SOLVENT EXTRACTION BY ALKYL BIPYRIDINES

by

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ABSTRACT

A series of 4,4'-dialkyl-2,2'-bipyridines and 4,4',5,5'-quatro-alkyl-2,2'-bipyridines with alkyl chain lengths 1C - 9C and varying in complexity has been prepared. Various synthetic routes were used and two were optimized for the synthesis of the new alkyl bipyridines. Structures and purity of products were confirmed by chromatographic techniques, infrared and nuclear magnetic resonance spectroscopy, and some samples were assessed by elemental analysis.

The solvent extraction properties of the range of alkyl bipyridines in organic solution, as reagents, was investigated for the metal ions Ni(II), Cu(II), Co(II), Fe(II) and Fe(III). Preliminary tests with one reagent defined the conditions for possibly selective extractions. The most suitable diluent, acid conditions and nature of anions affecting the extraction were found.

A routine of shake-out tests for the full range of alkyl bipyridines prepared was established. The results showed the relationships between metal extractability, acid solubility of reagent, rates of extraction and selectivity, all related to alkyl chain length and overall molecular structure of the reagent. They suggested the possibility of design of a selective reagent by small alterations in molecular structure or conditions of extraction.

Extraction tests were designed to investigate the mechanism of the extraction reaction. The effects of pH, metal loading, reagent concentration and anion concentration were evaluated. The structures of the metal complexes have been suggested, but the complexity of extractions from acid precluded any proposal of equilibrium equations for the extractions.

ACKNOWLEDGEMENTS

I am grateful to all those people who have helped to make this thesis a reality.

Firstly, thank you to my supervisor, Dr John Monhemius, for the guidance and interest shown in my project and its compilation into a thesis.

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As a chemist in a metallurgy department, I have needed some equipment and facilities of the chemistry department. I wish to thank the staff and students there for allowing me the freedom of their laboratories and use of instruments.

I would like to thank my sponsors, N.R.D.C., who allowed me to use the work I did in their employment for this degree.

Finally, thank you Laurie, for your instigation to take this degree course and the encouragement throughout the experimental and writing up stages.

Karen Coulston.

CONTENTS

1. INTRODUCTION

The technique of solvent extraction is a very useful tool to the chemist. The difference in solubility of an organic compound in aqueous or organic solvents can enable it to be extracted between immiscible phases. Thus certain compounds can be isolated from their reaction mixtures and also purified according to their solubility properties relative to those of the impurities. Solvent extraction is a useful analytical procedure when a compound can be completely transferred to another phase where it is more easily manipulated and its physical properties are more easily measured.

Simple ions, most especially metal ions, can be extracted from aqueous solutions into an organic diluent with the aid of certain organic molecules which can react with metal ions, forming a hydrophobic shell, which is then soluble in the immiscible organic phase.

The mechanisms of the extraction reactions vary with the nature of the extractant. Some extractant molecules are bonded to the metal ion as chelates, some in solvation shells, and some as ion pairs. Some extracted complexes are formed by a combination of these types of bonds.

The analytical chemist uses many of the various types of complex. He is usually isolating trace amounts of the metal and can measure its coloured complexes by spectrophotometric methods. He can isolate the complex for study of its composition or physical properties.

As an extension of the chemist's approach, metallurgists have found that solvent extraction of metal ions from leach liquors into organic solvents is a good method of isolation and purification of a metal from its mineral source or from mining residues. The simple laboratory solvent extraction procedure can be automated and enlarged to commercial scale plants, producing up to 300,000 kg of metal per day. The metallurgist has different requirements for his organic extractants than the chemist. There does not necessarily have to be a coloured complex formed. The extraction must be fast; the extractant must have a high loading capacity; the extraction reagent must be relatively cheap, aqueous insoluble, but soluble in a common organic diluent (so it is not lost to the system), and the metal complex must dissociate easily under controlled stripping conditions such that the metal is in a usable form and the reagent can be recycled.

The various solutes in the aqueous phase must be considered. Extraction processes may produce strongly acid or alkaline leach liquors containing various electrolytes usually sulphate or chloride.

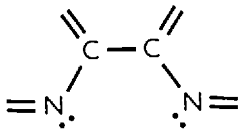
Various organic compounds have now been produced as commercial extractants: tributylphosphate, carboxylic acids, amines, the hydroxy oximes (LIX), and Kelex reagents.

No extractant has been found to be specific for one metal only, but some are selective under defined conditions. These conditions may include pH, the elimination of metals which may interfere or co-extract, time of extraction, temperature. Thus iron, aluminium and manganese can be extracted separately from an aqueous mixture by 8-hydroxy quinoline in chloroform, by changing the pH. Iron is extracted at pH 2.8, then aluminium at pH 5.0, then manganese at pH 10.0.

Chemists have found colour reactions specific to individual metals in complexes, thus they can determine the amount of a metal by its complex absorbance at a certain wavelength even when other metal complexes are present, providing their absorbances do not overlap the required one. Various metals are extracted as their complexes but each can be identified in the organic solvent by their individual absorbances. For example, the 1,10-phenanthroline complex with ferrous ions is a strong red colour (λ=435 nm). Other metals do not form strongly coloured complexes with 1,10-phenanthroline. The metallurgist wants not just a measure of how much metal is present, but a complete isolation of it.

Selective nickel extraction has been a problem to the metallurgist in all solvent extraction research. Any selective extraction systems investigated have been slow. Nickel-cobalt separation is difficult.

In the search for a nickel selective reagent for commercial solvent extraction, many of the organic chelating agents used in analytical chemistry to extract metals, were studied with a view to modifying one to the metallurgist's needs and to extract nickel commercially. In a study of the stability constants of various transition metal complexes with 2,2'-bipyridine, the nickel complex was found to be the most stable thermodynamically,



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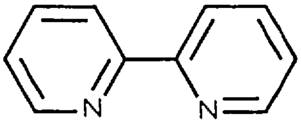

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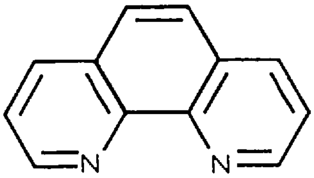


(III)

Compounds incorporating the "ferroine" functional group (I), e.g. 2,2'-bipyridine (II) and 1,10-phenanthroline (III) are well established chelating reagents, particularly for the analytical determination of Fe(II) and Cu(I) as highly coloured complexes in the presence of other metals. The structures have been modified by the addition of substituent groups on various positions of each molecule, such that they are more selective for different metals. Thus the ferroine structure is suggested to be a suitable basis for the design of an extractant which is selective for nickel in the presence of other metals in an aqueous phase.

Hydrometallurgical methods of nickel extraction involve leaching with ammonia or acid, sulphuric acid being the usual leaching solution. Analytical extractions of metals by 2,2'-bipyridine are usually from acid solutions, so a modification of this molecule to extract metals from sulphuric acid solutions may be feasible. A particularly important property of the ferroine grouping is that it does not form a complex with Fe(III), which is generally present in acidic process liquors and is extracted by many of the extractants used at present. This gives one degree of favourable selectivity to the ferroine group compounds to be studied.

The ferroine group reagents are neutral bidentate chelating agents. Co-ordinate bonds are formed between the metal and nitrogen atoms. Two or three ligands are bound to the metal, the number depending on the metal and the steric hindrance that the ligands experience around the metal. As neutral extractants they form cationic complexes with metal ions, so for extraction into another phase, they need to form ion pairs with anions from the aqueous phase. This means that the aqueous electrolyte composition must be well defined for a serious study and its control could promote selectivity. The anions participate in the complex extraction. An alternative is to build an anion, say in the form of a carboxylate group, which can exchange its proton at the interface, into the reagent molecule.

The known ferroine reagents are acid soluble, and some of their metal complexes also stay in the aqueous phase rather than being extracted from it. Thus for further study, in a metallurgical field, a hydrophobic reagent which is soluble only in the organic phase in its free form and which forms organic soluble complexes is required. This can be achieved by building bigger (hydrophobic) groups onto the basic molecule.

Thus changes in the basic molecule, without changing the chelating ability through its ferroine group, variation in organic diluent and variations in the aqueous phase including anion type, ionic strength and pH are steps proposed for study in the design of a solvent extraction reagent, based on the ferroine group, to selectively extract nickel. The project should produce a pattern for design of selectivity, through the experimental results, whether a new commercial reagent is discovered or not.

Many new bipyridine compounds have been prepared in this work. Some are not pure, but they have been used for simple extraction tests. The extraction mechanism for these complexes is very complicated, but some results may help to elucidate it.

The study falls into three main sections :

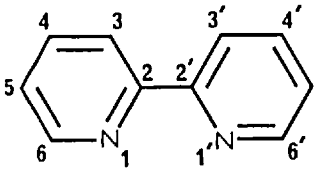
1. Synthesis of the bipyridines,
2. Solvent extraction tests,
3. Study of the mechanism.

These are treated separately but interrelate so much that the discussion of each overlaps.

2. NOMENCLATURE

The nomenclature of organic compounds employed in the present work follows the International Union of Pure and Applied Chemistry rules [1]. Some trivial names are used when cited from a reference which has used them.

The numbering of the bipyridine system is shown below.



Where structural formulae have been presented the shortened notation for alkyl groups (e.g. $-C_3H_7$ rather than $-CH_2.CH_2.CH_3$) has been used to denote unbranched isomers. The longer form has been used where necessary for detailed structural descriptions.

Several accepted notations and abbreviations have been used to simplify structural representations. They are:

R = saturated alkyl group, e.g. C_4H_9,

C_6H_5 = phenyl group,

bipy = 2,2'-bipyridine,

phen = 1,10-phenanthroline,

nC(in chain length descriptions) = number of carbon atoms in the alkyl chain. If a bracket follows nC, the bracketed figures mean,

n = normal,

t = tertiary,

½ = one side only, 4- or 4'-, of the bipyridine is substituted, 2 = double substitution in each of the 4- and 4'-positions of the bipyridine.

Many chemical equations have not been balanced when the stoichiometry and nature of the side products are not important to an understanding of the reaction in the text.

3.BACKGROUND

3.1. History of the Technique of Solvent Extraction in Chemistry

The differences in the liquid-liquid distribution behaviour among various organic substances was recognized by many early chemists, who used solvent extraction as a fundamental technique without understanding its principles. There are several nineteenth century reports of the extraction of metals into organic solvents. The extraction of uranyl nitrate into diethyl ether was reported by Péligot [2] in 1842, and a method that was to be much applied in the ensuing years for the separation of iron in hydrochloric acid with diethyl ether, by Rothe [3] and by Hanroit [4] in 1892. Around the turn of the century there were several studies on distribution equilibria in progress. Nernst [5] published his distribution law: "When a material is distributed between two mutually immiscible liquid phases, the concentration ratio in the two phases at a given temperature is independent of the total amount", in 1891.

The important breakthrough in the extraction of metal ions was made when Fischer [6], in 1925, discovered the use of dithizones to precipitate metal ions as stable chelate complexes. The physical and chemical interpretations of these metal chelate systems were much simpler than the inorganic metal complex systems. The extraction equilibria could be related to metal, reagent and hydrogen ion concentrations. Quantitative descriptions of the extraction process were given by Kolthoff and Sandell [7], then more extensive theoretical treatment was applied by Irving and Williams [8], in 1949, then Dyrssen [9], Stary [10] and Ringbom [11] in the 1950s.

Since then the interest in solvent extraction systems has broadened considerably. The principles and use of the technique in analytical chemistry have been reviewed extensively by Morrison and Freiser [12], who used much of their own work, Stary [13], Zolotov [14], Marcus and Kertes [15], De, Khopkar and Chalmers [16] and Sekine and Hasegawa [17]. Various reports of current research on the fundamentals and application of solvent extraction chemistry presented to the International Conferences on Solvent Extraction Chemistry have been compiled and published [18] and more recently the International Solvent Extraction Conferences [19] have brought together reports on the applications and related technology of solvent extraction.

The solvent extraction reagents can be classified in various ways, but this report has grouped them into four types of complex formation:

A. Solvation

$$M^{m+} + mA^- \xrightarrow{S} [MS_nA_m]_{org}$$

where S is the organic solvent and A^- is a free anion.

$$(C_4H_9O)_3P{=}O \text{ --- } M^{m+} \quad mA^- \qquad \text{(IV)}$$

This group is represented by tributylphosphate (IV) [20] which is used as the organic solvent or diluted with a non-polar diluent. Tributylphosphate molecules solvate the metal ion, replacing water, and in this shell it can be taken into the organic phase with a free anion as an ion pair. The solvation shell interaction with the metal ion is electrostatic and is not as close as a co-ordination shell around the metal ion. The nature of the diluent is important.

B. Ion exchange without chelation

a. Proton exchange by monobasic carboxylic acids (HA)

$$M^{m+} + mHA \longrightarrow [MA_m]_{org} + mH^+$$

Carboxylic acids can exchange their protons for the metal ion. They cannot form chelate rings as a four-membered ring so formed would be unstable. The forces holding the metal ion and extractant are again electrostatic. There is often polymerization of the extractants and the extracted species. An example is the extraction of copper by caproic acid (V) in benzene[21].

$$CH_3(CH_2)_4COO^- \text{---} M^+ \qquad (V)$$

b. Anion exchange by amine salts

$$n\left[(R_3NH^+)A^-\right] + ML_m^{n-} \longrightarrow \left[(R_3NH)_nML_m\right]_{org} + nA^-$$

where A^- is a free anion and L is an anionic ligand such as Cl^-, CN^-, SCN^-.

The extraction order is as follows for extraction of metal chlorides by quaternary ammonium salts[66]:

Cd(II) > Zn(II) > Pb(II) > Fe(III) > Cu(II) > Co(II) > Mn(II) > Ni(II)

Thus most transition metals can be extracted leaving nickel in the aqueous phase.

A free amine, quinoline, in chloroform was used for the extraction of silver perchlorate from solutions of high pH[22], but most amines extract as polymerized amine salt complexes, for example trilaurylamine salt (VI) with thiocyanate[23].

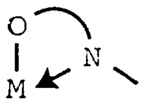
$$\left[(C_{12}H_{25})_3NH^+\right] \text{---} M^+\ 2SCN^- \qquad (VI)$$

C. Ion exchange with chelation

$$M^+ + mHL \longrightarrow (ML_m)_{org} + mH^+$$

where HL is a bi- or poly-dentate ligand.

This group comprises chelating compounds which bond to a metal ion through a deprotonated position (-OH, -COOH, $-SO_3H$, $-AsO_3H_2$, $-PO_3H_2$, -NH-, $-NH_2$, =NOH, -SH) and another electron donor group (=O, -OH, -O-, -N=, $-NH_2$, =NOH, =S, -S-) to form a stable heterocyclic ring incorporating the metal ion.

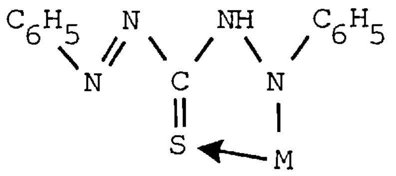


Most chelating reagents are weak acids with dissociation constants of 10^{-3} - 10^{-4} or less. The number of acidic groups and the dentation of the reagent may vary, but most are monobasic, bidentate weak acids. The distribution of their molecules in the undissociated form must favour the organic phase.

The fundamental equilibrium of metal chelate extraction can be followed by the proton exchange.

There has been much research into these complexes and many reviews have been written[12-17]. Some examples are:

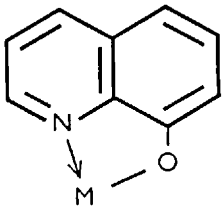
a. Dithizone (diphenylthiocarbazone) (VII)



(VII)

A comprehensive review on dithizone was published by Iwantscheff[24] and there are many by Fischer[25+refs cited therein]. The metal dithizonates are strongly coloured so it has been useful for the determination of small amounts of metal ions. Dithizone reacts with metals which form stable sulphides[26] - Hg, Ag, Pd, Cu, Pb, Zn, Cd - but not with rare earth elements, Al or Zr. Accordingly, elements of the "dithizone" group can be separated from any amounts of aluminium, lanthanides and alkaline earth elements. It has been a useful reagent for qualitative determination of a group of heavy metals of considerable industrial and especially toxicological importance [27].

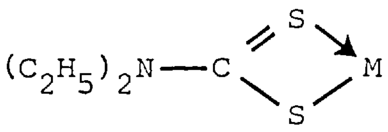
b. 8-Hydroxyquinoline (VIII)



(VIII)

8-Hydroxyquinoline and its derivatives are amphoteric: they are ionic in both acid and basic aqueous solutions. Thus these reagents, from an organic solvent, are readily transferred into the aqueous phase not only at high pH, as are all acidic extractants, but also at low pH. 8-Hydroxyquinoline is a very effective extractant. It extracts many metal ions including Mg, Ca, Al which are not easily extracted with other extractants. It has been extensively reviewed [28,29]. The commercial reagent Kelex is based on this molecule.

c. Sodium diethyldithiocarbamate (IX)



(IX)

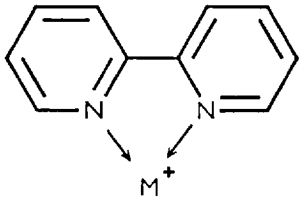
Sodium diethyldithiocarbamate can be used as a selective reagent. It forms complexes with many metals in a limited pH range, but with the use of masking agents, the separations become very selective. Stary [30] and Bode [31] have reported on systematic studies of this reagent.

D. Ion pair formation with chelation

$$M^{m+} + nL + mA^{-} \longrightarrow \left[(ML_n)A_m\right]_{org}$$

The extractant (L) is a neutral bi- or poly-dentate molecule which co-ordinates with the metal ion to form a large cationic complex, extractable into organic solvents if accompanied by a free anion (A), as an ion pair.

This group is represented by molecules containing the ferroine functional group $(=N-\overset{\|}{C}-\overset{\|}{C}-N=)$. It is found in 2,2'-bipyridine (II), 2,2',2"-terpyridine (X) and 1,10-phenanthroline (III) and their derivatives.



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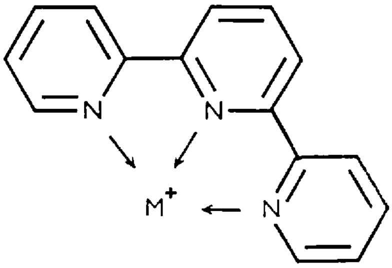

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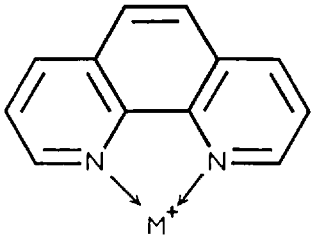


(III)

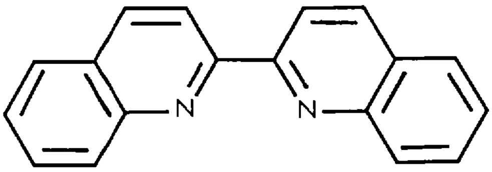
The stable heterocyclic 5-membered rings formed by co-ordinate bonds from the nitrogens to the metal ion contribute to stable bis and tris complexes. This group is the subject of this study and the background studies will be detailed in a later section.

3.2. Selectivity of Reagents

None of these extractants mentioned is specific for one element. Some are selective in that they do not take some elements at all and others only under defined physical conditions or at variable rates, which make them separable.

Gillis [32] has discussed the various terms associated with selectivity of analytical reagents and the possibility of designing selective reagents. Feigl [33] studied specific, selective and sensitive reactions with the aim of employing those unique or different characteristics in analysis and separation.

The many possible modifications of known extraction reagents are now being investigated to introduce specificity into already useful tests. One example of the principle is the discovery of the action of "cuproine" in the work by Hoste [34-36] and coworkers. The ferroine functional grouping of 2,2'-bipyridine and 1,10-phenanthroline had been given that name because of its selectivity for Fe(II). Other metal ions reacted with the grouping but without the distinctive colour of the ferrous complex. Hoste found that 2,2'-biquinoline (XI), with the same ferroine chelating group was "specific" for Cu(I), the bright purple complex being extractable into immiscible solvents, but there were no coloured Fe(II), Ni(II) or Co(II) complexes formed. The bivalent ion in the FeL_3^{2+} cation is 6 co-ordinated, the three ligands being chelated in octahedral configuration. The CuL_2^+ ion is 4 co-ordinated and the two ligands are in a tetrahedral arrangement. Hoste concluded that substitution at the extremities of the molecule, (6,6'-positions for 2,2'-bipyridine and 2,9-positions for 1,10-phenanthroline), caused the tris complex formation to be sterically hindered. Three ligands could not fit octahedrally around a metal ion, but two in a tetrahedral configuration could. Thus di(2,2'-biquinolyl)-Cu^{+}could be formed with this big ligand, but tri(2,2'-biquinolyl)-Fe^{2+}could not. A selectivity for metals which form only tetrahedral complexes had been found. Ferroine complexes become cuproine complexes by addition of sterically hindering alkyl groups to the ligands.



(XI)

Smith and his co-workers [37,38] prepared 25 mono-, di-, tri- and tetra-methyl derivatives of 1,10-phenanthroline to study the effect of methyl group substitutions on physical constants such as molecular extinction co-efficients and redox potentials of ferrous complexes of these derivatives. They looked at the corresponding Cu(I) complexes. They found simple rules to predict the wavelengths of maximum absorption for each methyl substituted derivative with good accuracy.

