridyl complexes of nickel(III) perchlorate, which have not previously been reported. The complexes were formed in good yield in a pure state as indicated by the analytical data. The complexes were sufficiently stable to be handled by normal glove-box methods and even on exposure to a moist atmosphere, reduction back to the corresponding nickel(II) complex was slow. Although polypyridyl complexes of iron(III) and cobalt(III) perchlorate have been prepared successfully by conventional methods, the present technique is a useful alternative to chemical oxidation, giving pure anhydrous products in very good yields. Normally, the method would not be considered in the preparation of iron(III) complexes, which can be obtained directly from reactions of iron(III) compounds without the need for any oxidation process. As stated earlier, it was hoped that the inclusion of iron(III) preparations would provide additional evidence for the general usefulness of the technique by giving known products; this has been achieved.

The isolation of nickel(I), cobalt(I) and iron(I) polypyridyl complexes was found to be much more difficult than for the corresponding metal(III) complexes. The reasons for this are, firstly, that metal(I) polypyridyl complexes are much more soluble in acetonitrile than the corresponding metal(II) and metal(III) complexes and, secondly, that the metal(I) complexes are extremely sensitive to molecular oxygen and are rapidly reoxidised even when handled in a nitrogen atmosphere containing only traces of oxygen. Despite these difficulties, it has been possible to isolate both $\{\text{Ni}(\text{bipy})_2\}(\text{ClO}_4)$ and $\{\text{Co}(\text{bipy})_2\}(\text{ClO}_4)$ from acetonitrile

solutions and obtain analyses which, considering the practical difficulties involved, are remarkably good. The nickel(I)-bipy complex has not previously been reported and the composition of the cobalt(I)-bipy complex (previously reported¹⁰⁰⁻¹⁰³) has been in doubt. In the case of the other attempted metal(I) complex preparations, isolation has unfortunately not been possible, although there seems little doubt that the complexes are formed in solution.

5.5. Electronic Spectra

Electronic spectral studies of polypyridyl complexes of iron, cobalt and nickel have been concerned mainly with 2,2'-bipyridyl and 1,10-phenanthroline complexes of iron(II), cobalt(II), nickel(II), iron(III) and cobalt(III). Only a limited amount of information is available for terpyridyl complexes. In the present study, new data have been obtained for iron(I), cobalt(I), Nickel(I) and nickel(III) complexes.

The electronic spectra of polypyridyl complexes of transition metal ions are characterised by extremely strong absorption bands in the u.v. region if the spectrum which have been associated with intraligand transitions. For example, of the bands in the vicinity of 42000cm^{-1} and 33000cm^{-1} in bipyridyl complexes the latter has been assigned to a $\pi \rightarrow \pi^*$ transition.³¹³ Charge transfer bands appear in the near u.v. region and in many cases are present also in the visible region giving intense colours which are utilised in colorimetric determinations. Iron(II)-bipyridyl complexes show a charge transfer band in the region of 28000cm^{-1} for which a $\pi \rightarrow eg^*$ (ligand to metal) transition has been assigned and a band at lower frequencies ($\sim 19000\text{cm}^{-1}$) associated with a $t_{2g} \rightarrow \pi^*$ (metal to ligand) transition.²⁶⁴

The presence of intraligand and charge transfer bands (ϵ_M values $\sim 10^3 - 10^4 \text{mol}^{-1}\text{cm}^{-1}$) will obliterate any d - d transitions (ϵ_M values $\sim 10 - 10^2$) expected to occur in the same frequency regions. Of the group of complexes examined in the present study, transitions of the d - d type could be observed only in bipyridyl complexes of cobalt(II), cobalt(III), nickel(II), nickel(III) and the terpyridyl complexes of nickel(II) and nickel(III).

The present data for the visible and near i.r. spectra determined in acetonitrile solutions can best be presented for comparative purposes by dealing separately with charge transfer bands and d - d transitions.

Charge transfer bands

Table XIV gives a summary of the present data and where available literature data are included.