"Bathophenanthroline" (4,7-diphenyl-1,10-phenanthroline) forms extractable coloured complexes with Cu(I) and Fe(II), but the complexes are easily analysed separately. At pH 4 the CuL_2^{+} cation is converted to the colourless mono-complex CuL^{+}, so that under these conditions, iron can be determined without interference by copper.

Some of these selectivity results are useful for photometric measurement of metals in solution, but most still do not actually isolate one metal by extraction of it, only, into the organic phase.

So the factors to be considered in the design of a selective reagent are:

a. order of stability of metal complexes,
b. solubility in aqueous or organic phases and effect of substituents in nature and position on solubility,
c. colour, for photometric analysis in analytical separations,
d. steric hindrance in co-ordination complexes,
e. oxidation-reduction potentials.

3.3. Solvent Extraction in the Commercial Extraction and Refining of Metals

Mineral ores contain a mixture of metals in common groupings, so the alkaline or acid leach solutions contain various metal ions in solution. Solvent extraction on a large scale can be very useful for isolating one or all of these metals from the leach liquor. Where one element is the major component there are two alternatives for separating it from its impurities. Firstly the impurities may be removed, leaving the product as a pure salt in the aqueous phase. This is useful for solutions of high required metal concentration. Or secondly, the required metal can be extracted, as selectively as possible, leaving the impurities behind in the raffinate. The latter process is more usual;

the metal is concentrated in a purer form in the organic phase. This allows for leaching of low grade ores where the aqueous solution will have low metal concentration. Stripping of the organic solution can also be done selectively if more than one component was extracted.

Hydrometallurgy is not taking over from pyrometallurgy but there is now a profitable partnership between the two. Processes involving solvent extraction can treat low grade ores effectively and also the tailings from other processes. Companies are now being set up to develop, manufacture and sell new reagents for solvent extraction of metals, combining the skills of the metallurgist and synthetic organic chemist.

Solvent extraction processes have been set up for the removal of metals and acids from process waste waters, for economic and environmental value [39-42].

The considerable efforts made by oil companies to remove nickel and vanadium from petrol have resulted in many patents [43-51] for the extraction of metals involving various compounds. These compounds include polyethylene glycol, dimethyl sulphoxide, pyridine, furfural, butyrolactone, acetonitrile, N,N-dimethyl formamide, 2-pyrrolidine, sulphonic acids and hydrofluoric acid.

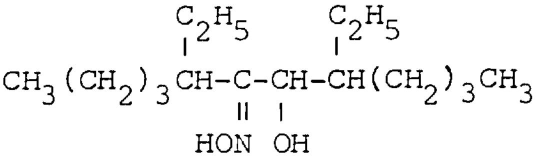
Flett has reviewed the commercial solvent extraction scene over various periods [52,53]. He also reviewed the many patents produced over recent years for potentially commercial scale use.

There are commercial plants in operation for the solvent extraction of copper, nickel/cobalt and uranium and it is feasible that other metals (Mo, W, V, Cr, Cd, Zn, Au, Mn, rare earths) can be treated on appropriately smaller scales.

The copper plants can produce up to 300,000 kg/day[54,55]. The copper source can be leach liquors, scrap copper or tailing liquors. The metal is recovered from strip solutions by electrowinning plants. All of the plants use the LIX reagents, some in conjunction with Versatic Acid. The Kelex reagents and new Shell Metal Extractants are strong competitors.

Commercial extraction reagents are usually modified versions of reagents that have been used for analytical separations for many years. Reagent insolubility in the aqueous phase and increased solubility in the organic phase, an economic necessity for commercial processes, is attained by addition of alkyl chains to parent molecules with known extractive properties.

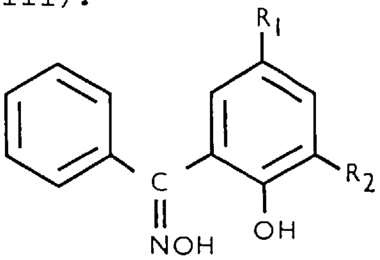
The LIX series of reagents are mostly substituted 2-hydroxy benzophenone oximes. The first LIX reagent, LIX 63 manufactured in 1964, was reported [56] to be 5,8-diethyl-7-hydroxy-6-dodecanone oxime (XII).



$$CH_3(CH_2)_3\overset{C_2H_5}{\overset{|}{CH}}-\underset{HON}{\underset{\|}{C}}-\underset{OH}{\underset{|}{CH}}-\overset{C_2H_5}{\overset{|}{CH}}(CH_2)_3CH_3$$

(XII)

This reagent had insufficient discrimination for copper over iron and inadequate loading characteristics at the normal pH of dump leach liquors. LIX 64, a 2-hydroxy benzophenone oxime substituted in the 5-position with an alkyl group, gave better extraction than LIX 63 over a range of conditions, but its extraction was slow. Further modifications for different conditions, have given a range of LIX reagents, mostly combinations of 5- and 3-substituted 2-hydroxy benzophenone oximes (XIII).

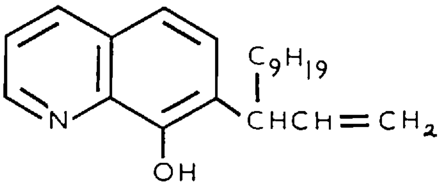


$R_1 = C_9H_{19}$ or $C_{12}H_{25}$

$R_2 =$ H or Cl

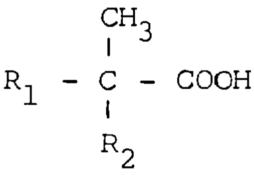
(XIII)

Two Kelex extractants are made [57]. Kelex 100 is a 7-alkenyl-8-hydroxyquinoline (XIV), and Kelex 120 is a 20 vol per cent solution of Kelex 100 in p-nonylphenol.



(XIV)

Versatic acids [58] are highly branched synthetic carboxylic acids produced by Shell (XV).



$$R_1 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle R_2}{|}}{C}}} - COOH$$

$R_1 + R_2 = C_7H_{15}$
for Versatic 10 (XV)

Although they exhibit some disadvantages in performance as compared with chelating cation exchangers, these carboxylic acids are relatively inexpensive and offer good performance in many specialized areas of solvent extraction. Ferric ions can be removed well from say, zinc solutions by Versatic Acid.

Shell Metal Extractant (SME) 529 is a β-hydroxyphenone alkyl oxime similar to the LIX reagents in a hydrocarbon diluent[59].

Alkyl amines, tributylphosphate, di(2-ethylhexyl)-phosphoric acid are in commercial use for isolation and separation of many metals, including cobalt from nickel.

Other extractants that have been proposed for use with various metals on large scales are the LIX related alkoxy-2-hydroxy benzophenone oximes [60], acetylacetone, perfluoroalkane sulphonic acids, quaternary ammonium salts and tertiary amines.

Some mixed solvent systems have been shown to exhibit synergistic properties in the extraction of metals. Thus a mixed system of LIX reagents and di(2-ethylhexyl)-phosphoric acid [61,62] or aliphatic carboxylic acids [63,64] extracts copper more efficiently than any component alone. The mechanism involves a mixed ligand complex with better solution properties than either single ligand-metal complex.

Ashbrook [65] has reviewed the 1975 position on chelating reagents used in solvent extraction processes.

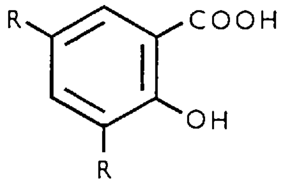
3.4. Extraction of Nickel

The LIX reagents have proved invaluable for the commercial extraction of copper. Nickel leach liquors could similarly be treated by solvent extraction if only an economically viable, efficient reagent could be found for it. At present it is isolated only as a residual salt when other metals are extracted from it. Nickel extraction is renowned to be slow [66] and a lot of work is in progress on additives to existing extraction systems to increase nickel extraction rates[67-69].

Sulphuric acid leaching is considered economically the best treatment of low grade lateritic ores. Sulphuric acid is a cheap reagent and the leaching is selective when performed at high temperatures and pressures [70]. Most reagents proposed for commercial solvent extraction processes are suitable for ammoniacal leach solutions but not sulphuric acid leach liquors.

Nickel does not form anionic complexes, therefore it is not extracted by amine extractants. In most reports concerned with nickel refining by liquid amines [71,72], all other metals are removed and nickel is left in a pure salt solution. This forms the basis for the nickel/cobalt separations in current commercial use.

Nickel can be extracted by large carboxylic acids and alkyl derivatives of phosphoric or phosphonic acids, but extraction is most efficient from alkaline solution. There are only small separation factors between the metal complexes but counter current separations have been reasonable [73]. An attempt to modify the solvents and shift their extraction to higher acidities was made by the preparation of salicylic acid derivatives [74] (XVI) and sulphur analogues of carbamic acid such as pyrrolidine carbodithioate [75] (XVII).



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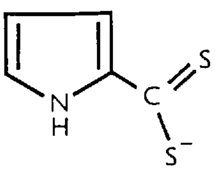


(XVII)

One solvent extraction process of importance in the separation of nickel and cobalt employs di(2-ethylhexyl)-phosphoric acid as the extractant [76-78], but there is interference by Fe, Cu, Zn and Ca if they are not removed from the feed solution prior to the nickel/cobalt separation by solvent extraction.

Similarly tributyl phosphate will extract cobalt from nickel [79].

The chelating reagents extract nickel into the organic phase but in competition and combination with many other metals, and from alkaline solutions. For instance, the LIX reagents will extract copper from acidic solutions but nickel only from ammoniacal solutions. Various dioximes have been regarded as selective reagents for nickel because of the intense colour of the insoluble dimethylglyoxime complex,but other metal dimethylglyoxime complexes are more stable than the nickel complex. The low carbon glyoximes are insoluble both in water and organic diluents, the higher ones are very expensive, therefore they have not been developed for industrial applications.

The β-diketones extract only from alkaline solution. Trifluoroacetylacetone (TTA) synergistically with amines extracts Ni, Co, Cu, Zn, Cd and Pd [80]. The extracted nickel species were identified as $Ni(TTA)_2$amine and $Ni(TTA)_2amine_2$

Sabot and Bauer [67] have described a separation of nickel in sulphuric acid medium by liquid-liquid extraction with dialkylphosphorodithioic acids. The slow rate of nickel extraction and stripping can be improved by the addition of a critical amount of octanol [81]. Cobalt and zinc were co-extracted and were removed by further extraction with tributylphosphate or ion exchange.

Development of other reagents to extract nickel selectively and quickly from acid solution is desperately needed.

3.5. Acid Extraction

There is another problem associated with research work into extraction of metals from acid leach liquors. The extraction of the acid itself complicates an understanding of the mechanism of many extractions. When extraction of a strong acid occurs, the extracted acid changes the nature of the solvents and the solutes in the system. The estimation and correction of these activities is not easy, therefore no definite conclusions can be drawn about the mechanism. Qualitative approaches have been made [82,15] to try to understand the extraction equilibria.

Strong acids are not extractable into non-polar solvents. The extraction is usually a solvation process, transferring the protons from a water solvation shell to a solvent or solvent/water shell in the organic phase. In the aqueous phase the protons and their anions are completely dissociated. In the organic phase the hydrogen bonding forces are not so strong but still exist between the solvated proton and the solvent molecule or water molecules in the organic phase.

Acids can be extracted with basic extractants such as amines or neutral extractants such as tributylphosphate and ethers, ketones and alcohols. All are solvating reactions. Amine-acid salts, like trilaurylamine-hydrobromic acid salt have been studied [83]. In the extraction of a given acid, primary amines extract better than secondary which are better than tertiary [84].

In extraction by a neutral extractant (E), a similar salt is formed in the organic phase.

e.g. $H^+ + NO_3^- + H_2O + E_{org} \rightleftharpoons HNO_3H_2O.E_{org}$

Water molecules associated with the free proton in the aqueous phase (as H_3O^+ or $H^+(H_2O)_3$) may be incorporated into the organic solvent. A species, $H_9O_4^+$, has been suggested, as in the extraction of perchloric, hydrochloric and hydrobromic acids, where a co-extraction of four molecules of water into tributylphosphate was found [82]. The hydration of the acid anion is weaker than that of the proton and it may be extracted as a free anion, but it is known that sulphate and phosphate are strongly solvated. Various solvents solvate to different extents and the dissociations of acids differ in different solvents.

In some systems, e.g. methyl isobutyl ketone, as acid concentration increases in the organic phase, mutual solubility increases and finally the acid and organic solvents become a single liquid phase [85]. This indicates the great effect of acids on the organic phase. Co-extraction of water, polymerization or dissociation of extracted species, high ionic concentrations in the aqueous phase, change in activity co-efficients of chemical species in the system, all complicate analysis of the extraction process.

Electrolyte salts can also be extracted into the organic phase in the same way. Sodium perchlorate is extracted with tributylphosphate to concentrations of 0.01M in polar organic diluents and 0.1M in undiluted tributylphosphate.

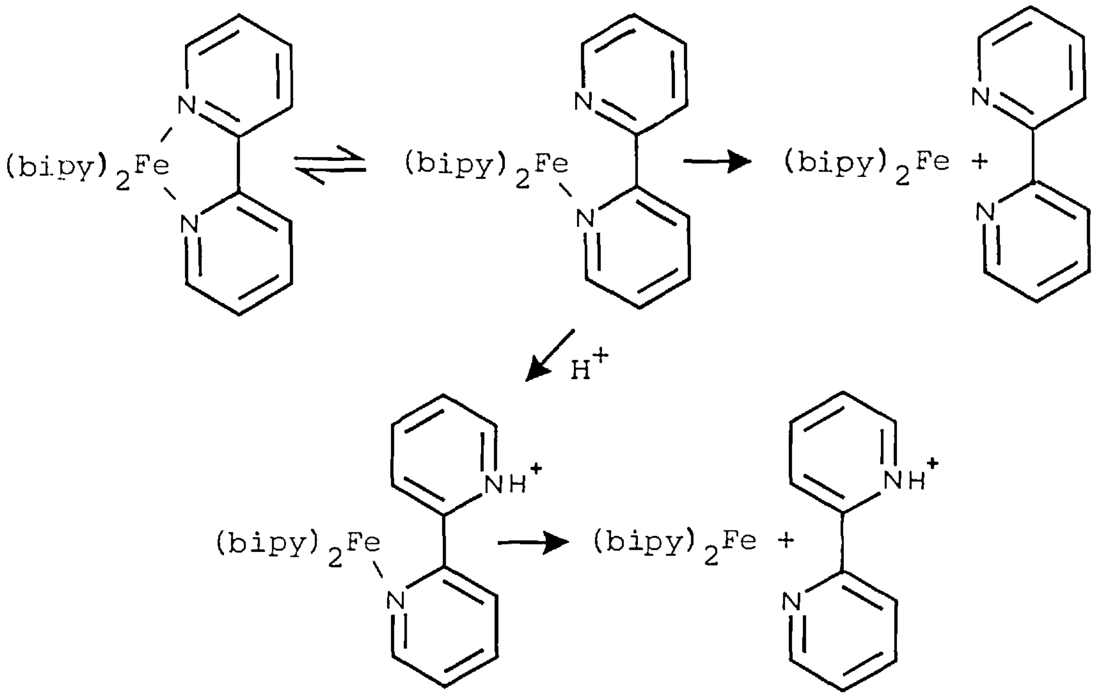
The extraction of metal ions in a strong acid solution with neutral solvating extractants is always accompanied by an extraction of that strong acid. Thus the nature of the extracted species and solvent, and activity co-efficients of the aqueous species, change dramatically. Qualitative analysis of the equilibria is impossible. Some anions are complex-forming themselves. Thus chloride ions from hydrochloric acid complex the metal ion before it is extracted (possibly as H_aMCl_{m+a} where m is the charge on the metal ion).

There is little information on the effect of acid on the extraction of metals by neutral chelating reagents such as 2,2'-bipyridine. It should not affect the actual metal complex extraction process as the chelation complex is much stronger than a solvation complex. Free complexing anions, such as chloride, may interfere by occupying co-ordination sites in the complex formation. Reaction of the acid with the weakly basic nitrogens of the bipyridine molecule certainly affects the extraction.

2,2'-Bipyridine gives a mono-equivalent titration curve on titration with strong acid. The acid dissociation constant of the bipyridinium ion in aqueous solution is 4.35. In concentrated sulphuric acid, however, ultraviolet spectra indicate formation of diprotic species. The pK_a value reported for bipy-$2H^+$ is -0.2 [86]. The conjugate acids of bipyridine are reported not to show evidence of any appreciable hydrogen bonding effect [87].

Basolo has suggested a scheme for the acid hydrolysis of the iron chelate $Fe(bipy)_3^{2+}$ [88].

The process is catalysed by hydrogen ions [89], unlike the acid hydrolysis of the 1,10-phenanthroline complex $Fe(phen)_3^{2+}$ where there is no free rotation in the molecule.



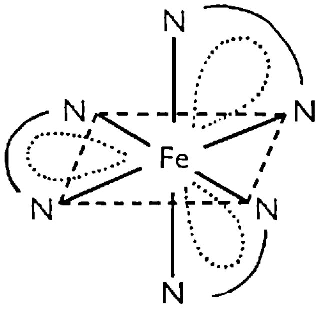
Some work suggests that complex species $H(phen)^+$, $H(phen)_2^+$ and $H(phen)_3^+$ are extracted with 1,10-phenanthroline with log β_n for each, 5.11, 7.22 and 9.03 respectively [90]. The compound $[H(phen)_2][OSO_2C_{10}H_7]2H_2O$ has been isolated [91].

Other chelation extractions cannot be performed from strongly acidic media so this interference is not relevant to them.

3.6. Ferroine Group Complexes

Late in the nineteenth century the Austrian chemist Fritz Blau synthesized 2,2'-bipyridine and 1,10-phenanthroline, and discovered that these compounds react with ferrous salts to produce water-soluble compounds of an intense red colour[92,93]. Blau isolated numerous salts of the red, positively charged ions produced in these reactions: $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ and showed that the bivalent iron compounds could be oxidized with strong oxidizing agents to the corresponding ferric ions $Fe(bipy)_3^{3+}$ and $Fe(phen)_3^{3+}$, intensely blue in colour, and that the oxidation-reduction couples were reversible. He did not, however, understand the bonding within his ionic salts. Co-ordination and ionic dissociation theories were in their infancy at that time.

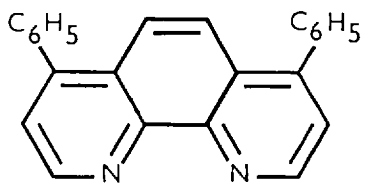
In 1912, Alfred Werner [94] proved that the six nitrogen atoms of the three bipyridine molecules of $Fe(bipy)_3^{2+}$ were attached to the iron atom at the apices of a regular octahedron around the metal, thus forming stable heterocyclic rings with the metal ion as one member. Such ring structures were later designated "chelate" rings.



The uses of 2,2'-bipyridine and 1,10-phenanthroline in analytical chemistry began about 1930 with the application of 2,2'-bipyridine as a reagent for the colorimetric determination of iron and the use of the couple, $Fe(phen)_3^{3+} + e^- = Fe(phen)_3^{2+}$, as a high potential oxidation-reduction indicator [95]. Morgan and Burstall [96] studied the synthesis and other metal complexes of 2,2'-bipyridine and 2,2',2"-terpyridine and Pfeiffer [97,98] carried out a similar investigation of the 1,10-phenanthroline complexes. Work in three laboratories[99-101] proved the superiority of the use of 1,10-phenanthroline over 2,2'-bipyridine for routine colorimetric determination of small amounts of iron.

Most information on the synthesis and use of 2,2'-bipyridine and 1,10-phenanthroline and their derivatives have been published by two groups, those of Smith and Case. The two groups, working in conjunction, have prepared and studied 150 compounds derived from or closely related to 2,2'-bipyridine or 1,10-phenanthroline [102-104]. Schilt has reviewed the analytical application of 1,10-phenanthroline and related compounds [105].

Three important iron reagents have been reviewed by Diehl and Smith [106]. 4,7-Diphenyl-1,10-phenanthroline (bathophenanthroline) (XVIII) and 2,4,6-tripyridyl-s-triazine (XIX) are very sensitive to iron and make possible a colorimetric determination of iron in the parts per billion.



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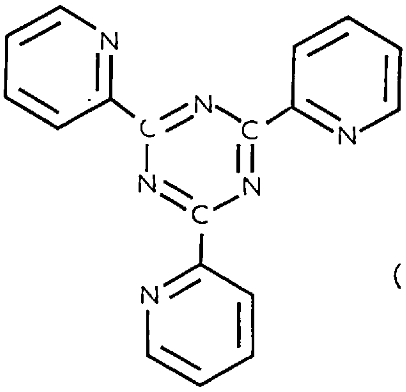

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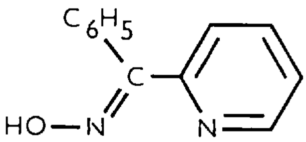
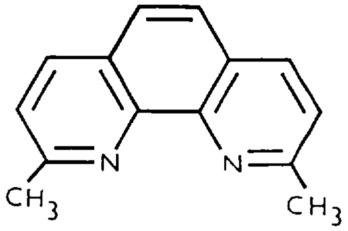


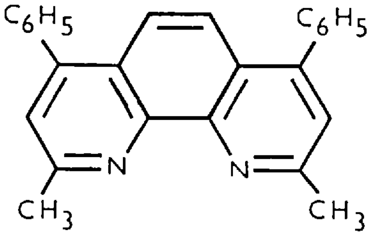
(XX)

syn-Phenyl-2-pyridyl ketoxime (XX) makes possible the direct determination of iron in the presence of strong alkali and the determination of oxidized iron in the presence of metallic iron. The ferrous complexes of all three of these reagents are soluble in organic solvents, immiscible with water, so the coloured complex can be extracted and concentrated into a favourable diluent.

Those studies also found some compounds which are suitable for the determination of copper[107]. Those 2,2'-bipyridines and 1,10-phenanthrolines which are substituted in the 6,6'- or 2,9-positions respectively do not give the "ferroine" reaction, i.e. strongly coloured complex formation with ferrous ions, but some do react to give a coloured cuprous complex. This has been called the "cuproine" reaction. 2,2'-Biquinoline[108] (cuproine) was the first reagent used for the cuprous determination[34-36], then other substituted bipyridines and phenanthrolines were developed to give higher molecular extinction co-efficients in the cuprous colour determination. "Neo-cuproine"[109] is 2,9-dimethyl-1,10-phenanthroline (XXI) and "bathocuproine" is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline[110,111] (XXII).



(XXI)



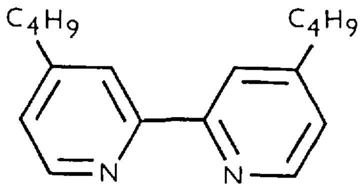
(XXII)

These reagents are not "specific" for ferrous or cuprous ions. They are useful in analytical chemistry only because of their own intensely coloured complexes, with which complexes of other metals in solution do not interfere. The cuproine reagents do not form ferrous complexes at all[62]. This has been explained in the previous section on selectivity. The steric hindrance which the α-substitutions on 2,2'-bipyridine or 1,10-phenanthroline cause between chelating molecules does not allow an octahedral or square planar configuration around a metal ion, therefore only those metal ions which allow a tetrahedral configuration can make a complex.

Research work on the complexes of other metals has been secondary to that for iron and copper. 2,2'-Bipyridine and 1,10-phenanthroline extract Ni(II) and Co(II) as coloured complexes and Zn(II), Cd(II) and Hg(II) as colourless complexes. Fe(III) complexes do not form directly from ferric ions and the ligand but oxidation of the Fe(II) complex will give these complexes. The $Ni(phen)_3^{2+}$ complex is the most stable of the transition metal 1,10-phenanthroline complexes [112], but its determination is difficult in the presence of iron and cobalt which also form stable complexes. However Ducret and Pateau [113] found that the trichloroacetate salt of $Ni(phen)_3^{2+}$ can be separated from the oxidized forms of the iron and cobalt complexes by extraction with 1,2-dichloroethane.

Potential selectivity of reagent molecules with varying substitution gives scope for the design of metal selective reagents.

Hart and Newbery [114] found that 2,2'-bipyridine and 1,10-phenanthroline formed lanthanide complex salts but their lack of solubility in inert solvents and ready dissociation in polar solvents deterred investigations. They found they could make lanthanide complexes, which were soluble in inert solvents, with 4,4'-dibutyl- and 5,5'-dibutyl-2,2'-bipyridine (XXIII) (XXIV).



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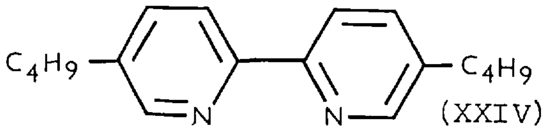
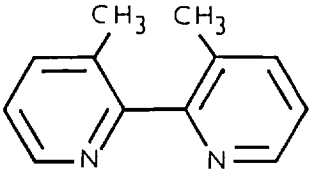


(XXIV)

Therefore changing the size of the extractant molecule, thus changing its solubility and extractability, without changing its chelating ability, is useful in designing an extraction reagent.

Substitution in the 6,6'-positions of 2,2'-bipyridine causes steric hindrance to the formation of tris complexes. Similarly substitution in the 3 and/or 3'-position discourages coplanarity of the heterocyclic rings, resulting in a loss of resonance energy and chelating ability [115,116]. This is seen in 3,3'-dimethyl-2,2'-bipyridine (XXV) and 1,1'-biisoquinoline (XXVI).



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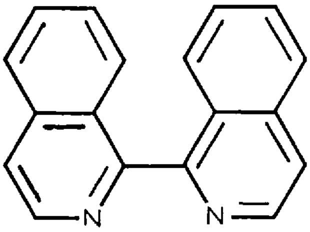


(XXVI)

Substitution of a hydrogen atom in an aromatic compound invariably gives rise to a change in electron distribution throughout the molecule, and thus to alterations in chemical reactivity and spectral characteristics. A methyl substituent at position 4 or 6 in 2,2'-bipyridine increases the basicity of the nitrogen atom appreciably, at position 3 only slightly. Thus 4,4'-dimethyl-2,2'-bipyridine forms more stable complexes than 2,2'-bipyridine.

Halide substitutions produce strong inductive effects [117].

Substituent groups have predictable effects on the extractions by these molecules. Alkyl or aryl substituents tend to decrease the water solubility of the ligand and the metal complex. Hence extractability into organic solvents is enhanced. Polar substituents, e.g. amino, nitro, hydroxy, tend to give the opposite effect and decrease extractability. A readily ionizable substituent group such as sulphonic acid increases water solubility of both the ligand and metal chelate salts [118].

The extraction of these complexes into an organic phase is the extraction of an ion pair. The complex is a large hydrophobic cation which can take an anion with it into the organic phase. The extraction is easiest with a large anion, for example a long chain alkyl sulphate or sulphonate [119], but a smaller inorganic anion, such as perchlorate is acceptable, though the rate of extraction may be slower. The diluent also has a strong influence on the extraction. Extraction into a polar diluent, such as nitrobenzene, is often more complete than into a non-polar diluent[120].

The stable ferrous complexes of iron with 2,2'-bipyridine and 1,10-phenanthroline have been used as extractants for various anions. The extracted anion can be determined by measurement of the absorption of the organic phase due to the metal complex. Thus, for example, perchlorate concentration has been measured by extraction with $Fe(bipy)_3^{2+}$ in nitrobenzene [121].

The literature gives no details of mechanisms involved in these extractions. General treatments [122] of ion pair extractions rely on an accurate determination of the activity co-efficients. This is very difficult in solutions of high ionic strength and acidity.

The thermodynamic eqilibrium constant must include the activity co-efficients as shown overleaf.

$$M^{m+} + nL + mA^{-} \rightleftharpoons (ML_nA_m)_{org}$$

$$K = \frac{[ML_nA_m]_{org}}{[M^{m+}][L]^n[A^{-}]^m} \times \frac{\gamma_{ML_nA_m}}{\gamma_M \gamma_L^n \gamma_{A^-}^m}$$

3.6.1. Stability of Complexes

Several studies have been made of the stabilities of the bipyridine and phenanthroline metal complexes [112,123,124]. The stability of the chelate complexes can be related to the acid dissociation constants of the ligands [125], and measured by means of potentiometric pH titration.

A table of stability constants of many metal complexes with 2,2'-bipyridine and 1,10-phenanthroline and related compounds is given in Schilt's review [105].

Yasuda [123] found that the complexes of the methyl substituted bipyridines and phenanthrolines were more stable than the parent molecules except for α-substituted compounds which were less stable because of steric hindrance in the complexes. The 1,10-phenanthrolines were more stable than the 2,2'-bipyridines.

The stability constants of several metal complexes with 2,2'-bipyridine and 1,10-phenanthroline ligands are listed in Table 1. [112].

Table 1.

Stability constants of $M(bipy)_3^{2+}$ and $M(phen)_3^{2+}$ complexes in 0.1M $NaNO_3$ solutions

Metal ion	log β_3 $M(bipy)_3^{2+}$	log β_3 $M(phen)_3^{2+}$
Fe^{2+}	17.45	21.3
Co^{2+}	16.02	19.90
Ni^{2+}	20.54	24.8
Cu^{2+}	17.0	21.35
Zn^{2+}	13.63	17.55

The nickel complex is the most stable for both 2,2'-bipyridine and 1,10-phenanthroline.

If this order can be maintained for more highly alkylated bipyridines, a reagent selective for nickel is favoured throughout the system.

3.6.2. Lability of Complexes

The rate constants for formation and dissociation of metal-bipyridine and phenanthroline complexes divide the complexes into two types. The inert type, with low rates of dissociation are Co(II), Ni(II), Fe(II). The labile type are Cu(I), Cu(II), Zn(II). The rates of formation are not so easily divided but nickel is the slowest [126]. A table of rate constants from various sources was compiled in Schilt's review [105].

3.6.3. Synthesis of Bipyridines

2,2'-Bipyridine is a white crystalline solid, melting point 69.5°C. Studies of the crystal structure reveal that the two pyridine rings are co-planar with nitrogen atoms in a trans configuration [127]. In solution the coplanarity and trans configuration are retained [128], but the cis form is adopted for chelate ring formation with metal or hydrogen ions.

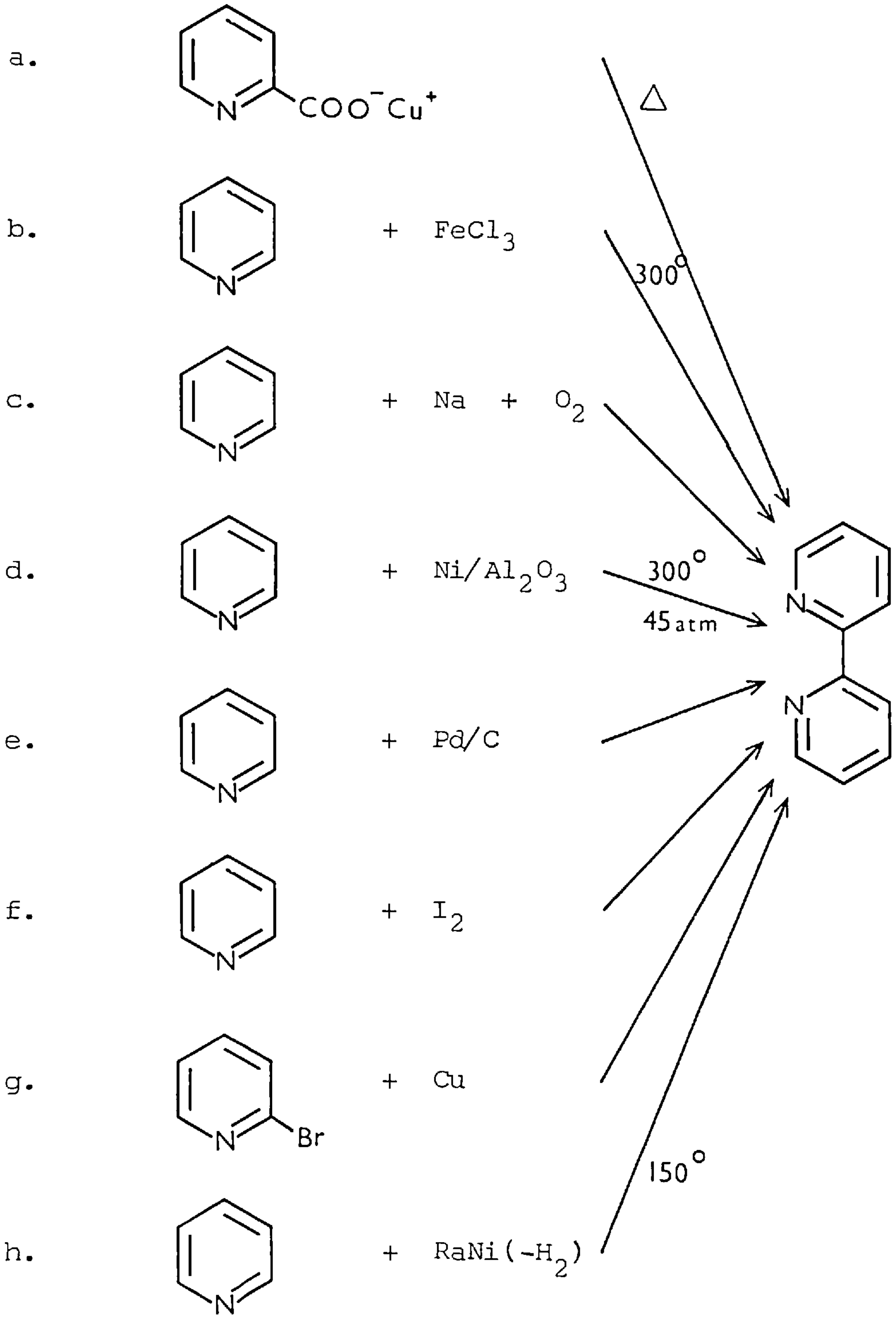
The chemical reactivity of 2,2'-bipyridine is similar to that of pyridine which is notably less reactive than any type of compound excluding saturated hydrocarbons. Bipyridines can be subjected to great heat and oxidizing or reducing conditions with no change.

2,2'-Bipyridine has been prepared by the following different methods:

a. Pyrolysis of copper picolinate [93],
b. Action of anhydrous ferric chloride on pyridine at 300° [129,13
c. Action of sodium on pyridine followed by oxidation [131],
d. Dehydrogenation of pyridine by a nickel-alumina catalyst at 300° and 45 atmospheres pressure[132,133],
e. Action of palladium-on-carbon catalyst (and some other carbon supported catalysts [134]) on pyridine [135],
f. Dehydrogenation of pyridine by iodine [133],
g. Action of copper powder on 2-bromopyridine in the Ullmann reaction [136],
h. Action of a degassed Raney Nickel catalyst on pyridine [137,138].

Each method gives only low yields of 2,2'-bipyridine. Small amounts of polypyridines are usually formed too. The

Synthetic routes to 2,2'-bipyridine



last preparation, (h), has superseded all of the other methods, apart from the Ullmann reaction, (g), which is still used with reasonable success. The particular value of the Raney Nickel method is that it produces reasonable yields and can be easily used, often with even better yields, on substituted pyridines to give symmetrically substituted 2,2'-bipyridines.

The first catalyst prepared by Badger and Sasse [137] for this reaction was prepared by heating a W-7 Raney Nickel catalyst [139] to 100° prior to treatment with pyridine. It was also found advantageous to heat the catalyst in vacuo to produce an anhydrous catalyst which would react with bases less water soluble than pyridine. In subsequent work the authors found that this catalyst often exploded during the degassing procedure, so a modified preparation was published[140]. Further studies [140,141] on the conditions and role of hydrogen in the reaction showed that the catalyst was poisoned by pyrrole, a side product in the reaction, and that the W7-J Raney Nickel catalyst containing only 5% of its original hydrogen is the most efficient. Dilution of the pyridine with an inert diluent also lowered the yield.

Badger and Sasse have reviewed their work on the action of metal catalysts on pyridines [142].

3.6.4. Substituted Bipyridines

The preparation of substituted 2,2'-bipyridines may involve reactions which condense two substituted pyridines in the 2-position, or substitution onto 2,2'-bipyridine itself.

The reactions used for the preparation of 2,2'-bipyridine can be used to prepare most disubstituted 2,2'-bipyridines from the substituted pyridines. Thus reaction of the methyl pyridines with catalysts produces the 5,5'-, 4,4'- or 6,6'-dimethyl-2,2'-bipyridines. The 3,3'-dimethyl- derivative is not formed in these reactions. It is not favoured as its formation would distort the coplanarity of the pyridine rings. 3,3'-Dimethyl-2,2'-bipyridine can be produced in low yield by the Ullmann reaction of 2-bromo-3-methyl-pyridine with copper.

The degassed Raney Nickel method has been used to produce a great range of symmetrically alkylated 2,2'-bipyridines and some phenyl, benzyl and carboxy derivatives [142,143]. Sasse and co-workers have studied the infrared spectra of these compounds [144]. No long chain alkyl derivatives were reported apart from 4,4'-dipentyl-2,2'-bipyridine. Hart and Newbery [114] prepared 4,4'- and 5,5'-dibutyl-2,2'-bipyridines by this method. Some of the reactions were carried out in xylene as diluent, and some were conducted under reduced pressure at 150°. Many reactions gave yields of 0.5g/g catalyst, but the yields were not consistently high.

Some halo- and nitro- substituted bipyridines have been prepared by the Ullmann reaction from the dihalo- or halo-nitro-pyridines. Thus 5,5'-dichloro-2,2'-bipyridine was prepared from 2-bromo-5-chloro-pyridine and copper, and similarly 5,5'-dibromo-2,2'-bipyridine from 2,5-dibromo-pyridine and 5,5'-dinitro-2,2'-bipyridine from 2-iodo-5-nitro-pyridine [145].

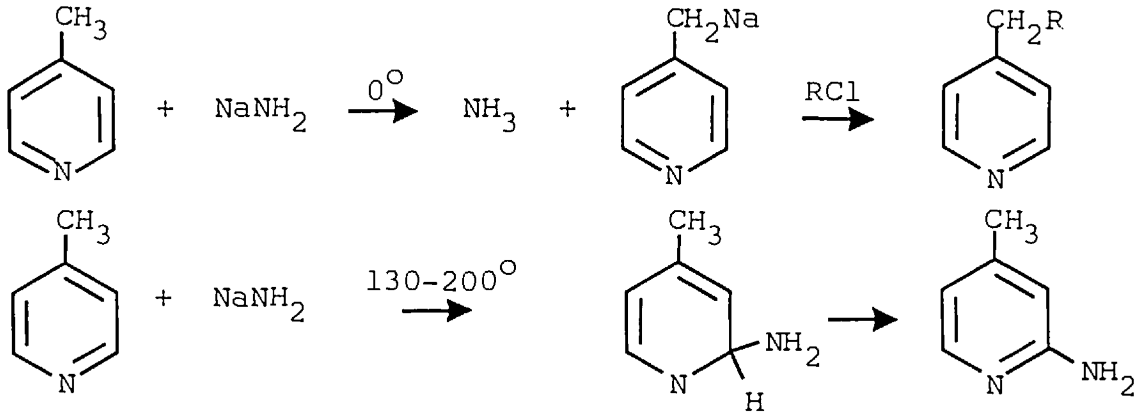
Substitutions on 2,2'-bipyridine itself are few as it is a very unreactive compound. If substitution occurs it is always only in the 6-positions, the most reactive sites. It has been brominated at 500^{o} to yield 6-bromo- and 6,6'-dibromo-2,2'-bipyridine [146]. These in turn can be substituted by cyanide at the bromo-position to give the corresponding nitriles which can be hydrolysed to the carboxylic acids.

Amination of 2,2'-bipyridine with sodamide yields 6,6'-diamino-2,2'-bipyridine [133]. Phenyl lithium will add phenyl groups at one or both of the 6-positions [147,148].

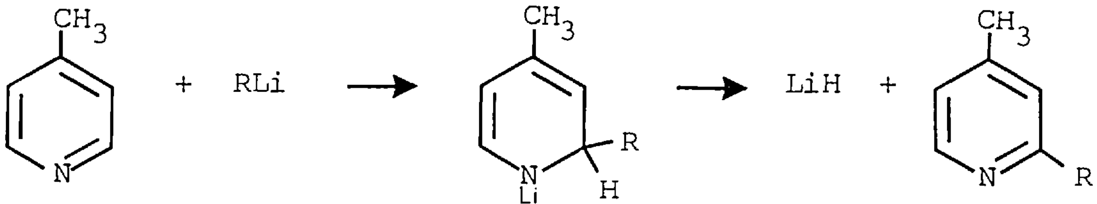
2,2'-Bipyridine-1,1'-dioxide is more easily substituted than 2,2'-bipyridine. It is prepared by the action of hydrogen peroxide in glacial acetic acid on 2,2'-bipyridine[149], and after substitution the oxide can be reduced back to the bipyridine base with phosphorous trichloride. Nitration of the dioxide yields 4,4'-dinitro-2,2'-bipyridine-1,1'-dioxide, which on treatment with iron and acetic acid is converted to 4,4'-diamino-2,2'-bipyridine [150]. 4,4'-Dinitro-2,2'-bipyridine-1,1'-dioxide is the starting material for reactions to produce 4,4'-dichloro-, 4,4'-dibromo-, 4,4'-diethoxy-, 4,4'-dimethoxy- and 4,4'-diphenoxy-2,2'-bipyridines [150].

The dimethyl-2,2'-bipyridines, prepared by a methyl pyridine condensation, are a better base for substitution than the parent bipyridine. These compounds have similar reactivity to the methyl pyridines [151] so that reactions used to substitute methyl pyridines give a corresponding reaction with dimethyl-2,2'-bipyridines, except where steric hindrance at the 3,3'-positions prevents this.

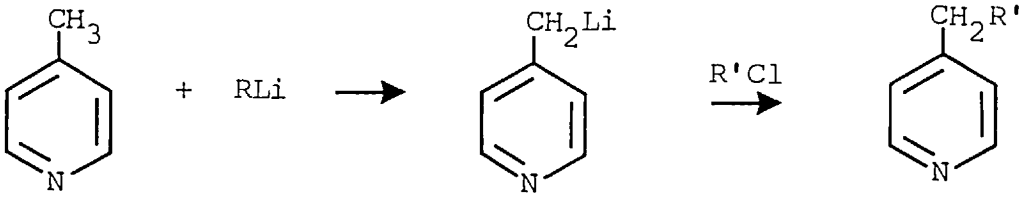
Tschitschibabin [152] found that sodamide metallated the methyl group of methyl pyridines rather than aminating the 2- and 6-positions, as for pyridine and 2,2'-bipyridine, if the reaction was performed at 0° rather than 100°. The reaction of the picolyl lithium with alkyl halide is now used to prepare long chain alkyl pyridines [153,154]. Two alkyl groups are sometimes introduced into the methyl group.