The band in the vicinity of 19000cm^{-1} in Fe(II) bipyridyl complexes has been assigned to a $t_{2g} \rightarrow \pi^*$ transition, a similar band having been observed in Fe(II)-phenanthroline complexes.³¹⁴ It is reasonable to assume that such metal oxidation bands will appear at lower frequencies in metal(I) complexes due to their greater ease of oxidation. (Waind and Martin¹⁰² have assigned the band at about 16000cm^{-1} in $\text{Co}(\text{bipy})_2^+$ as a metal oxidation transition). Bands in the spectra of iron(I), cobalt(I) and nickel(I) polypyridyl complexes in the region of 16000cm^{-1} can therefore be tentatively assigned to $t_{2g} \rightarrow \pi^*$ transitions.

Bands in the region of 28000cm^{-1} in Fe(II) complexes may be due to metal reduction transitions ($\pi \rightarrow eg^*$) as suggested by Fergusson and Harris.²⁶⁴ If present in iron(III) complexes, the $\pi \rightarrow eg^*$ transitions would be expected to occur at much lower frequencies than for Fe(II) complexes; in fact, the band observed at 17000cm^{-1} by Day and Sanders³¹⁴ in the tris(1,10-phenanthroline) iron(III) complex ion has been attributed to such a transition. By comparison with the present data for Fe(III)-bipyridyl complexes the prominent but distinct shoulders appearing in the same frequency region might be similarly assigned.

The spectra of Fe(III)-bipyridyl complexes call for some explanation. It will be seen from Table XIV that with the exception

of the shoulders mentioned above, the spectra of Fe(III)-2,2'-bipyridyl and Fe(III)-4,4'-dimethyl-2,2'-bipyridyl complexes are almost identical to those of the corresponding Fe(II) complexes; both sets of spectral data include bands in the region of 28000cm^{-1} and 19000cm^{-1} which have already been discussed in the case of Fe(II) complexes. The presence of such bands with similar assignments would not be expected for the iron(III) complexes. It was thought, at first, that Fe(II) might be present as an impurity in the Fe(III) complexes. However, several important factors do not support this hypothesis. Firstly, values of the molar extinction co-efficient (calculated on the basis of pure Fe(III)) for the bands in question are of the same order of magnitude as those determined for the pure Fe(II) complexes. Secondly, tests for the presence of Fe(II) in the Fe(III) samples were negative and further, the analyses of the samples and their magnetic susceptibilities were consistent with Fe(III) and not Fe(II). Surprisingly, spectral data for iron(III)-bipyridyl complexes are not available in the literature with the exception of one study²⁶⁸ which quotes for the complex ion $\{\text{Fe}(\text{bipy})_3\}^{3+}$ a band at 16000cm^{-1} (observed in the present work) and a shoulder at 25000cm^{-1} . Clearly, further investigation of the spectra of Fe(III)-bipyridyl complexes is required.

d - d transition bands

Table XV gives details of possible d - d bands which are compared with literature data where available.

Of the compounds described in the present work only the electronic spectra of $\{\text{Co}(\text{bipy})_3\}^{2+}$ and $\{\text{Ni}(\text{bipy})_3\}^{2+}$ have previously been studied in detail. Palmer and Piper²⁷² examined the polarised crystal spectra of $\{\text{Co}(\text{bipy})_3\}\text{Br}_2 \cdot 6\text{H}_2\text{O}$ and was able to make confident

Table XIV

Charge Transfer Bands

Complex	Absorption	ϵ_M	Literature data
	Maximum (cm^{-1})	($\text{mol}^{-1} \text{cm}^{-1}$)	
*{Fe(bipy)} ₂ ClO ₄	25510	9000	
	20410	6300	
	19140	7100	
	(16530)	4600	
*{Fe(dimbipy)} ₂ ClO ₄	27470	13000	
	19870	11500	
	18690	12500	
	(16400)	3900	
Fe(I)-terpy perchlorate	23530	7000	
	(18870)	9800	
	18180	10750	
{Co(bipy)} ₂ ClO ₄	(25600)	6500	25640 ($\epsilon_M = 6720$) - in aqueous solution. ²⁶⁸

cont/d ...