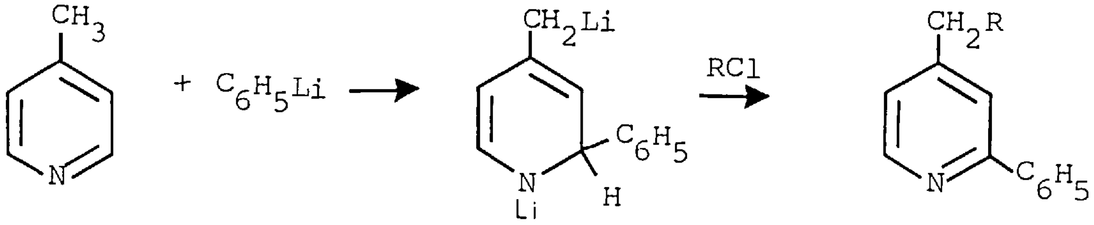
Reactions of organolithium compounds with methyl pyridines are well reported [155-157]. Alkyl lithiums and phenyl lithium readily add to the -N=C- bond of the pyridine ring and a methyl pyridine substituted in the 2-position is obtained [158].



However, the metallation of the methyl group also competes with this reaction under some conditions.



Both reactions can occur in the same molecule [159].



Wibaut and Hey [160] found that the reaction could be restricted to an introduction of an alkyl group into the methyl group of 4-methyl pyridine if the organolithium reagent was added very slowly to 4-methyl pyridine before the equivalent quantity of alkyl halide. Choice of solvent influences the reaction to favour one or other substitution [161]. There are no reported reactions of organolithium compounds with 4,4'-dimethyl-2,2'-bipyridine.

Sasse and Whittle [143] have given details of the styryl derivatives of the alkyl bipyridines that they prepared. They used a standard method [162]. Reaction of 4,4'-dimethyl-2,2'-bipyridine with benzaldehyde produced di(2-phenylethenyl)-2,2'-bipyridine. This product was hydrogenated to give 4,4'-(diphenylethyl)-2,2'-bipyridine.

4. RESULTS AND DISCUSSION

4.1. Syntheses of bipyridines

Substituted 2,2'-bipyridines have been chosen as suitable potential extraction reagents for transition metal ions from acidic solutions. Each compound based on 2,2'-bipyridine contains the "ferroine" group and has the ability to form complexes with metals through nitrogen-metal co-ordination bonds, but substitution in the 6,6'- and 3,3'-positions restricts this ability due to steric hindrance. Substitution in the 6- and 6'-positions interferes with the other co-ordinated ligands in octahedral or square planar configurations around the metal ion. Thus Ni(II), Cu(II), Co(II) and Fe(II), those metals of most interest in this study, will not allow 6,6'-substitution on their bipyridine ligands. Substitution in the 3,3'-positions forces the ligand molecule out of coplanarity, a feature essential for stable complex formation with metal ions. The 4,4'- and 5,5'-positions are therefore the suitable substitution positions for a bipyridine ligand designed to extract nickel. Substitution of the parent 2,2'-bipyridine in the 4,4'-positions is easier than the 5,5'-positions because of the electronic distribution in the pyridine rings caused by the electron withdrawing nitrogen atom.

Alkyl substitution is desirable to increase the size and the hydrophobic nature of the bipyridine base such that it and its metal complexes are soluble only in the organic phase in extraction reactions. An inert alkyl group will affect the electron distribution very little compared to halide, nitro and oxygen containing groups, but there may be subtle differences in complex formation, enough to promote selectivity of metal ions.

4.1.1. Coupling of alkyl pyridines with Raney nickel

The Badger and Sasse method [137] of alkyl bipyridine synthesis involving the coupling of alkyl pyridines using a Raney nickel catalyst, was considered the most suitable in ease and directness of application and gave relatively high yields, compared to the more traditional methods of dialkyl bipyridine synthesis. For the bipyridine and substituted bipyridines, yields were highest from 3- and 4-alkyl pyridines as their increased basicity and lack of sterically hindering groups facilitate chemisorption on the nickel catalyst surface [143].

Badger and Sasse prepared W7-J Raney nickel catalyst by heating and degassing a W7 Raney nickel catalyst. Their original procedure was modified as explosions often occurred in the degassing of the catalyst. They incorporated a number of large traps and non-return valves into their vacuum line, as safety precautions against sudden releases of hydrogen. In the present work one large trap was fitted into the system and no explosions ever occurred. Extreme care was always taken to keep the catalyst wet when exposed to air as the dry catalyst is pyrophoric.

The highest yields of 4,4'-dimethyl-2,2'-bipyridine were obtained when the catalyst was prepared by fast addition

(15 minutes) of the nickel-aluminium alloy to the vigorously stirred sodium hydroxide solution, followed by 6 hours' digestion at 100° and 18 hours' standing at room temperature. The catalyst was washed well with water to remove all traces of alkali, then degassed at 100-120° for 2-3 hours.

A catalyst to pyridine ratio of approximately 1:2 (based on dry Ni-Al alloy : pyridine base) was used for optimum performance of the catalyst.

The optimum reaction time of alkyl pyridine over the catalyst varied with the pyridines, as did the maximum yields. Over-long reaction times resulted in complex formation and no appreciable increase in bipyridine formation. Badger and Sasse reported better yields of bipyridine from 3-ethyl-4-methyl pyridine when the mixture was refluxed under reduced pressure. This was not the case here. A slightly lower yield was obtained under those conditions.

Badger and Sasse had reported the preparation of 4,4'- and 5,5'-dimethyl-, 5,5'-diethyl-4,4'-dimethyl-, 4,4'- and 5,5'-diethyl- and 4,4'-dipentyl-2,2'-bipyridines, all in good yields [142]. Hart and Newbery reported the synthesis of 4,4'- and 5,5'-dibutyl-2,2'-bipyridine by this method [114]. It is here reported that 4,4'-dipropyl-2,2'-bipyridine, 4-methyl-4'-propyl-2,2'-bipyridine and 4,4'-di(1,1'-dimethyl ethyl)-2,2'-bipyridine have been prepared by this method also. 4-Methyl-4'-propyl-2,2'-bipyridine was a byproduct of the 4,4'-dipropyl-2,2'-bipyridine reaction. The 4-propyl pyridine was contaminated with some 4-methyl pyridine, thus 4,4'-dimethyl-, 4-methyl-4'-propyl- and 4,4'-dipropyl-2,2'-bipyridine could form in the coupling reaction on the catalyst.

Two different forms of crystals, blue needles and colourless plates, separated from a recrystallization mixture of 4,4'-di(1,1'-dimethylethyl)-2,2'-bipyridine. The physical properties of the two sets of crystals were identical. Melting points and mixed melting points, and elution properties on thin layer chromatography plates showed no differences and neither did the nuclear magnetic resonance or infrared spectra of each set. Another recrystallization gave homogeneous blue needles. The cis and trans forms of the bipyridine appear to have been crystallized in this one instance.

Sasse prepared 4,4'-dipentyl-2,2'-bipyridine by a Raney nickel coupling of 4-pentyl pyridine at 150°. This preparation could not be reproduced with the Raney nickel used to prepare the lower chain length alkyl bipyridines in good yield in this work. There was similarly failure to produce any trace of bipyridine from 4-nonyl pyridine over W7-J Raney nickel catalyst. The temperature and duration of the reactions were varied but made no difference, only the starting alkyl pyridine was recovered. The alkyl pyridines were purified to remove any pyrrole which is known to be an inhibitor of the coupling reaction.

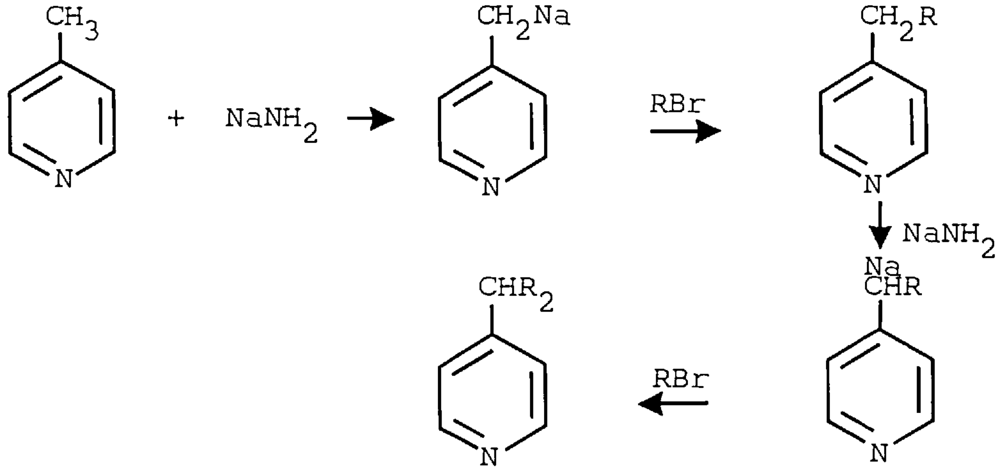
These findings suggest that the longer chain 4,4'-dialkyl-2,2'-bipyridines cannot be formed by coupling of the appropriate pyridines over degassed Raney nickel. The longer chain on the 4-position may interfere with the chemisorption of the pyridine base onto the catalyst or the orientation of the pyridine molecules on the catalyst, for

2,2'-bonding, may be more difficult where a long alkyl chain deters easy rotation.

4.1.2. Alkylation of bipyridines by the Tschitschibabin method

The longer chain alkyl bipyridines can be prepared by alkylating the methyl groups of 4,4'-dimethyl-2,2'-bipyridine. Tschitschibabin's method [152] of alkylation of methyl pyridines with sodamide and alkyl bromide can be used relatively well for the addition of alkyl chains to 4,4'-dimethyl-2,2'-bipyridine.

Before using it to alkylate bipyridines the Tschitschibabin method was used to prepare the 4-alkyl pyridines required for the attempted Raney nickel couplings. Thus 4-propyl, 4-butyl, 4-pentyl and 4-nonyl pyridines were prepared from 4-methyl pyridine, sodamide and the appropriate alkyl bromide. The original method recommended the use of diethyl ether as a diluent, but other workers have obtained better results for higher alkyl pyridines by performing the reaction without a diluent and sometimes at higher temperatures. For the 3C - 9C chain length range the best results were obtained when there was no dilution of the pyridine and the reaction was performed at 0^{o}. In each reaction, whenever good yields of alkyl pyridine were obtained, there were also some more highly substituted pyridines formed. The methyl group is subject to multiple attacks by sodamide.



The starting material, mono-alkylated and dialkylated products could be separated by fractional distillation but the boundaries were not sharp.

The sodamide quality affects the reaction. New, finely ground sodamide is necessary for good results.

The Tschitschibabin reaction was modified for the alkylation of bipyridines. 4,4'-Dimethyl-2,2'-bipyridine is a white solid, insoluble in diethyl ether, so a suitable diluent was required for its contact with solid sodamide. Dry xylene proved suitable. 4,4'-Dimethyl-2,2'-bipyridine is quite soluble in hot xylene and some will stay in solution as it cools. It was also found that there was no reaction at 0^{o}, but moderate heat (up to 100^{o}) would promote the metallation. The progress of the reaction was indicated by the colouring and darkening of the mixture associated with metallation reactions. Near the end of the alkyl halide addition the colour disappeared as the metallated species was alkylated. No amination products were detected in these reactions at higher temperatures in contrast to the alkyl pyridine aminations in the 2-position at 100^{o}.

The reaction gave a mixture of products. They were mono-, di-, tri- and tetra-alkylated species formed through the metallation of one or both methyl groups either singly or doubly. Fractional distillation could separate some fractions of the mixture, but the boiling points were very high and separation under the conditions of reduced pressure was not good. Small samples could be purified by elution through a column of alumina with non-polar eluants.

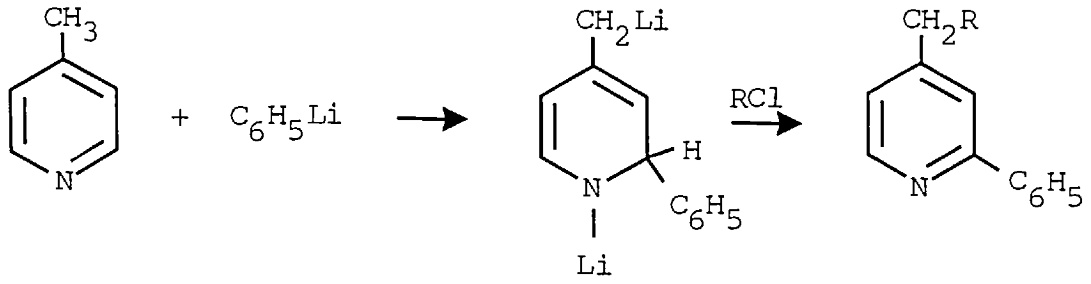
Gas liquid chromatography and nuclear magnetic resonance spectra gave good indications of the purity, nature and quantities of side products, but complete separations could not be effected.

When the reaction was performed on 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine only the 4-methyl groups were attacked by sodamide to produce 5,5'-diethyl-4,4'-dipentyl-2,2'-bipyridine and side products. The 4-substituted position is known to be the most reactive of the pyridine positions and this is shown even with sodamide metallation reactions.

Reasonably pure samples of 4,4'-dipentyl-, 5,5'-diethyl-4,4'-dipentyl-, 4,4'-diheptyl- and 4,4'-dinonyl-2,2'-bipyridines were synthesized by this method, along with the side products of mono-, tri- and tetra-alkylated bipyridines.

4.1.3. Organolithium reactions

Organolithium reagents have been used to metallate methyl pyridines prior to alkylation in a manner similar to the sodamide reactions. However they also substitute the ring.



The direction of the metallation is dependent on the nature of the organolithium reagent, solvent and general conditions.

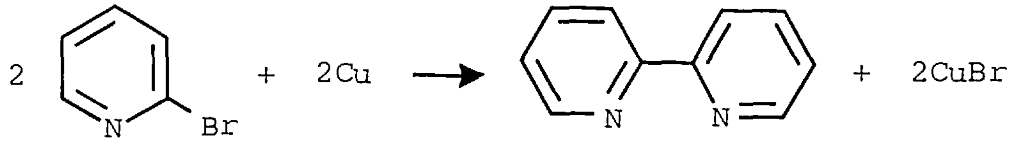
In an attempt to alkylate the methyl groups of 4,4'-dimethyl-2,2'-bipyridine, it was reacted with phenyl lithium, then 1-bromo octane. A mixture of products was obtained, with phenyl substitution in the ring on the 6-position and alkylation on one or both of the methyl groups. The acid-soluble product consisted of 4,4'-dimethyl-6-phenyl-2,2'-bipyridine.

Reactions of the dimethyl bipyridine with methyl lithium were inconclusive. It has been reported [158] that methyl lithium does not substitute the pyridine ring to the extent that phenyl lithium does. The bipyridine reaction with methyl lithium and 1-bromo octane in diethyl ether and tetrahydrofuran produced a very low yield of product. Nuclear magnetic resonance spectra suggested the product to be only partially alkylated at the methyl groups and there was some 6-methyl substitution.

4.1.4. Ullmann reaction

Before the introduction of the Raney nickel method of bipyridine synthesis from pyridines, the coupling of

2-bromo pyridines through the Ullmann reaction was the most accepted synthetic route.



The reaction has been used only with short chain 4-alkyl-2-bromo-pyridines. When the coupling reaction was attempted on 4-pentyl-2-bromo-pyridine, no bipyridine products could be detected. The carbon chain in the 4-position may have an interfering effect on the alignment to correct orientation for the copper reaction and coupling at the pyridine 2-position.

4.1.5. Oxidation products of bipyridines

The bipyridines being prepared were to be tested for their suitability as solvent extraction reagents. The alkyl bipyridines are neutral molecules and chelation with a metal ion results in a positively charged complex. To maintain charge neutrality in the transfer of the metal complex between phases, an anion must accompany the complex across the interface. If the ligand were ionizable itself, without any change in its chelating ability, this necessity would be eliminated as the metal-ligand complex would be neutral. To make such a ligand a carboxylated bipyridine was synthesized.

5,5'-Diethyl-4,4'-dimethyl-2,2'-bipyridine was oxidized with potassium permanganate. The isolated product was

2,2'-bipyridine-4,4',5,5'-quatrocarboxylic acid. This compound is very soluble in water. It has too many easily dissociable protons to make it useful as an ionizable ligand, but the reaction could not be controlled to carboxylate only the 4-methyl group.

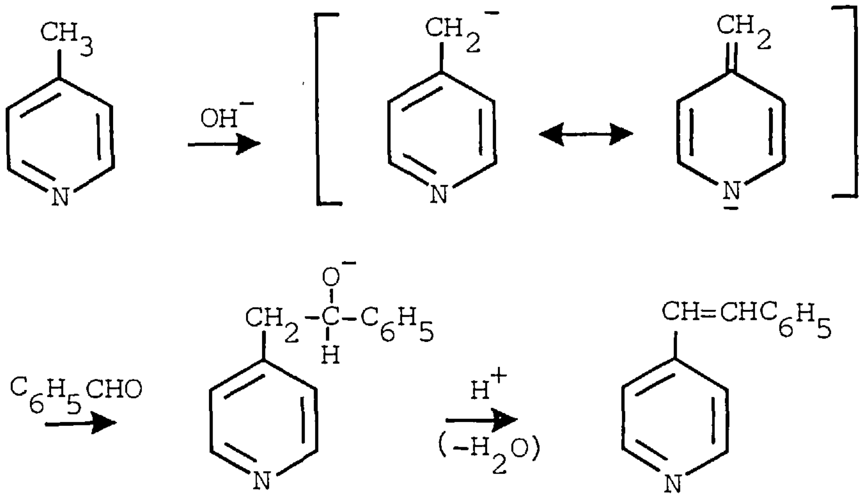
The oxidation of 3-ethyl-4-methyl-pyridine to pyridine-3,4-dicarboxylic acid confirms that both the carbons attached to the 3- and 4-positions are oxidized easily and without discrimination. The end of a chain could not be carboxylated, it would be cut off.

It is not possible to make a water-insoluble long chain alkyl bipyridine carboxylic acid in this manner.

Subsequent extraction tests showed that the ion pair extraction worked well and so the ionizable ligand research was not followed up.

4.1.6. Increase in substituent size by reaction with an aldehyde

Aromatic aldehydes can extend an alkyl chain of a pyridine by an "aldol"-like condensation.



4,4'-Di(2-phenylethenyl)-2,2'-bipyridine and 5,5'-diethyl-4,4'-di(2-phenylethenyl)-2,2'-bipyridine, (styryl derivatives of the parent compounds), were prepared by the condensation of benzaldehyde with 4,4'-dimethyl-2,2'-bipyridine and 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine.

4,4'-Di(2-phenylethenyl)-2,2'-bipyridine was found to be insoluble in all common diluents and aqueous mixtures, so it was not investigated further.

5,5'-Diethyl-4,4'-di(2-phenylethenyl)-2,2'-bipyridine was soluble in chlorinated hydrocarbon diluents but salts precipitated from both acid and organic phases when an organic solution of it was shaken with sulphuric or hydrochloric acids.

These solubility properties are not compatible with those of a potential solvent extraction reagent.

The aldehyde condensation is recorded only for aromatic aldehydes. The same reaction with 4,4'-dimethyl-2,2'-bipyridine was attempted using 2-ethyl butyraldehyde as the aldehyde. No condensation product could be detected. Similarly, when 4-methyl pyridine was treated with 2-ethyl butyraldehyde, there was no condensation reaction.

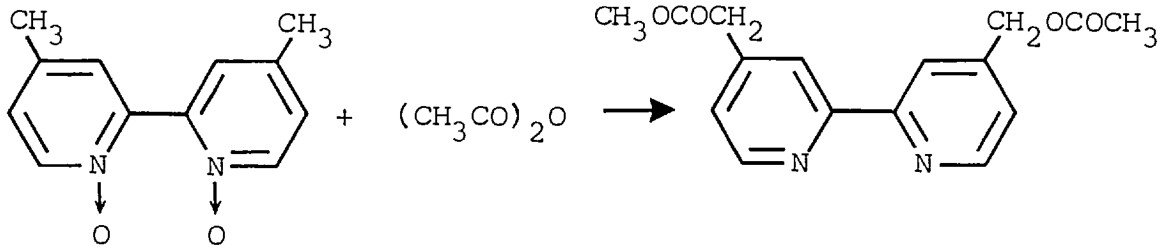
This was not a suitable method for preparing long chain alkyl bipyridines.

4.1.7. N,N-Dioxides of the bipyridines

Many substituted bipyridines have been prepared through substitution reactions on 2,2'-bipyridine-1,1'-dioxide. The methyl groups of N-oxides of 2- and 4-methyl pyridines are more reactive than those of the methyl pyridines. The increased acidity should also be applicable to the methyl groups of 4,4'-dimethyl-2,2'-bipyridine-1,1'-dioxide, and the 4- and 4'-positions could have their reactivities enhanced.

4,4'-Dimethyl-2,2'-bipyridine-1,1'-dioxide was reacted with sodamide but no coloured metallation product was formed and no alkyl bipyridine could be isolated after addition of 1-bromo octane.

Alkyl pyridine-N-oxides react with acetic anhydride to form acetates [163,164]. 4,4'-Dimethyl-2,2'-bipyridine-1,1'-dioxide was reacted with acetic anhydride to produce a small amount of a diacetate.



The ester is acid-soluble so is not useful for solvent extraction tests.

4.2. Solvent extraction tests

The metals of main interest in this study were Ni(II), Co(II), Cu(II), Fe(II) and Fe(III). A few tests were performed for Zn(II), Pb(II) and Cd(II). These closely related transition metals are often all extracted by known extraction reagents. The nickel complex is the most stable of the 2,2'-bipyridine complexes of these metals, so conditions to promote selectivity towards nickel were sought in these studies.

4.2.1. Initial tests

Simple shake-out tests were performed with 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine to determine the general behaviour of the bipyridines with various diluents, electrolytes and additives to aqueous and organic phases. The conditions of extraction of various metals by 2,2'-bipyridine and some derivatives have been investigated only for colorimetric determination of iron and copper. Extraction for isolation and recovery of the metal requires its own optimum conditions, and variations in them, for selection of metals.

The extraction tests were simple shake-outs of equal volumes of 0.1M 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine in chloroform and a solution of metal salt, 100 ppm metal, in water, acid or alkali as detailed. The amount of metal in the aqueous phase before and after extraction was measured by atomic absorption, and the percentage extraction into the organic phase calculated from this.

a. Anions

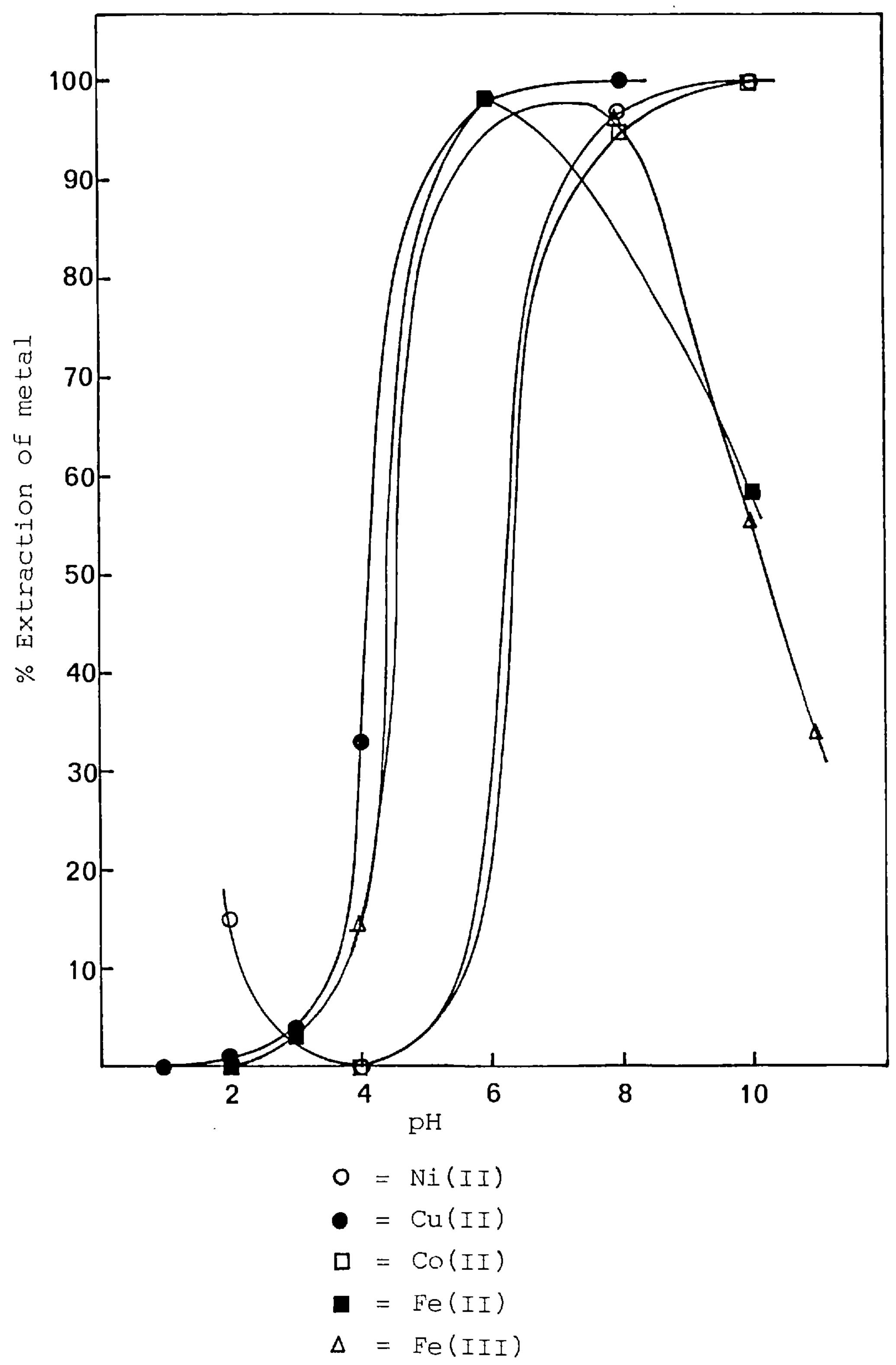
In the first studies the only anions available as pairs to the cationic complex were supplied by the metal salt. The aqueous phase was simply a solution of the metal salt in water. From these neutral solutions, 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine in chloroform extracted all of the metal perchlorates, no metal sulphates and all metal chlorides though nickel chloride was extracted only very slowly.

When acetic acid was added to the metal sulphate solutions to provide acetate anions there was partial extraction of all metals. When Versatic acid was added to the organic phase there was again partial extraction of all metals. Versatic acid is an extraction reagent itself. Its extractions are pH dependent. To determine the extent of Versatic acid extraction and bipyridine extraction, some extraction tests were performed over a range of pH. Extraction of all metals increased with increasing pH just as extractions by Versatic acid alone do. Graph 1 shows the extraction behaviour over a wide pH range. The extraction of nickel shows slight differences from the other metals. There is some extraction at pH 2 then no extraction at higher pH until a sudden extraction at pH 7 and higher. The extraction at low pH is very unusual.

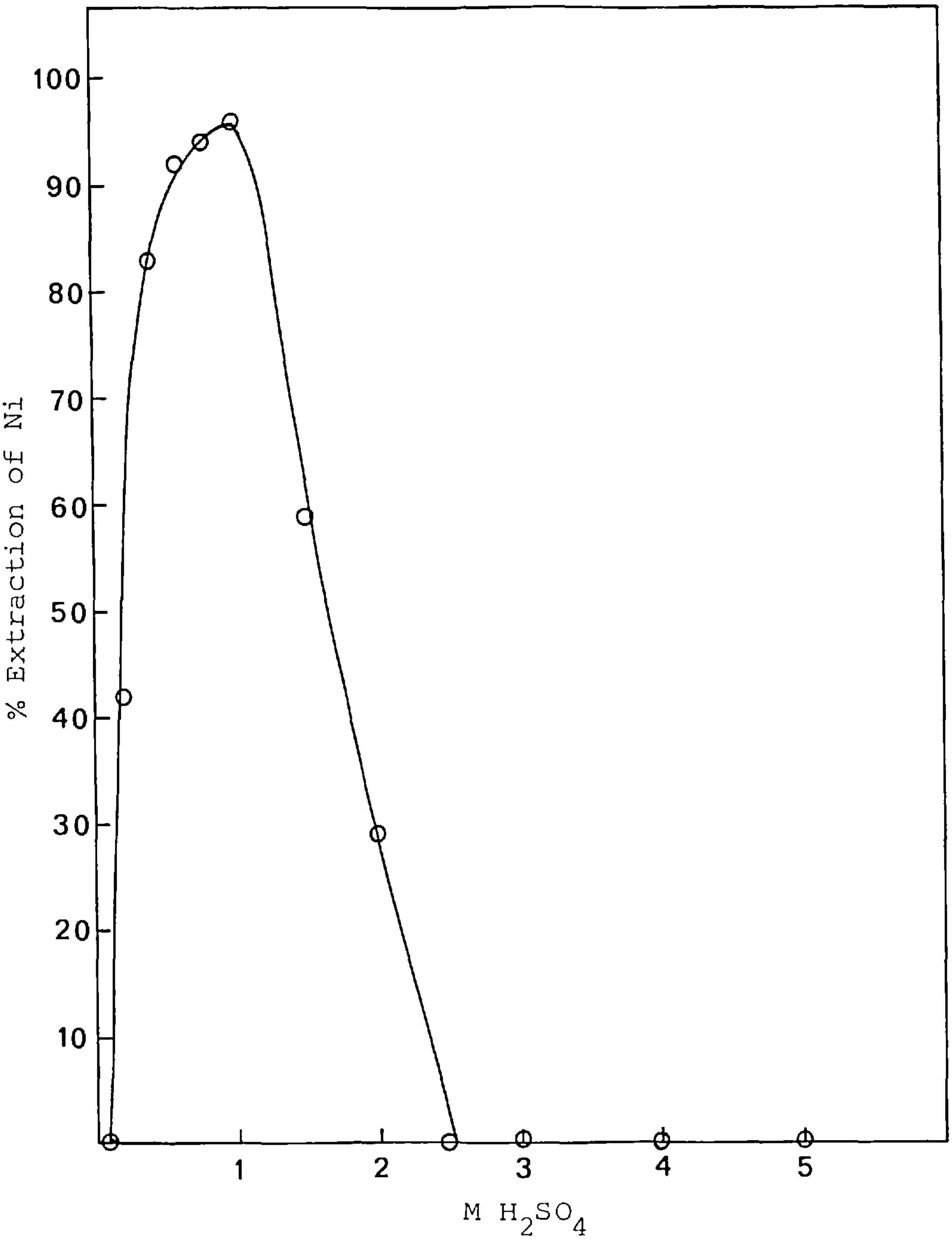
b. Extraction by bipyridines with pH variation

The mixed reagent behaviour complicates the study of extraction by bipyridines as Versatic acid was acting as an extractant itself. It was not useful as an anion source. The behaviour of the bipyridine itself, as an extractant, with change in pH and sulphate as anion was investigated. The anomalous behaviour of nickel in the mixed reagent system was clarified here. Nickel was extracted by 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine in chloroform from 1.0 M sulphuric acid and no other metal was extracted at all from 0.1 to 5.0 M sulphuric acid. The extraction curve is shown in Graph 2. There is no extraction of any metal by

GRAPH 1. Extraction of metal sulphates by Versatic acid and 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine.



<u>GRAPH 2.</u> The extraction of Ni(II) from sulphuric acid by 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine.



the bipyridine alone from neutral or basic aqueous phases.

Similar tests were performed for the extraction of metal chlorides from hydrochloric acid. Graph 3 shows the extraction curves over the acid range for each metal. All metals were extracted at low acidity and only copper was extracted from very strong acid equally well. Many complexes are known where metals include both 2,2'-bipyridine and chloride ions in their co-ordination spheres. Chloride incorporation into complexes as well as the bipyridine causes this variation in extraction behaviour.

c. Diluents

Chloroform was not the most suitable diluent for the nickel sulphate extraction. The complex concentrated at the phase interface rather than dissolving in the organic phase. Various other organic diluents were tested in the nickel sulphate extraction.

Solvesso 150 would not dissolve the complex. Perchlorate complexes were also insoluble in Solvesso 150.

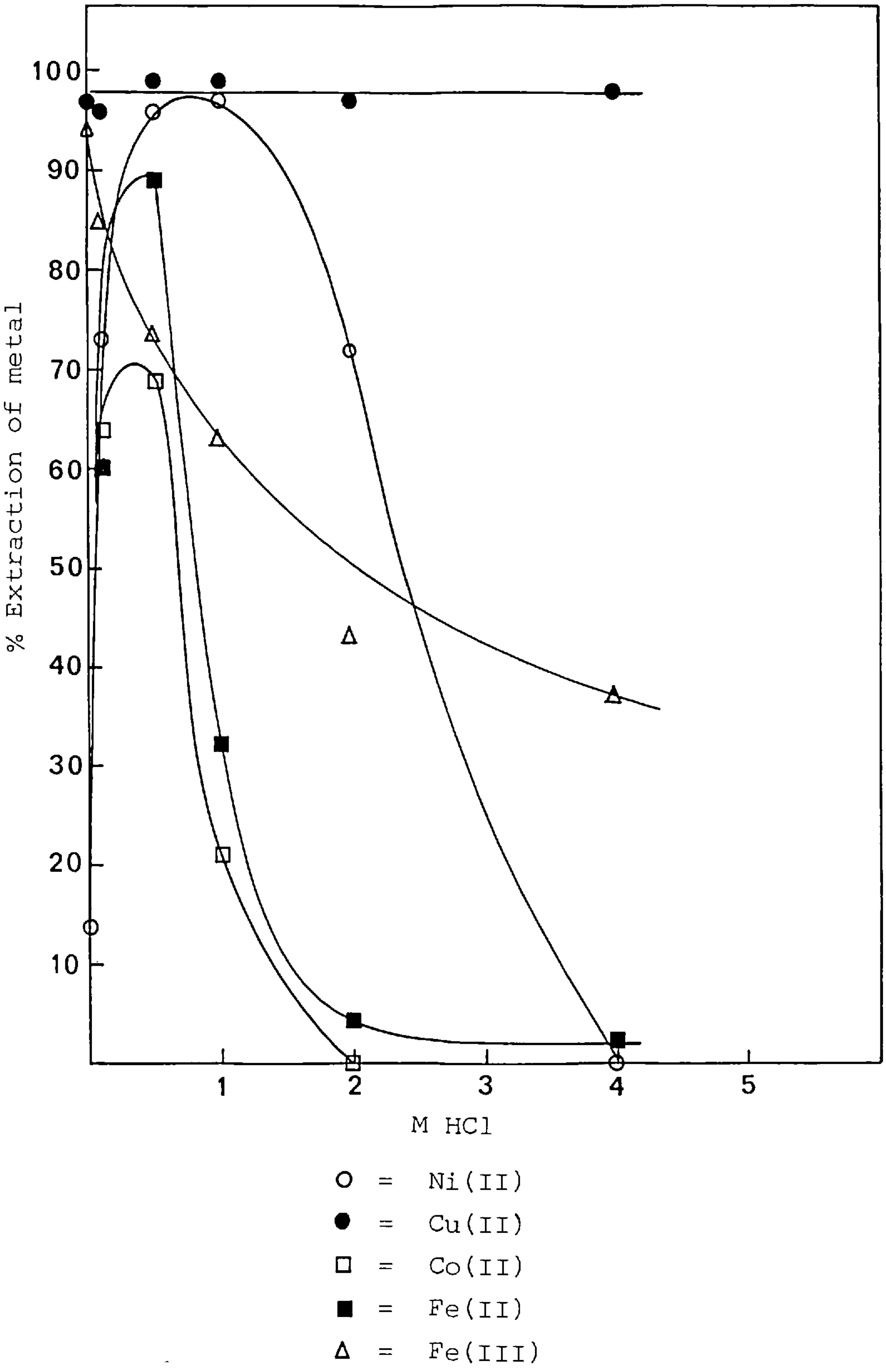
1,2-Dichloroethane is a suitable diluent for the bipyridines and there is no third phase in the nickel sulphate extraction.

Nitrobenzene is also a good diluent for the extraction but its use is not practical, from safety considerations and difficulty of reclamation of the bipyridine.

Toluene allowed no extraction of nickel sulphate at all. It is too non-polar to allow ion-pair extraction.

Petroleum ether was tried with some of the higher alkyl bipyridines, but it would not dissolve the complex at the

GRAPH 3. The extraction of metal chlorides from hydrochloric acid by 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine.



interface. The addition of isodecanol does not help to dissolve the precipitate.

Isodecane, also, is too non-polar a diluent for these extractions, and isodecanol will not change its properties sufficiently for dissolution of the complex.

1,2-Dichloroethane is the most suitable diluent for these tests. The lower alkyl bipyridines are all reasonably soluble in it; it is not so volatile as to cause changes in volumes during tests; the phases separate easily after shaking with aqueous solutions; the metal bipyridine complexes are soluble in it; it can be easily removed for recovery of the dry reagent.

d. Extraction behaviour of other lower ferroine group compounds

To determine whether 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine is unique in its extraction of nickel sulphate, the extraction test was performed using the closely related bipyridines and phenanthrolines which were available. All are about the same size and have the same functional groups.

2,2'-Bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 5,5'-dimethyl-2,2'-bipyridine and 1,10-phenanthroline in 1,2-dichloroethane did not extract nickel from any sulphuric acid solutions. 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine is unique in its extraction of nickel from 1.0 M sulphuric acid. This is certainly a discovery of specificity of a reagent for one metal to the exclusion of all others in a set of commonly found conditions. However its use as a commercial reagent is not viable as the ligand is soluble in the acid phase and is completely lost from the organic to the aqueous phase in the shake-out. Only the complex is returned to the organic phase. Such a loss of reagent is not acceptable.

4.2.2. Extraction by higher alkyl bipyridines

A range of long chain alkyl bipyridines was prepared for extraction tests. The addition of bigger alkyl groups on the 4-positions should decrease the solubility of the reagent in acid and keep the chelating ability of the ferroine functional group. The change in extraction properties with chain length can be related to acid solubility and the selectivity of the ligand.

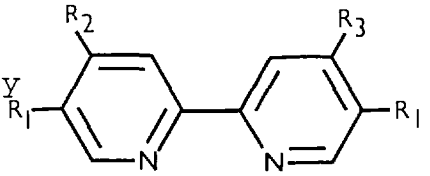
The 4,4'-dialkyl-2,2'-bipyridines are the most easily prepared and theoretically are the most easily varied without changing the chelating ability of the ligand as the 4-position is the most remote from the nitrogen co-ordination atom and the possibility of steric hindrance is least for this position.

Bipyridines of 4-alkyl carbon chain length 1C to 9C have been prepared, some also containing a 5-ethyl group. Some asymmetrical molecules where only the 4- and not the 4'-position has been substituted are included.

The extractions were carried out from both sulphate and chloride acid aqueous phases, to see if trends were similar where different complexes, (the chloride being incorporated into the complex), were involved.

Table 2. Extraction of metal sulphates from sulphuric acid by alkyl bipyridines.

% ext^n after 5 min shake (( )60 min shake) by



0.1 M in $(CH_2)_2Cl_2$

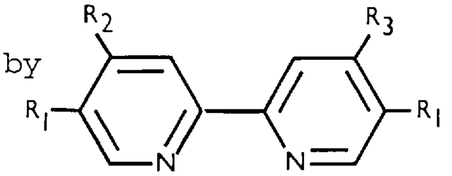
chain length $^4_5$ pos^n	Alkyl groups in 2,2'-bipyridine	Ni(II) 100 ppm in H_2SO_4			Co(II) 100 ppm in H_2SO_4		
		0.1M	1.0M	2.0M	0.1M	1.0M	2.0M
C_1	R_1=H R_2=R_3=CH_3	0	0	0	0	0	0
C_1 C_2	R_1=C_2H_5 R_2=R_3=CH_3	0	96	29	0	0	0
C_3(½)	R_1=H R_2=CH_3 R_3=C_3H_7	0	14 (31)	33 (54)	0	0	0
C_3	R_1=H R_2=R_3=C_3H_7	0 (0)	92 (98)	99	0	6 (7)	0
C_4(t)	R_1=H R_2=R_3=$C(CH_3)_3$	96 (98)	100	100	1 (41)	(5)	9 (12)
C_4(n)	R_1=H R_2=R_3=C_4H_9	77 (99)	100	100	14 (20)	87 (89)	55 (62)
C_5(½)	R_1=H R_2=CH_3 R_3=C_5H_{11}	92 (92)	99 (99)	22 (73)			
C_5	R_1=H R_2=R_3=C_5H_{11}	8 (79)	39 (100)	25 (100)	3 (5)	37 (66)	(44)
C_5 C_2	R_1=C_2H_5 R_2=R_3=C_5H_{11}	0 (0)	1 (11)	0 (6)	0 (6)	2 (30)	3 (25)
C_7	R_1=H R_2=R_3=C_7H_{15}	21 (95)	80 (100)	69 (99)	4 (8)	50 (56)	20 (25)
C_7(2)	R_1=H R_2=R_3=$CH(C_6H_{13})_2$	7 (58)	33 (97)	18 (86)	22 (33)	59 (94)	22 (85)
C_9(½)	R_1=H R_2=CH_3 R_3=C_9H_{19}	15 (58)	59 (99)	78 (99)	12 (14)	79 (90)	78 (83)
C_9	R_1=H R_2=R_3=C_9H_{19}	15 (50)	39 (96)	49 (98)	14 (14)	61 (78)	61 (83)
C_9(2)	R_1=H R_2=R_3=$CH(C_8H_{17})_2$	2 (5)	2 (6)	5 (7)	7 (9)	8 (24)	12 (31)

Table 2.(cont.)

chain length 4 pos^n 5	Cu(II) 100 ppm in H_2SO_4			Fe(II) 100 ppm in H_2SO_4			Fe(III) 100 ppm in H_2SO_4		
	0.1M	1.0M	2.0M	0.1M	1.0M	2.0M	0.1M	1.0M	2.0M
C_1	0	0	0	0	0	0	0	0	0
C_1 C_2	0	0	0	0	0	0	0	0	0
$C_3(\frac{1}{2})$	0	0	0	0	0	3	0	4	0
C_3	0	2	4	0	21 (73)	0	0	0	0
C_4(t)	2 (4)	40 (41)	35 (29)	7 (59)	36 (92)	7 (50)	1 (2)	2	1
C_4(n)	33 (34)	97	96	18 (74)	46 (88)	19 (75)	0 (2)	0 (5)	0 (0)
$C_5(\frac{1}{2})$	0 (0)	8 (10)	4 (5)						
C_5	81 (80)	98 (99)	98	0 (23)	31 (66)		0 (0)	0 (0)	
C_5 C_2	100	100	100	0 (3)	0 (1)	0 (0)	0	0	0
C_7	59 (59)	95 (95)	92 (94)	25 (57)	33 (91)	15 (59)	0	0 (2)	1
C_7(2)	95	100	100	2 (32)	12 (64)	8 (44)	0	5 (22)	0 (12)
$C_9(\frac{1}{2})$	90 (91)	100	100		14 (76)			0 (0)	
C_9	91 (91)	96	99		10 (34)			0 (0)	
C_9(2)	95	99	100		0 (0)			0 (0)	

Table 3. Extraction of metal chlorides from hydrochloric acid by alkyl bipyridines.