Complex	Absorption Maximum (cm^{-1})	ϵ_M ($\text{mol}^{-1} \text{cm}^{-1}$)	Literature data
	16640	7800	16400 ($\epsilon_M = 7480$) ²⁶⁸ 15625 ($\epsilon_M = 5230$) - in aqueous solution, assigned to a $t_{2g} \rightarrow \pi^*$ transition. ¹⁰²
*{Co(dimbipy) ₂ }ClO ₄	23810	11000	
	16440	8000	
*Co(I)-terpy perchlorate	23200	8500	
	19420	6200	
	18110	5800	
{Ni(bipy) ₂ }ClO ₄	25000	9000	
	17540	6900	
*{Ni(dimbipy) ₂ }ClO ₄	23420	9800	
	16260	5440	
Ni(I)-terpy perchlorate	21980	13000	
	15410	6800	

cont/d ...

Complex	Absorption Maximum (cm^{-1})	ϵ_M ($\text{mol}^{-1}\text{cm}^{-1}$)	Literature data
{Fe(bipy) ₂ }(ClO ₄) ₂	28170	8000	28570 ($\epsilon_M = 6600$) assigned to a $\pi \rightarrow eg^*$ transition. ²⁶⁴
			28600 ($\epsilon_M = 9960$) ²⁶⁸
	(20410)	8800	(20120)
	19150	9590	19190 ($\epsilon_M = 8000$) assigned to a $t_{2g} \rightarrow \pi^*$ transition. ²⁶⁶
			19000 ($\epsilon_M = 9590$) ²⁶⁸
{Fe(dimbipy) ₂ }(ClO ₄) ₂	28170	9000	
	(20410)	8860	
	18870	9830	
{Fe(terpy) ₂ }(ClO ₄) ₂	27770	8000	
	18050	11900	18100 ($\epsilon_M = 11600$) ²⁷¹
{Co(terpy) ₂ }(ClO ₄) ₂	27027	1800	
	24096	1350	
	22520	1420	22500 ($\epsilon_M = 1620$) ²⁷¹
	19840	1250	19800 ($\epsilon_M = 1420$) ²⁷¹
	18120	420	18100 ($\epsilon_M = 600$) ²⁷¹

Complex	Absorption Maximum (cm^{-1})	ϵ_M ($\text{mol}^{-1} \text{cm}^{-1}$)	Literature data
{Fe(bipy) ₃ }(ClO ₄) ₃	28170	8500	(25000) ($\epsilon_M = 1000$) in aqueous solution²⁶⁸ 16000 ($\epsilon_M = 462$)
	(20620)	9000	
	19150	10200	
	16700	670	
{Fe(dimbipy) ₃ }(ClO ₄) ₃	28170	8000	
	(20410)	10000	
	18870	11000	
	16400	700	
{Fe(terpy) ₂ }(ClO ₄) ₃	(19610)	3500	
	18180	5800	
	(16130)	1600	
	14290	700	

*Expected composition.

Absorption maxima in parentheses denote unresolved shoulders.

Bracket } denotes split band.

assignments to the transitions observed. (c.f. Table XV).

$\{\text{Co}(\text{bipy})_3\}(\text{ClO}_4)_2$. The spectrum of this high spin complex in acetonitrile shows bands which correspond to two of the bands obtained by Palmer and Piper²⁷² in the crystal state. Although the present investigation included the near infra-red region, the reported band at 11000cm^{-1} (assigned ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$) was not observed. By comparison with Palmer and Piper's²⁷² assignments, the bands at 22730cm^{-1} and 18250cm^{-1} were taken as ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ and ${}^4\text{T}_1(\text{F}) \rightarrow {}^2\text{T}_1(\text{P,H})$ transitions respectively. On this basis, values of Δ and B were calculated as 13100cm^{-1} and 813cm^{-1} respectively using the d^7 Tanabe-Sugano diagram presented by Offenhartz.³¹⁵

$\{\text{Co}(\text{dimbipy})_3\}(\text{ClO}_4)_2$. Using the same assignments as for $\{\text{Co}(\text{bipy})_3\}(\text{ClO}_4)_2$, values of Δ and B were calculated as 13450cm^{-1} and 820cm^{-1} respectively.