% ext^n after 5 min shake (( )60 min shake) by



0.1 M in $(CH_2)_2Cl_2$

chain length 4 pos^n 5	Alkyl groups in 2,2'-bipyridine	Ni(II) 100 ppm in HCl			Co(II) 100 ppm in HCl		
		0.1M	1.0M	2.0M	0.1M	1.0M	2.0M
C_1	R_1=H R_2=R_3=CH_3	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
C_1 C_2	R_1=C_2H_5 R_2=R_3= CH_3	73	97	72	64	21	0
$C_3(\frac{1}{2})$	R_1=H R_2=CH_3 R_3=C_3H_7	0 (1)	82 (81)	79 (86)	0 (0)	39 (37)	4 (2)
C_3	R_1=H R_2=R_3=C_3H_7	29 (49)	98	97	39 (55)	75 (73)	27 (28)
C_4(t)	R_1=H R_2=R_3=$C(CH_3)_3$	90 (99)	99	98	85 (88)	96	74 (76)
C_4(n)	R_1=H R_2=R_3=C_4H_9	45 (99)	90 (100)	86 (100)	87 (86)	95 (95)	85 (85)
C_5	R_1=H R_2=R_3=C_5H_{11}	4 (43)	22 (98)	22 (95)	25 (79)	81 (96)	87 (91)
C_5 C_2	R_1=C_2H_5 R_2=R_3= C_5H_{11}	0 (2)	0 (0)	0 (0)	0 (6)	2 (16)	11 (28)
C_7	R_1=H R_2=R_3=C_7H_{15}	8 (65)	34 (98)	36 (98)	33 (56)	70 (81)	
C_7(2)	R_1=H R_2=R_3=$CH(C_6H_{13})_2$	3 (32)	13 (85)	15 (84)	11 (87)	54 (98)	90 (94)
C_9	R_1=H R_2=R_3=C_9H_{19}	0 (2)	0 (4)	0 (4)	7 (0)	36 (36)	59 (76)

Table 3.(cont.)

chain length 4 5 pos^n	Cu(II)			Fe(II)			Fe(III)		
	100 ppm in HCl			100 ppm in HCl			100 ppm in HCl		
	0.1M	1.0M	2.0M	0.1M	1.0M	2.0M	0.1M	1.0M	2.0M
C_1	3 (2)	36 (51)	49 (66)	0 (0)	0 (0)	0 (0)	0 (0)	3 (3)	7 (7)
C_1 C_2	96	99	97	60	32	4	85	63	43
C_3(½)	52 (50)	98	96	5 (4)	29 (35)	4 (7)	2 (8)	57 (54)	45 (43)
C_3	91 (91)	100	100	47 (48)	80 (86)	18 (21)	32 (44)	81 (82)	75 (73)
C_4(t)	99	99	99	50 (93)	57 (81)	18 (20)	9 (35)	75 (75)	78 (75)
C_4(n)	99	99	99	46 (96)	72 (99)	68 (87)	18 (71)	93 (95)	95
C_5	100	100	100	11 (53)	41 (96)	72 (91)	8 (37)	94 (94)	97
C_5 C_2	100	100	100	0 (15)	14 (27)	21 (45)	25 (79)	73 (81)	85 (87)
C_7	99	100	100	8 (65)	29 (89)	33 (48)	4 (27)	80 (81)	89 (89)
C_7(2)	100	100	100	0 (33)	31 (96)	74 (93)	5 (61)	95 (97)	97
C_9	100	100	100	6 (57)	13 (80)	26 (80)	8	82	92

The results of these extraction tests are tabulated in Table 2 for extraction of metals from sulphuric acid and Table 3 for hydrochloric acid. The shaded areas indicate complete, fast extraction (greater than 90%) of the metal into the organic phase.

Percentage extractions were calculated from atomic absorption determinations of metal concentration in the aqueous phase before and after the shake-out tests. Samples were taken after 5 minutes and 60 minutes shaking of the organic reagent phase and aqueous metal phase together, to distinguish between slow and incomplete complex formation and/or extraction.

Some trends related to the effect of longer alkyl chains on the extraction behaviour of the bipyridine reagents can be drawn from the tables. They are best described separately for the different systems of extraction from sulphuric acid and extraction from hydrochloric acid.

Extraction of metals from sulphuric acid by alkyl bipyridines. Table 2.

1. Fe(III) is not extracted at all by any bipyridine reagent.
2. Fe(II) is partially and slowly extracted by bipyridines with alkyl chain lengths of 3C - 9C. The lower chain length bipyridines form red Fe(II) complexes in the aqueous phase.
3. Ni(II) is extracted quickly and completely by the lower chain length (3C - 5C) 4-alkyl bipyridines, and slowly but completely by the higher chain length (5C - 9C) 4-alkyl bipyridines.

4. Cu(II) is extracted quickly and completely by the higher chain length (5C - 9C) 4-alkyl bipyridines over the whole acid range, 0.1 M - 2.0 M sulphuric acid.

5. Maximum extraction for all metals occurs from 1.0 M sulphuric acid.

6. Ni-Co separation is good for 1C - 4C chain lengths, but Ni(II) and Co(II) are extracted similarly by the higher alkyl bipyridines.

7. Extraction behaviour of the 5,5'-diethyl-4,4'-dialkyl-2,2'-bipyridines differs from that of the purely 4-substituted bipyridines. Extraction of metals is poor except for extraction of Ni(II) by 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine from 1.0 M sulphuric acid and extraction of Cu(II) by 5,5'-diethyl-4,4'-dipentyl-2,2'-bipyridine.

Extraction of metals from hydrochloric acid by alkyl bipyridines. Table 3.

1. Cu(II) is extracted quickly and completely by the whole range of alkyl bipyridines.

2. Fe(III) is extracted well by the higher chain length 4-alkyl bipyridines (4C - 9C) and partially by the lower ones.

3. Ni(II) is quickly and completely extracted by 3C and 4C chain length 4-alkyl bipyridines and is slowly extracted by the higher alkyl bipyridines.

4. Maximum extraction of all metals occurs from 1.0 M hydrochloric acid.

5. There is only slight selectivity towards Cu(II) and Ni(II) over the other metals for the whole range of bipyridine reagents.

6. Co(II) is often extracted as well as and sometimes faster than Ni(II).

4.2.3. Rates of nickel extraction

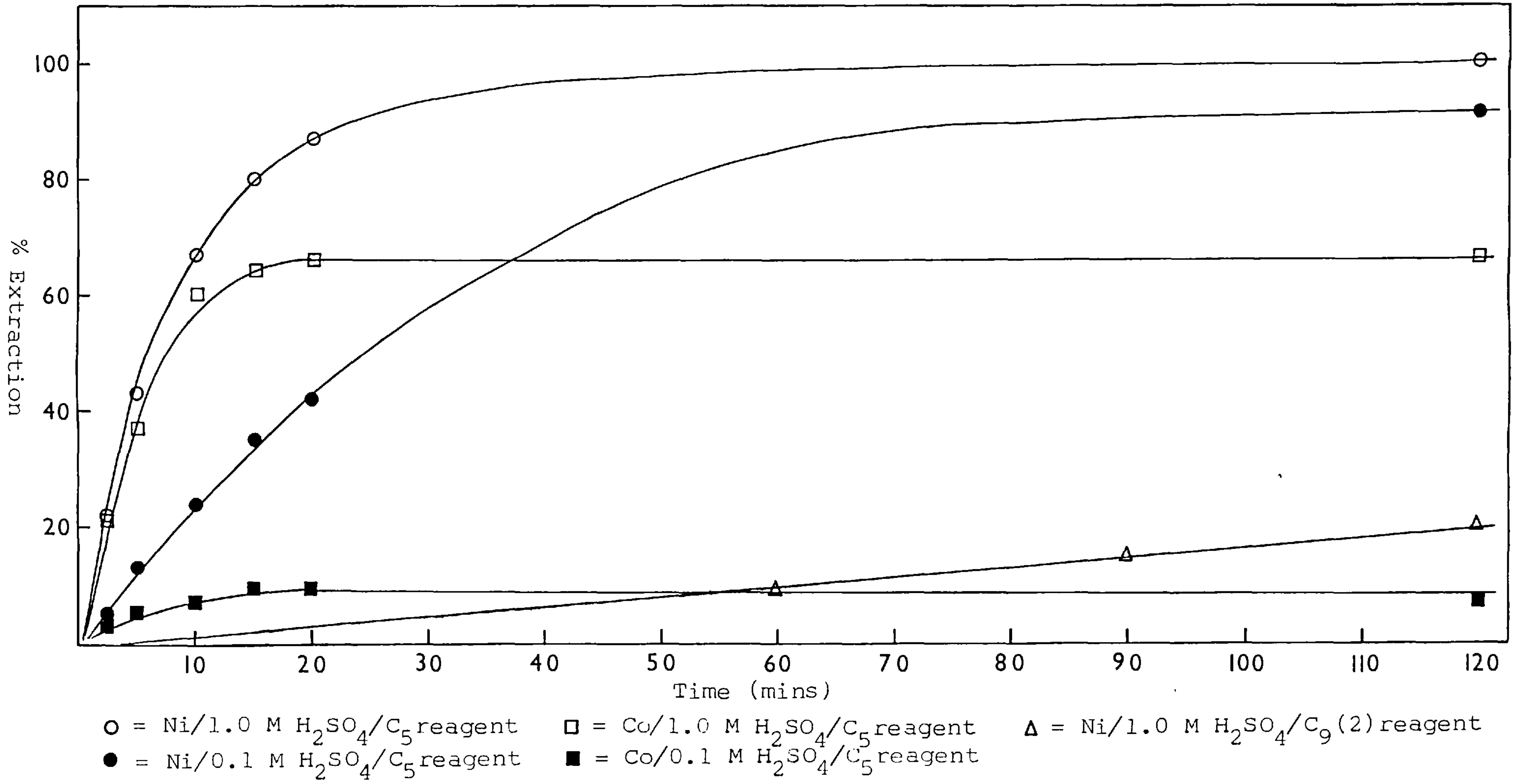
The rate of nickel extraction by alkyl bipyridines is slower for the higher alkyl bipyridines than the lower 3C - 5C chain length alkyl bipyridines. The smaller bipyridines extracted nickel completely in 5 minutes. Rates of extraction of Ni(II) and Co(II) by 4,4'-dipentyl-2,2'-bipyridine were measured from 0.1 M and 1.0 M sulphuric acid, and the extraction of Ni(II) by the tri- or quatro-substituted nonyl bipyridine was roughly assessed. The extraction curves are given in Graph 4.

The acidity of the aqueous phase affects the rate of extraction as suggested in Table 2. Extraction of both nickel and cobalt from 1.0 M sulphuric acid is faster than extraction from 0.1 M sulphuric acid. The extractions go to completion for nickel but different levels for cobalt, though the initial rate of cobalt extraction was equal to that of nickel from 1.0 M sulphuric acid.

Extraction of Ni(II) by 4,4'-di(1-octylnonyl)-2,2'-bipyridine was very slow but reached completion (greater than 90% extraction) after 36 hours. Extraction of other metals by this reagent appears to be equally slow, apart from the very fast extraction of Cu(II).

The general indications from 5 and 60 minute measurements of extraction levels in Tables 2 and 3 is that the rate of extraction decreases with increased alkyl chain

GRAPH 4. Rates of Ni(II) and Co(II) extraction from sulphuric acid by alkyl bipyridines.



length of the 4,4'-dialkyl-2,2'-bipyridine.

To study the effect of temperature on the rate of nickel extraction by 4,4'-dipentyl-2,2'-bipyridine, parallel shake-out tests were run at 25° and 50°, over a range of acidities. The rate of nickel extraction at 50° showed a 50% increase over that at 25°.

4.2.4. Acid solubilities of alkyl bipyridines

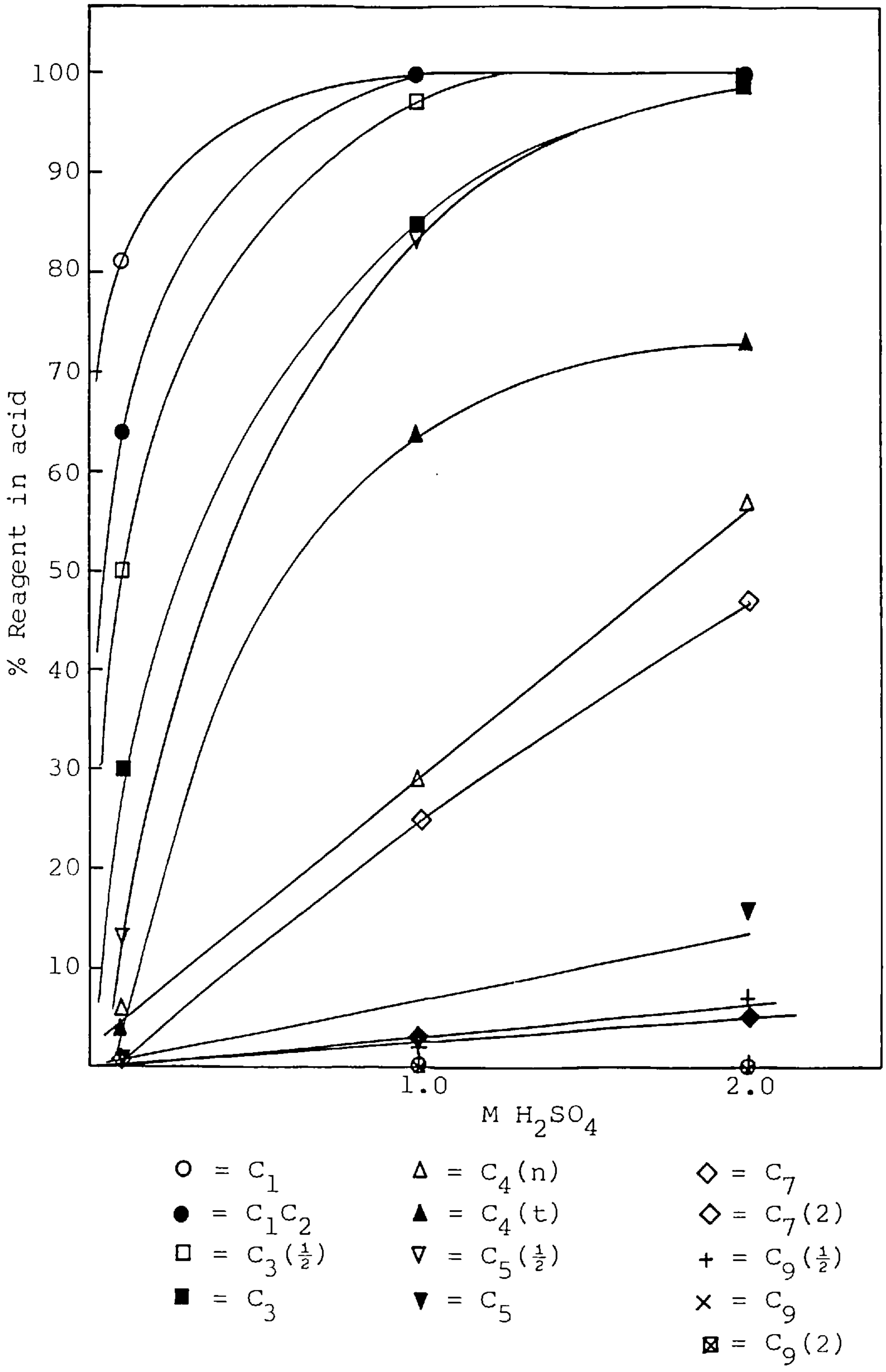
One prerequisite of a commercial solvent extraction reagent is its insolubility in the aqueous phase of the extraction system. 5,5'-Diethyl-4,4'-dimethyl-2,2'-bipyridine extracts Ni(II) selectively from 1.0 M sulphuric acid but because the free reagent is more soluble in the acid than organic phase, it is lost to the system with the spent aqueous phase and so is useless as a commercial extraction reagent. The increased alkyl chain lengths in the other bipyridines prepared make them increasingly insoluble in acid, but the extraction tests show that the extraction properties change with alkyl chain length too. An estimation of the acid solubility of each bipyridine prepared was obtained from ultraviolet spectra of the acid washes of each free base. The 0.1 M bipyridine solutions in 1,2-dichloroethane were shaken for 5 minutes with equal volumes of 0.1, 1.0 and 2.0 M sulphuric acid, then both phases were diluted (with 1,2-dichloroethane or water appropriately) and ultraviolet spectra taken. The absorptions follow Beer's law, so the relative heights of absorption peaks give a measure of amounts of reagent in aqueous and organic phases. Graph 5 shows the increase in aqueous solubility of the alkyl bipyridines with acid concentration, as percentages of the total bipyridine in each system in the acid phase.

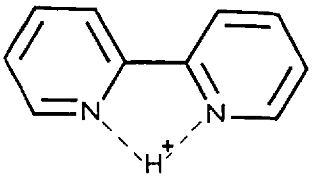
The dialkyl bipyridines are relatively soluble in acid solutions up to chain length 4C in the alkyl group. The solubility of 4,4'-diheptyl-2,2'-bipyridine is anomalous. It is expected to be less soluble than 4,4'-dipentyl-2,2'-bipyridine, but is not. The sample may have been contaminated with 4-heptyl-4'-methyl-2,2'-bipyridine as the mono-substituted product could not be separated from the main product during its preparation, as could be done in most preparations.

The bipyridines which extract nickel quickly and completely are those which are acid soluble i.e. have the same chain length upper limit of 4C. The acid soluble alkyl bipyridines extract nickel efficiently from sulphuric acid. Those which are acid insoluble (defined here as having a distribution ratio of less than 1:9 between 1.0 M sulphuric acid and the organic phase), extract nickel only slowly. This suggests that the complex formation is dependent on a reaction within the aqueous phase, before extraction into the organic of the hydrophobic complex.

The acid solubility is a measure of the protonation of the bipyridine as transfer to the acid increases with acid concentration. 2,2'-Bipyridine itself is mono-protonated easily. The usual trans form of bipyridines in solution probably converts to the cis form for bonding of the two nitrogen atoms to one hydrogen ion.

GRAPH 5. Acid solubility of alkyl bipyridines.





As the cis form is necessary for chelation, this may promote the first step to complex formation i.e. the necessary orientation for bonding of both nitrogen atoms to the metal ion is already attained by the rotation induced by bonding to a proton. Being aqueous insoluble, the longer chain alkyl bipyridines do not protonate and reorientate in the same way, and this fact along with the poorer contact between metal ions and reagent when they are not both acid soluble may be factors dictating the slower extraction rate of nickel. However these factors have not influenced copper extraction which is better by the higher alkyl bipyridines. The acid effect is certainly less in the copper case though; copper can be extracted from even neutral solutions by the higher alkyl bipyridines.

4.2.5. Nickel-cobalt separation

The possibility of using one of these bipyridine reagents to separate nickel and cobalt was assessed using 4,4'-dipentyl-2,2'-bipyridine, which is the smallest of the prepared reagents having a low acid solubility and thus potential value commercially, and sulphuric acid aqueous media. The percentage extraction figures of Table 2 and the rate of extraction details of Graph 4 suggest a possible separation by predominant extraction of nickel from 0.1 M sulphuric acid, leaving most of the cobalt in the aqueous phase. Nickel extraction is slow at this low acidity though, and at higher acidity cobalt is extracted at the same rate as nickel though not to the same extent.

Nickel will replace cobalt in the complex in an exchange reaction with a concentrated nickel aqueous solution. An organic solution of 4,4'-dipentyl-2,2'-bipyridine was loaded with nickel and cobalt (5:1). This organic solution was then shaken with an equal volume of aqueous nickel sulphate solution. All of the cobalt was transferred to the aqueous phase and an equivalent amount of nickel was taken into the organic.

This showed that 4,4'-dipentyl-2,2'-bipyridine extracts nickel preferentially over cobalt, but will still take both from 1.0 M sulphuric acid. A second extraction and bulk nickel solutions, which are consequently contaminated with cobalt, are necessary for any separation.

4.2.6. Stripping

Stripping the metal from the organic complex form with the alkyl bipyridines is a problem. As in the extractions, each metal behaves differently in extent and rate of stripping, though the stripping behaviour of each metal with the range of alkyl bipyridines is similar. Thus the stripping behaviour of each metal with the bipyridine chelation system has been observed.

Cobalt is stripped from 1,2-dichloroethane complex solutions completely and quickly by water.