$\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_2$. The bands observed at 12430cm^{-1} and 18980cm^{-1} correspond closely to the bands assigned by Palmer and Piper²⁷² to the ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ and ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{F})$ transitions respectively. Assuming the same assignments, values of Δ and B were calculated as 13200cm^{-1} and 725cm^{-1} respectively using the d^8 Tanabe-Sugano diagram.³¹⁵

$\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_2$. Taking the bands at 12880cm^{-1} and 19270cm^{-1} to correspond to ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ and ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{F})$ transitions respectively, as in the case of $\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_2$, values of Δ and B were calculated as 13000cm^{-1} and 685cm^{-1} respectively.

$\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_2$. Assignments for the visible and near infra-red spectrum of this complex have not previously been made. By comparison with the Ni(II) bipyridyl systems it would seem reasonable to assign the bands at 12500cm^{-1} and 19600cm^{-1} to ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ and

${}^3A_2(F) \rightarrow {}^3T_1(F)$ respectively. On this basis, values of Δ and B are calculated to be 15500cm^{-1} and 890cm^{-1} respectively. The higher value of Δ for the terpyridyl ligand compared to the bipyridyl ligands is in accordance with the accepted order of ligand field strengths.

The above values of Δ and B permit the expected frequency of the ${}^3A_2(F) \rightarrow {}^1A_1(G)$ transition to be determined; the calculated value of 22900cm^{-1} corresponds well with the observed band in the region of 22500cm^{-1} .

Cobalt(III) and nickel(III) complexes. Spectral data for these complexes is limited and in the absence of guide lines from previous assignments, it has not been possible to assign the transitions and make calculations of values of Δ and B.

Conclusions

Spectral data for the cobalt(II) and nickel(II) complexes are in agreement with previously published results and correlate well with the magnetic data. Calculated values of the crystal field splitting parameter, Δ and the Racah parameter, B, are summarised below:

Complex	Δ (cm^{-1})	B (cm^{-1})
$\{\text{Co}(\text{bipy})_3\}(\text{ClO}_4)_2$	13100	813
$\{\text{Co}(\text{dimbipy})_3\}(\text{ClO}_4)_2$	13450	820
$\{\text{Ni}(\text{bipy})_3\}(\text{ClO}_4)_2$	13200	725
$\{\text{Ni}(\text{dimbipy})_3\}(\text{ClO}_4)_2$	13000	685
$\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_2$	15500	890

Since the calculations of Δ and B are based on the absorption maxima of broad bands the limits of error will be of the order of

$\pm 10\%$. It can be seen, therefore, that within these limits, the values of Δ for Co(II) and Ni(II) complexes of 2,2'-bipyridyl and 4,4'-dimethyl-2,2'-bipyridyl are essentially the same but significantly less than the value for the Ni(II)-terpyridyl complex. It would be expected from these results that if the bipyridyl complexes of Co(III) and Ni(III) are spin paired, then the Ni(III)-terpyridyl complex should also be spin paired assuming an octahedral structure. Now it has been noted that of the Ni(III) complexes prepared in the present work, the terpyridyl complex was the only one found to be spin-free (c.f. page 150) which is at variance with the spectroscopic data. The tentative suggestion is put forward that the complex $\{\text{Ni}(\text{terpy})_2\}(\text{ClO}_4)_3$ might be tetrahedral and not octahedral as originally supposed. The fact that the molar extinction co-efficient for the lowest frequency band of the complex is high ($\epsilon_M = 114 \text{ mol}^{-1} \text{ cm}^{-1}$) compared to the values obtained for octahedral polypyridyl complexes in acetonitrile ($\epsilon_M = 10-50 \text{ mol}^{-1} \text{ cm}^{-1}$) supports this argument. A tetrahedral structure would imply that only two nitrogen atoms of each ligand are involved in the co-ordination. Unfortunately, the analytical data for this complex were in some doubt and clearly more work will be required to resolve the problem.