Ferrous ions can be partially stripped from the organics which take it, by water, and not by ammonia.

Nickel and copper can be stripped by ammonia, copper quickly and nickel slowly, as in the extractions, from the higher alkyl bipyridines.

Various other stripping agents were tested with the bipyridine system. These were sodium hydroxide, sodium carbonate, ammonium carbonate and ammonium sulphate in ammonia, but none worked as well as ammonia and water, though all of the bases took 50% of the copper.

The stripping of cobalt by water from a loaded nickel-cobalt organic is a potential separation technique in the bipyridine system. The cobalt is removed easily, but the nickel is only very slowly stripped by ammonia.

4.3. Mechanism of the bipyridine extractions

4,4'-Dipentyl-2,2'-bipyridine was chosen as the most suitable of the reagents prepared, to study the mechanism of the extraction of nickel and copper. 4,4'-Dipentyl-2,2'-bipyridine has a low acid solubility, it extracts Ni(II) completely, though slowly, and Cu(II) quickly. It is the easiest of the higher alkyl bipyridines to prepare and purify and can be made in a reasonable yield. Study of its extraction may elucidate the reasons for those bipyridines smaller than it extracting nickel preferentially and those with longer alkyl chains taking copper.

Several aspects of the Ni(II) and Cu(II) extractions have been investigated: the metal loading capacity of the reagent and thus the ligand to metal ratio in the complex, the effect of pH on extractability, anion concentration and ionic strength effects and reagent concentration effects.

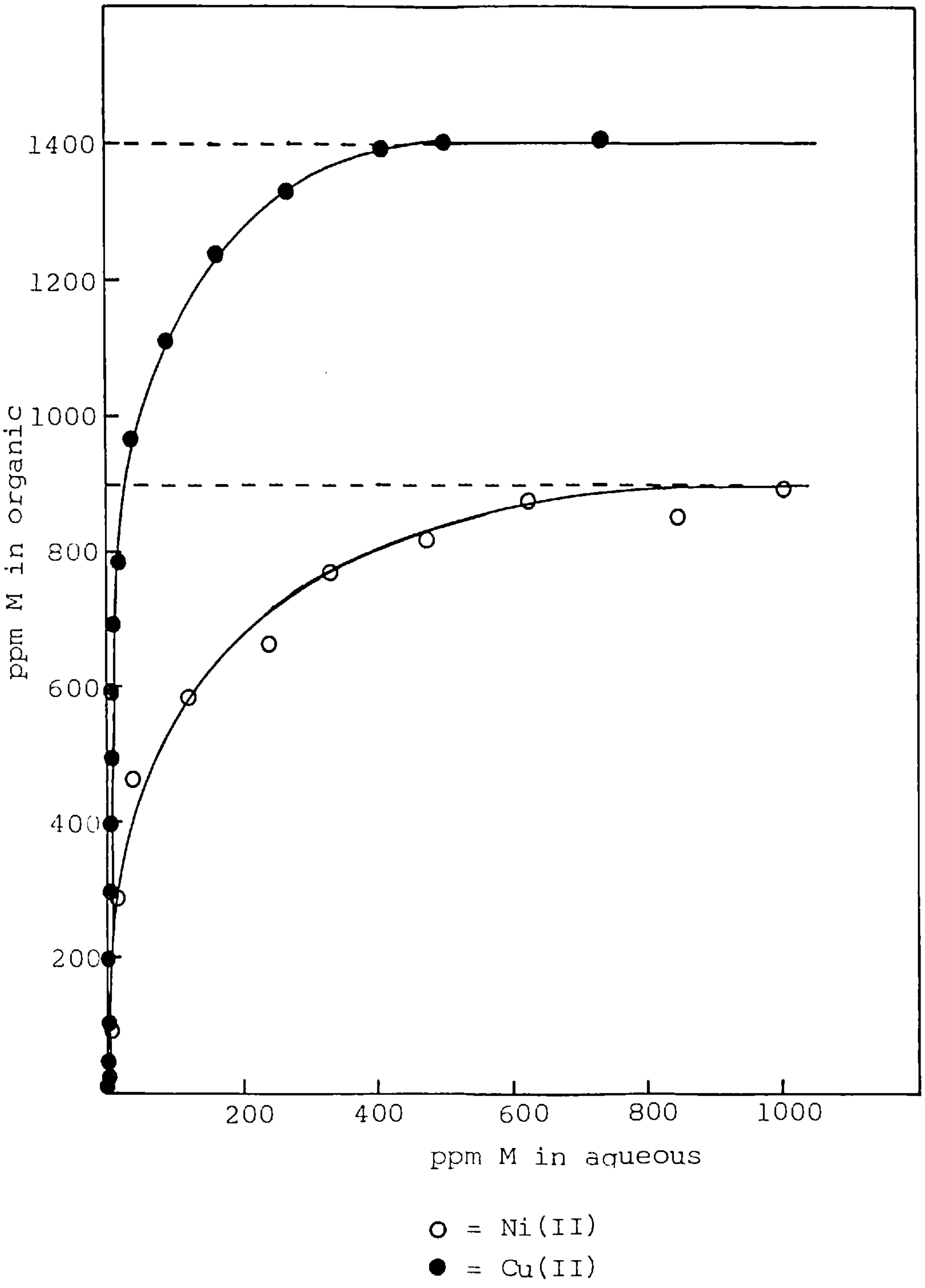
4.3.1. Metal loading capacity

Ni(II) generally forms 6-co-ordinate octahedral complexes. This is true for 2,2'-bipyridine ligands. Three ligands complex with one nickel ion, but bis- and mono-chelate complexes have been isolated too. Mixed ligand complexes, such as $\left[\mathrm{Ni(bipy)_2(phen)}\right]^{2+}$ are also common.[105]

Cu(II) generally forms 4- or 5-co-ordinate complexes arranged in a distorted square planar or trigonal bipyramidal structure. Two 2,2'-bipyridine molecules are co-ordinated in a slightly distorted square planar arrangement, often with an anion or a water molecule in a fifth co-ordination position. $\left[\mathrm{Cu(bipy)_2I}\right]\mathrm{I}$ and $\mathrm{Cu(bipy)SO_4.H_2O}$ are known.

To check the complex structure of Ni(II) and Cu(II) complexes with larger dialkyl bipyridines, the metal loading capacity of a set amount of 4,4'-dipentyl-2,2'-bipyridine was measured. 0.05 M solutions of 4,4'-dipentyl-2,2'-bipyridine were shaken with equal volumes of nickel and copper sulphate solutions in 1.0M sulphuric acid, the metal concentrations ranging from 10 ppm to 1900 ppm. Atomic absorption measurements against standard solutions gave the amounts of metal in aqueous and organic phases and the amount of metal in the organic phase was plotted against the amount in the aqueous phase in Graph 6. The maximum loading in the organic phase gives the number of ligands complexed

GRAPH 6. Metal loading capacity of a bipyridine reagent.



to each metal ion:

If there are three ligands to each metal, assuming complete reaction in complex formation and equal phase volumes:

0.05 M reagent will take $\frac{1}{3}(0.05)$ = 0.017 M metal
= 1000 ppm Ni
or 1080 ppm Cu.

If there are two ligands to each metal:

0.05 M reagent will take $\frac{1}{2}(0.05)$ = 0.025 M metal
= 1470 ppm Ni
or 1590 ppm Cu.

Graph 6 shows that the upper loading limit for nickel was 900 ppm Ni, nearly equal to 3 ligands/Ni, and the upper limit for copper was 1400 ppm Cu, nearly equal to 2 ligands/Cu. The values are a little lower than the theoretical yields because the reagent concentration was really lower than 0.05 M as it was contaminated by a little of the higher molecular weight tri- and **tetra**-pentyl-substituted bipyridines which could not be totally removed in the purification stages.

Thus it has been shown that the Ni(II) bipyridine complex is 6-co-ordinate and presumably octahedral and the Cu(II) complex is 4-co-ordinate, to the bipyridine ligand anyway, presumably in a square planar arrangement as in most Cu(II) complexes, possibly with H_2O or SO_4^{2-} in a fifth co-ordination position.

4.3.2. Extraction dependence on pH

As seen in the preliminary extraction tests, extraction by the alkyl bipyridines is dependent on pH, maximum extraction usually occurring from 1.0 M sulphuric acid and no extraction from neutral or alkaline aqueous solutions. Increased acidity up to 1.0 M sulphuric acid certainly gave increased extraction of Ni(II) by 4,4'-dipentyl-2,2'-bipyridine. The same trend was observed with Cu(II), but the dependence was not so extreme - copper is extracted to a small extent even from neutral sulphate solution.

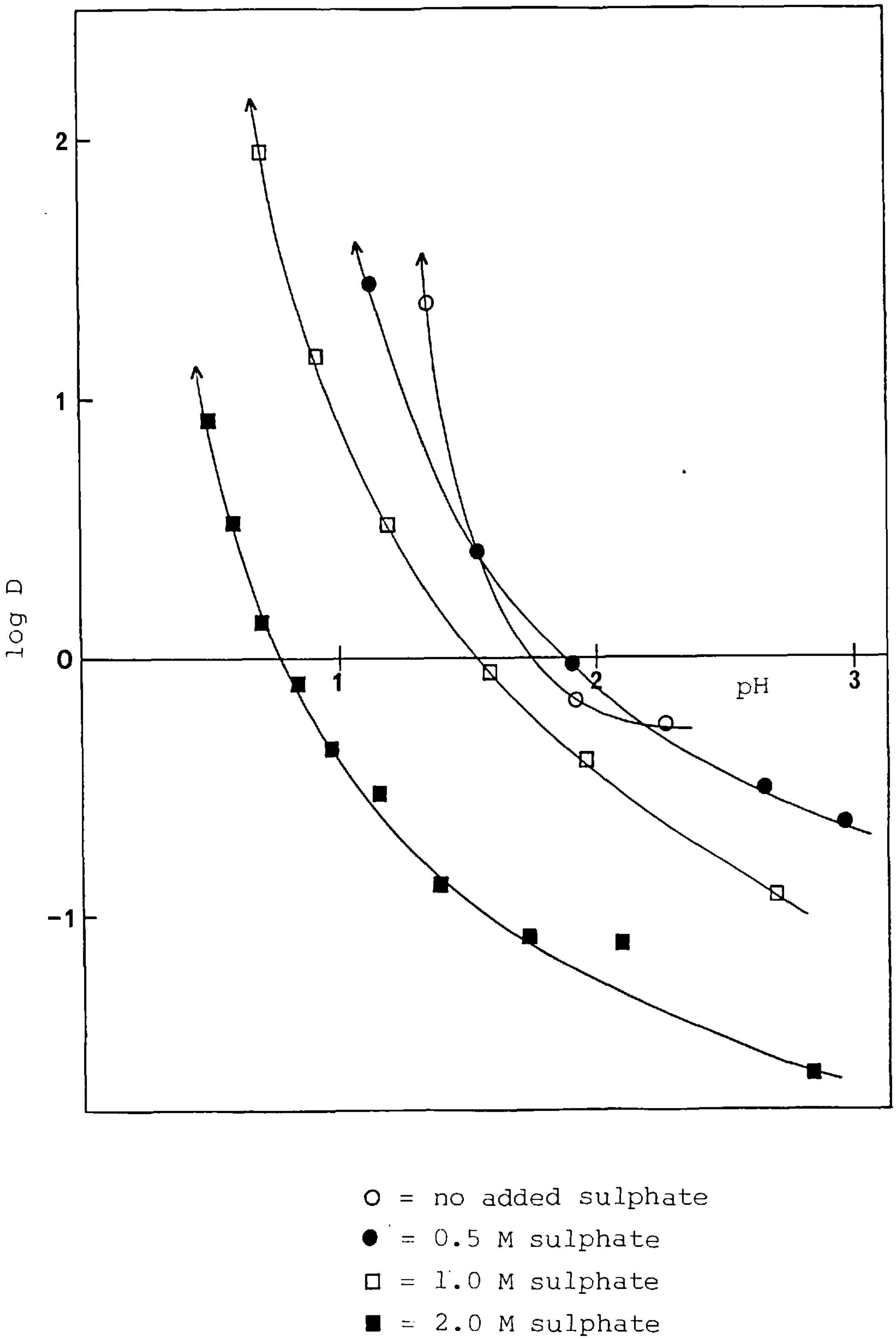
A series of extraction tests was made to determine the dependence on pH and sulphate concentration of the extractions of Ni(II) and Cu(II) by 4,4'-dipentyl-2,2'-bipyridine.

Graphs 7 and 8 show the dependence of log D (D is the distribution co-efficient equal to the ratio of the metal concentration in the organic phase to the metal concentration in the aqueous phase at equilibrium) on pH when the total sulphate concentration is contributed totally by the metal salt and sulphuric acid, so varying with pH, and when sodium sulphate was added to make the total sulphate constant at three different levels to eliminate anion concentration effects from the observation of pH effects.

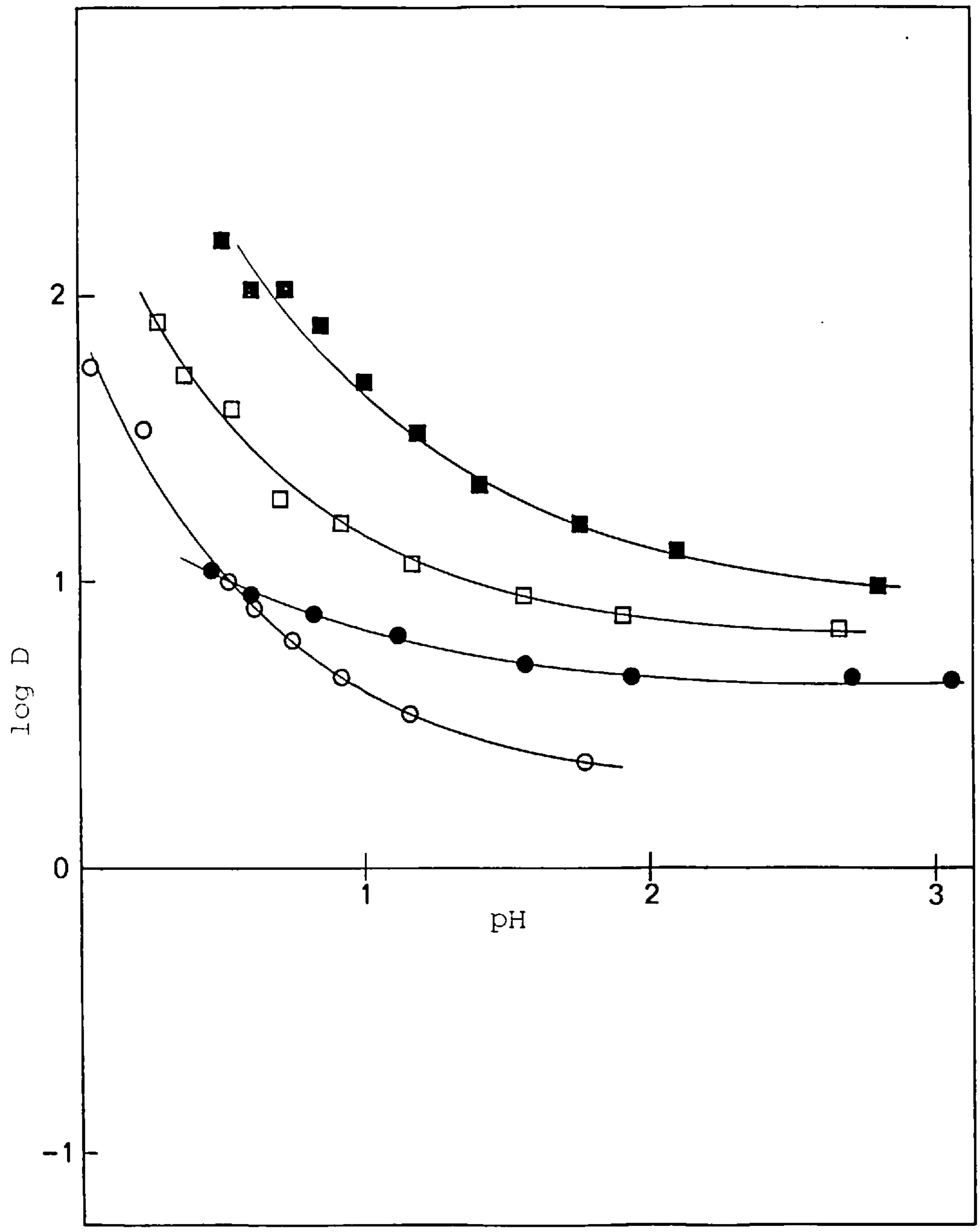
pH was measured before and after the extractions and found to be very nearly equal in the 0.01 M - 0.8 M sulphuric acid range. There is no measurable extraction of protons in this range.

The curves are difficult to understand.

GRAPH 7. Extraction of Ni(II) from sulphuric acid/sulphate solutions by 4,4'-dipentyl-2,2'-bipyridine.



GRAPH 8. Extraction of Cu(II) from sulphuric acid/sulphate solutions by 4,4'-dipentyl-2,2'-bipyridine.



○ = no added sulphate

● = 0.5 M sulphate

☐ = 1.0 M sulphate

■ = 2.0 M sulphate

In the Cu(II) extractions, Graph 8, extraction is clearly increased by decrease in pH and increase in sulphate level. It also has a threshold extraction independent of pH. Above pH 2 it is extracted at a constant level, dependent only on sulphate level.

From the nickel curves, Graph 7, it can be seen that log D decreases with increase in sulphate level, an opposite trend to that observed for copper, and the increase in extraction with pH less than 2 is dramatic.

It must be noted that at these low pH the background sulphate will be in the form of bisulphate as well as sulphate, dependent on pH. Bisulphate pK_a is 1.92 (Graph 9). The Ni(II) and Cu(II) extraction curves can not be related to the anion concentration of bisulphate or sulphate as it cannot be to original total sulphate concentration.

The equation expected for the Ni(II) extraction is:

$$Ni^{2+} + 3\ L + SO_4^{2-} \overset{K_{ex}}{\rightleftharpoons} \left(\left[NiL_3\right]SO_4\right)_{org}$$

where L is the alkyl bipyridine ligand. Charges are omitted for clarity.

$$K_{ex} = \frac{\left[\left[NiL_3\right]SO_4\right]_{org}}{\left[Ni\right]\left[L\right]^3\left[SO_4\right]}$$