Table XV

d - d transition bands

Complex	Absorption Maximum (cm^{-1})	ϵ_M ($\text{mol}^{-1} \text{cm}^{-1} \text{l}$)	Literature data	
{Co(bipy) ₃ }(ClO ₄) ₂	(22730)	30	(22000) ($\epsilon = 50$) ^{*272}	Assigned ${}^4T_1(F) \rightarrow {}^4T_1(P)$
	18250	6	18300 ($\epsilon = 10$) ^{*272}	${}^4T_1(F) \rightarrow {}^2T_1(P,H)$
			16000	${}^4T_1(F) \rightarrow {}^2T_1(G) {}^2T_2(G)$
			11000 ($\epsilon = 11$) ^{*272}	${}^4T_1(F) \rightarrow {}^4T_2(F)$
*All work on crystals of {Co(bipy) ₃ }Br ₂ ·6H ₂ O.				
Only band at 11260cm^{-1} found in aqueous solution, not observed in present study.				
{Co(dimbipy) ₃ }(ClO ₄) ₂	(23260)	34		
	18500	10		
{Ni(bipy) ₃ }(ClO ₄) ₂			(21000) ($\epsilon = 0.2$)	${}^3A_2(F) \rightarrow {}^1A_1(G)$ ^{*272}
	18980	96	18870 ($\epsilon = 20.7$)	${}^3A_2(F) \rightarrow {}^3T_1(F)$ ^{*272}
	12430	21	12740 ($\epsilon = 6.7$)	${}^3A_2(F) \rightarrow {}^3T_2(F)$ ^{*272}
			(11400) ($\epsilon = 2.1$)	${}^3A_2(F) \rightarrow {}^1E(D)$ ^{*272}
*{Ni(bipy) ₃ }Br ₂ ·6H ₂ O crystal				

cont/d ...

Complex	Absorption Maximum (cm^{-1})	ϵ_M ($\text{mol}^{-1}\text{cm}^{-1}$)	Literature data	
{Ni(dimbipy) ₃ }(ClO ₄) ₂	19270 12880	107 25	19200 ($\epsilon = 11$)	$\left. \begin{array}{l} {}^3A_2(F) \rightarrow {}^3T_1(F) \\ {}^3A_1(F) \rightarrow {}^3T_2(F) \\ {}^3A_2(F) \rightarrow {}^1E(D) \end{array} \right\} \begin{array}{l} [\text{Ni(bipy)}_3]\text{Br}_2 \\ \text{aqueous} \\ \text{solution} \end{array}$
			12650 ($\epsilon = 7$)	
			(11900) ($\epsilon = 7$)	
{Ni(terpy) ₂ }(ClO ₄) ₂	23000 21980 19600 (18180)	22 22 29 21	20000 ($\epsilon = 32$) ²⁷¹	$\left. \begin{array}{l} {}^3A_2(F) \rightarrow {}^3T_1(F) \\ {}^3A_1(F) \rightarrow {}^3T_2(F) \\ {}^3A_2(F) \rightarrow {}^1E(D) \end{array} \right\} \begin{array}{l} [\text{Ni(terpy)}_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O} \\ \text{in aqueous solution} \end{array}$
{Co(bipy) ₃ }(ClO ₄) ₃	21840	60	22100 ($\epsilon = 68$) ³⁰⁷	aqueous solution
			22000 ($\epsilon = 93$) ²⁶⁸	
{Co(dimbipy) ₃ }(ClO ₄) ₃	(24630) 22220	69 48		
{Co(terpy) ₂ }(ClO ₄) ₃	22570	280	22500 ($\epsilon = 340$) ³¹²	{Co(terpy) ₂ }Cl ₃ in ethanol

cont/d ...

Complex	Absorption	ϵ_M	Literature data
	Maximum (cm^{-1})	($\text{mol}^{-1} \text{cm}^{-1}$)	
{Ni(bipy) ₃ }(ClO ₄) ₃	(25900)	106	
	16590	60	
{Ni(dimbipy) ₃ }(ClO ₄) ₃	(24150)	125	
	16660	33	
{Ni(terpy) ₂ }(ClO ₄) ₃	24040 (centre of triplet band)	19	
	20240	114	

Frequencies in parentheses denote unresolved shoulders.

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