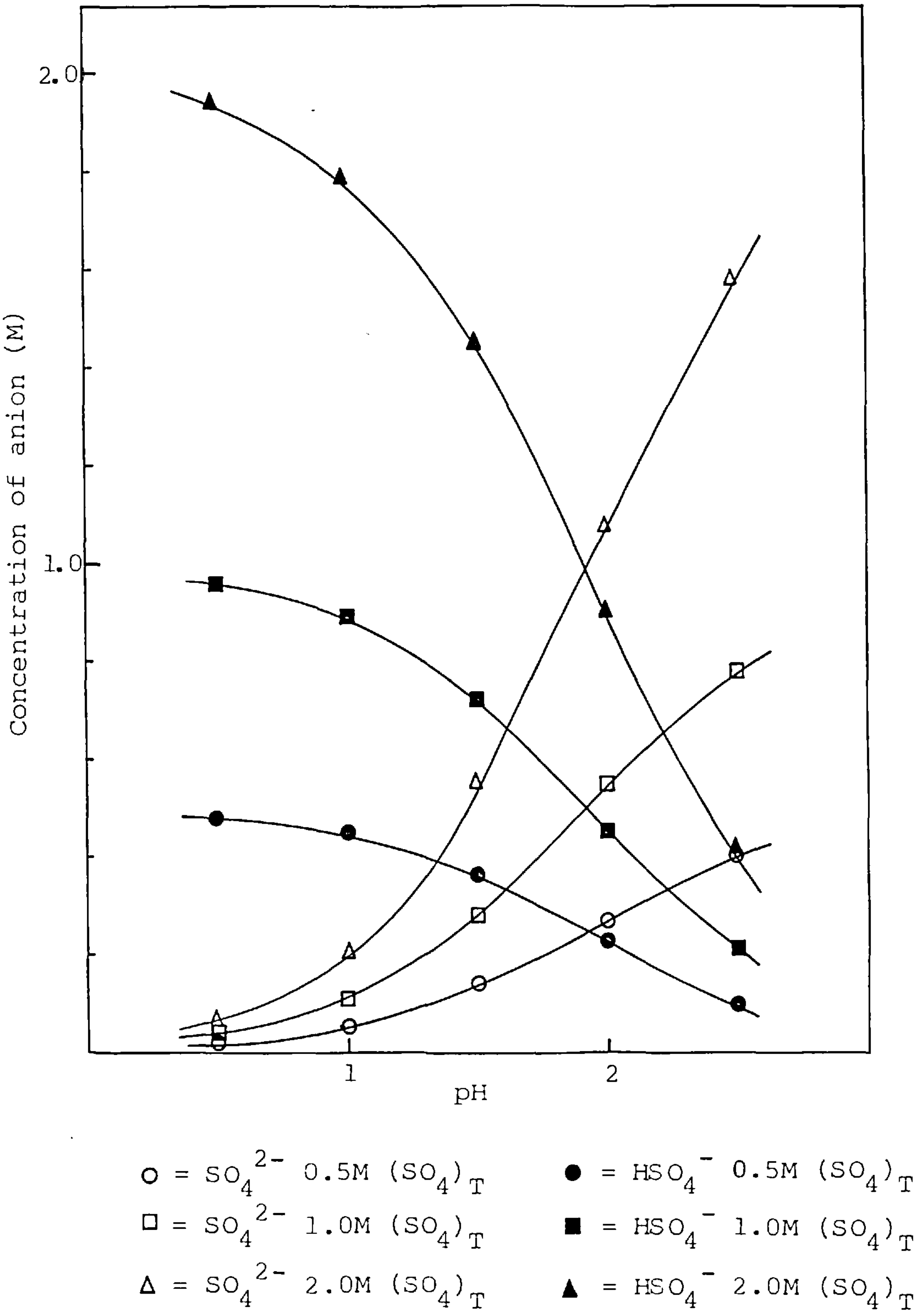
$$D = \frac{\left[\left[NiL_3\right]SO_4\right]_{org}}{\left[Ni\right]} \qquad \therefore \quad K_{ex} = \frac{D}{\left[L\right]^3\left[SO_4\right]}$$

$$\log K_{ex} = \log D - 3\log\left[L\right] - \log\left[SO_4\right]$$

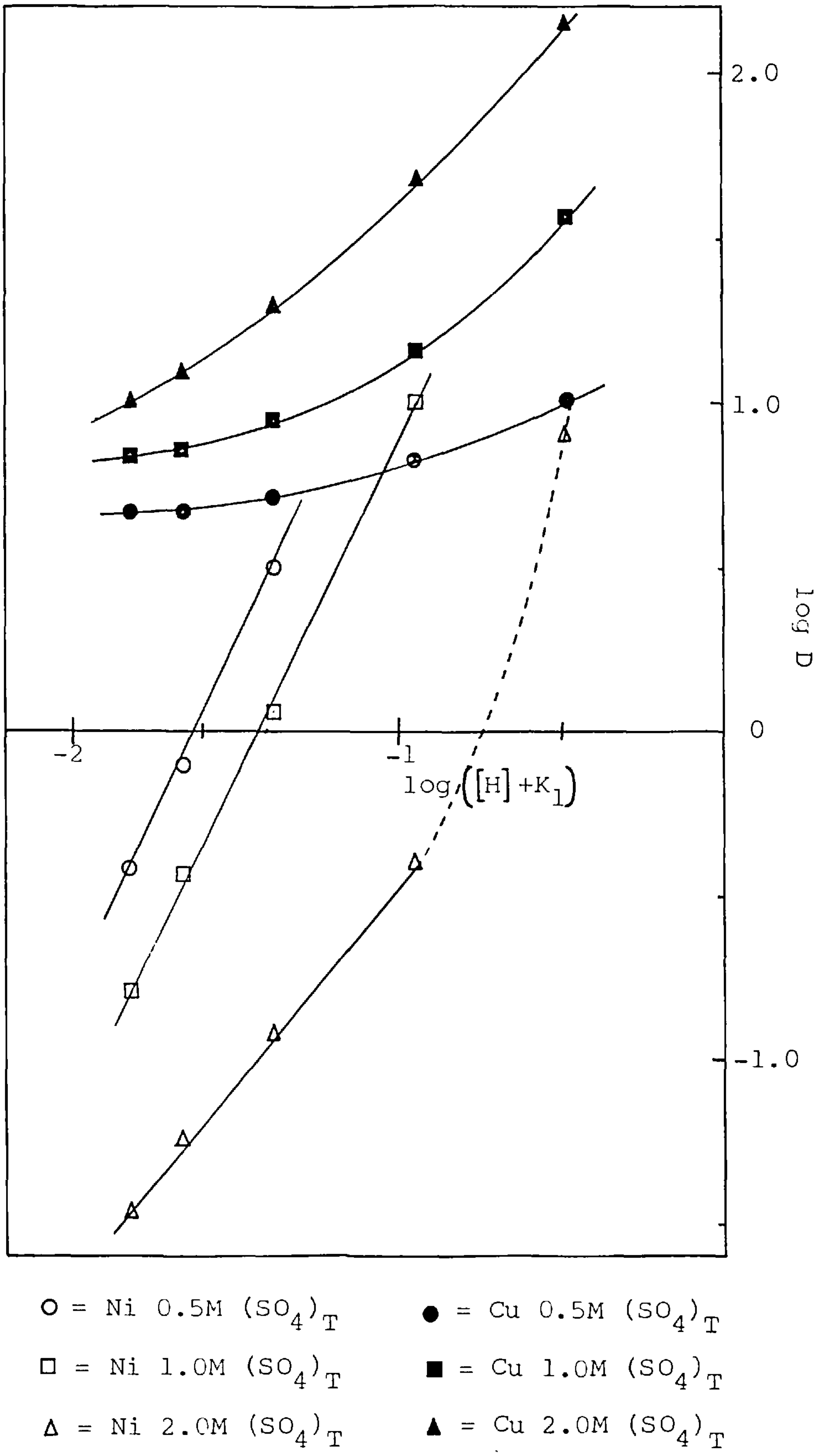
$$\therefore \quad \log D = \log K_{ex} + 3\log\left[L\right] + \log\left[SO_4\right]$$

if dependent on sulphate,

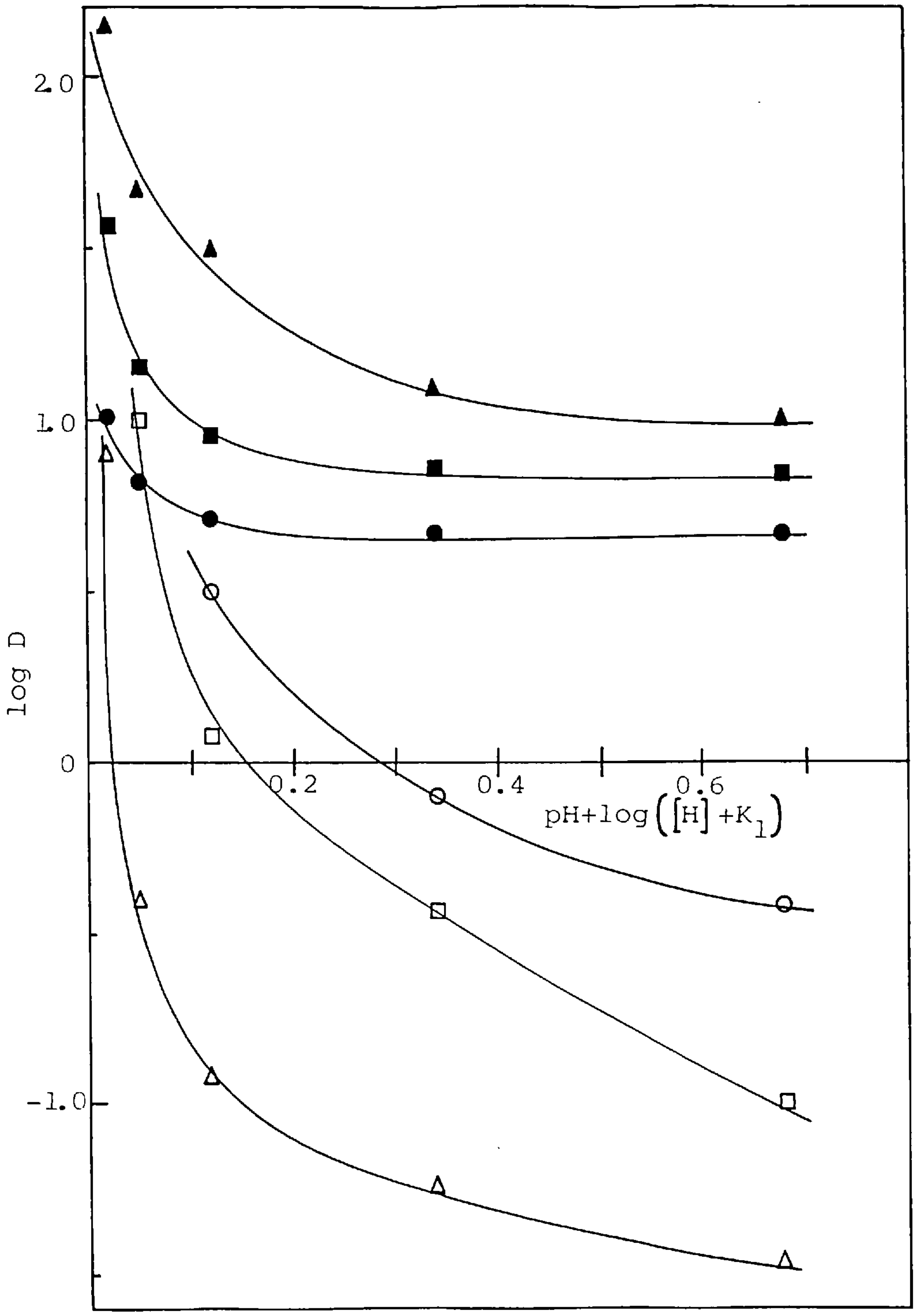
GRAPH 9. Change in anion concentrations with change in pH.



GRAPH 10. Log D vs $\log\left([H]+K_1\right)$ for the extraction of Ni(II) and Cu(II) by 4,4'-dipentyl-2,2'-bipyridine.



GRAPH 11. Log D vs pH+log$([H]+K_1)$ for the extraction of Ni(II) and Cu(II) by 4,4'-dipentyl-2,2'-bipyridine.



○ = Ni 0.5M $(SO_4)_T$

● = Cu 0.5M $(SO_4)_T$

□ = Ni 1.0M $(SO_4)_T$

■ = Cu 1.0M $(SO_4)_T$

△ = Ni 2.0M $(SO_4)_T$

▲ = Cu 2.0M $(SO_4)_T$

or $\log D = \log K_{ex} + 3 \log[L] + 2 \log[HSO_4]$

if dependent on bisulphate.

These expressions can be related to total sulphate concentration:

$$[SO_4]_T = [SO_4] + [HSO_4]$$

and $HSO_4^- \overset{K_1}{\rightleftharpoons} SO_4^{2-} + H^+$ $\qquad K_1 = \dfrac{[SO_4][H]}{[HSO_4]}$

Extraction with sulphate,

$$\log D = \log K_{ex} + \log[SO_4]_T + \log K_1 - \log\left([H]+K_1\right) + 3 \log[L]$$

$$\log D \;\alpha\; \log\left([H]+K_1\right) \qquad \text{slope} = -1$$

Extraction with bisulphate,

$$\log D = \log K_{ex} + 2 \log[SO_4]_T + 2 \log\left(\frac{[H]}{[H]+K_1}\right) + 3 \log[L]$$

$$= \log K_{ex} + 2 \log SO_{4\ T} - 2\,pH - 2 \log\left([H]+K_1\right) + 3 \log[L]$$

$$\log D \;\alpha\; pH + \log\left([H]+K_1\right) \qquad \text{slope} = -2$$

These were plotted from the previous graphs for Ni(II) and Cu(II) (whose extraction would be similar but with only 2 L / Cu) (Graphs 10 and 11). Neither clarified the situation. This simple extraction equation cannot be applied.

The presence of acid must alter the equilibrium equation dramatically. As discussed in the background, the acid causes major changes in each phase. The ionic activities of species in solution cannot be calculated accurately and the organic phase changes its whole nature when in contact with acid. There is no evidence of extraction of protons by the reagent in this case but the effect of the presence of acid on the extraction of metal ions is still great. The acid certainly plays some part in promoting the extraction, but it cannot be described in the equilibrium equations.

4.3.3. Reagent concentration effect

From the originally proposed reaction equations (1 and 2) a direct relationship is expected between log D and log $\left[\text{bipyridine ligand}\right]$.

$$Ni^{2+} + 3\,L + SO_4^{2-} \xrightleftharpoons{K_{ex1}} \left(NiL_3\right)SO_4 \qquad (1)$$

$$\log D_1 = \log K_{ex1} + 3\log\left[L\right] + \log\left[SO_4\right]$$

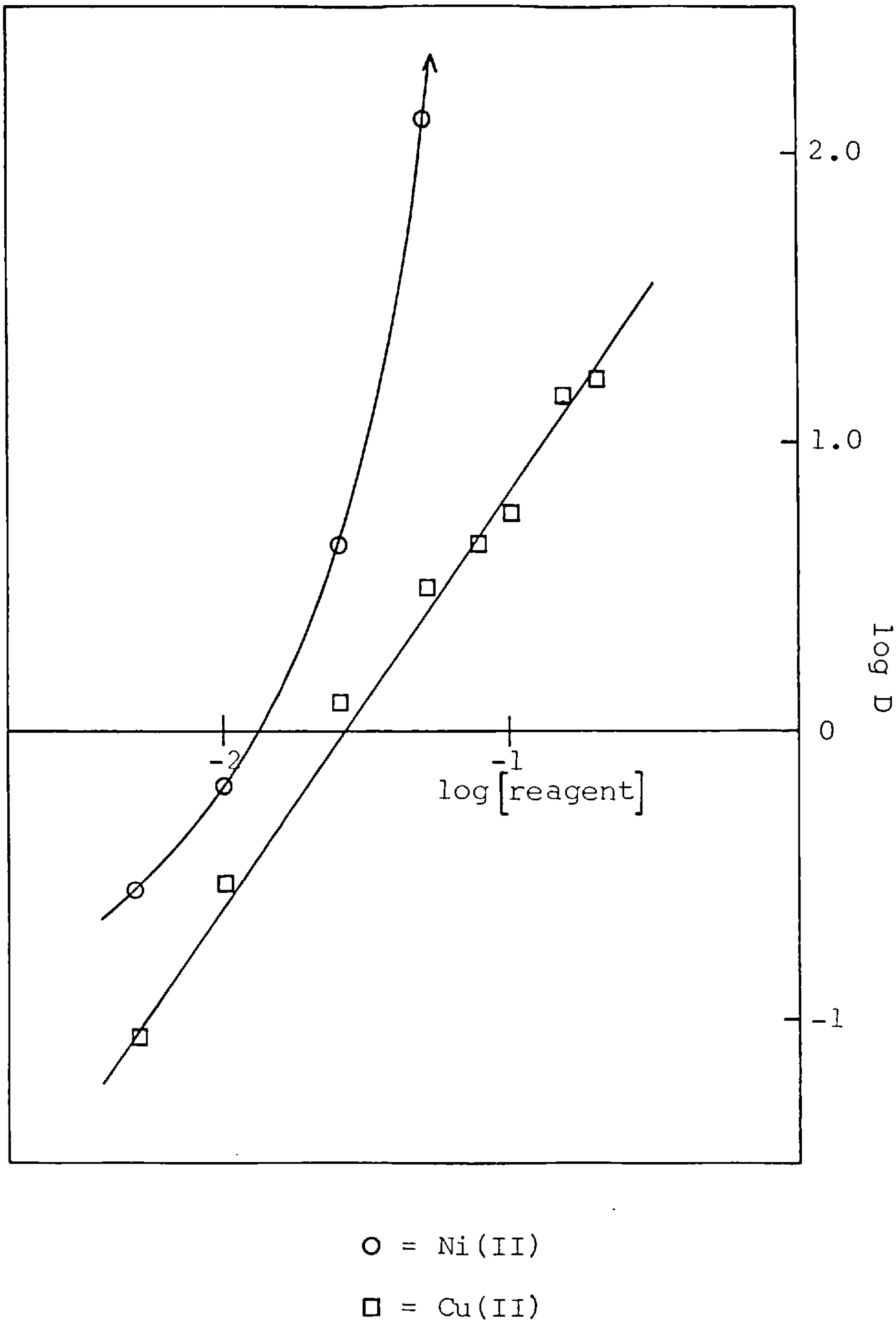
$$Cu^{2+} + 2\,L + SO_4^{2-} \xrightleftharpoons{K_{ex2}} \left(CuL_2\right)SO_4 \qquad (2)$$

$$\log D_2 = \log K_{ex2} + 2\log\left[L\right] + \log\left[SO_4\right]$$

Extraction tests were run with varying reagent concentration, 100 ppm metal, constant total sulphate (0.5 M) and from 0.05 M sulphuric acid. These constant conditions were chosen to provide a reasonable measurable log D range for both nickel and copper extractions.

Graph 12 shows the results. Only four values were obtained for nickel, as at reagent concentrations greater than 0.05 M complete extraction was obtained. This also meant that a straight line could not be drawn for those four values. However as an approximate calculation, the tangent to the curve at log D = 1 gave a slope of 3 which corresponds to equation (1).

The copper plot gave a relatively good straight line. The slope was 1.5, rather than the expected value of 2. The real reagent concentration being less than that recorded, GRAPH 12. Reagent concentration effect on extraction.



because of contamination by more highly substituted alkyl bipyridines, accounts for a small drop in this value, but not the full difference. Some mono-bipyridine-chelated copper complexes are probably present to cause the difference between experimental and theoretical slope values. At low reagent concentrations only one bipyridine ligand may be complexed along with anions or water which are commonly found in Cu(II) complexes.

Formation of aggregates in the organic phase may be a factor in the non-ideal behaviour of the complex extractions. Though 1,2-dichloroethane is a fairly non-polar diluent the dissolution of water and protons from the acid phase in the organic phase may contribute to hydrogen bonding between the reagent molecules, diluent, water and protons. The intermolecular interactions through hydrogen bonds can give rise to reagent dimers or larger aggregates, making the solvent abnormal.

The experimental slope values support the proposed complex structures of $Ni(bipy)_3^{2+}$ and $Cu(bipy)_2^{2+}$ and they add some credence to the proposed expected equilibrium equations.

5. CONCLUSION

The alkyl bipyridines have proven to be a very interesting family of extraction reagents. Only the methyl-, ethyl- and phenyl-substituted bipyridines have been used as metal chelates previously and then only for analytical studies. It has now been shown that there is great scope for their use as selective reagents on a larger scale.

Good synthetic routes have been found for the synthesis of alkyl bipyridines. Short chain length 4- and 5-alkyl pyridines can be coupled by a specially prepared degassed Raney nickel catalyst to form the dialkyl-2,2'-bipyridines. This synthesis was not suitable for the longer chain length (greater than 4C) bipyridines. These could be prepared by an alkylation, using Tschitschibabin's method, of the dimethyl-2,2'-bipyridines. Thus a range of 4,4'-dialkyl-2,2'-bipyridines and some 5,5'-diethyl-4,4'-dialkyl-2,2'-bipyridines were prepared for tests as solvent extraction reagents for Ni(II), Cu(II), Co(II), Fe(II) and Fe(III).

The preliminary solvent extraction tests with lower alkyl bipyridines showed that extraction by bipyridines was possible only from acid solutions. The choice of organic diluent, and the anionic composition of the aqueous phase affected the extractions. 1,2-Dichloroethane was found to be the most suitable diluent for the reagents as it dissolved both the reagents and the metal complexes and was easy to use practically. Perchlorate and chloride electrolytes provided suitable anion pairs for complex cations, promoting complete or partial extraction of all metals into the organic phase, but sulphate as anion was more suitable for selective extraction of some metals under finely defined conditions. 5,5'-Diethyl-4,4'-dimethyl-2,2'-bipyridine in 1,2-dichloroethane will extract Ni(II) from 1.0 M sulphuric acid, and no other metal ion, but because the reagent is more soluble in acid than in the organic phase it is lost to the system and so is unsuitable for consideration as a commercial solvent extraction reagent.

Within the range of alkyl bipyridines prepared the acid solubility decreases with increased size of the molecule. The extraction properties also vary with the size or solubility. The lower 4,4'-dialkyl-2,2'-bipyridines (carbon chain length 3C and 4C) extract Ni(II) quickly and completely along with Co(II), Cu(II) and Fe(II) partially. Extraction was best from 1.0 M sulphuric acid. The higher ones (5C - 9C) take Cu(II), quickly and completely, over the whole acid range, while the rate of Ni(II) extraction was decreased, though still complete. Co(II) and Fe(II) were also taken partially.

The change in the rate of Ni(II) extraction when the alkyl chain length reaches 5C may be because the Ni-bipyridine complex formation must occur in the aqueous phase, so an acid soluble bipyridine reacts with nickel ions in the aqueous phase and only the complex-anion pair is transferred to the organic phase. With the less acid soluble reagents the reaction is inevitably slower as complex formation must occur at the interface.

Cu(II) complex formation is not dependent on these conditions, and selective extraction of Cu(II) is best with the biggest alkyl bipyridine (9C(2)) which takes all other metals very slowly.

The mechanisms of the extraction reactions are thus different for these two metals. Equilibrium equations could not be confidently written for either reaction. An ion pair extraction should not be dependent on pH, but these certainly are. Acid interference in the organic phase, changing the physical properties of diluents and extractants, and in the aqueous phase where ionic strengths are complicated, causes the complexity in any understanding of the mechanism of the extraction. The anion concentration dependence is opposite for Ni(II) and Cu(II). Higher sulphate levels increase extraction levels for Cu(II) and decrease them for Ni(II). Reagent concentration dependence and metal loading capacities are consistent with a tris-bipyridine complex for Ni(II) and a bis-bipyridine (and mono- at low reagent concentration) complex for Cu(II). Anions or water may be incorporated into the Cu(II) complex.

Stripping of the metal from the organic complex solution requires different agents and conditions for each metal. Co(II) and Fe(II) are stripped by water, but Ni(II) and Cu(II) require ammonia and Ni(II) stripping is slower than its extractions.

A potential nickel-cobalt separation technique can be proposed from the stripping properties. Cobalt is stripped easily with water leaving the nickel complex in organic solution; however subsequent stripping of nickel is very slow. The difference in rates of extraction of nickel and cobalt from very dilute acid (0.1 M sulphuric acid) can be used to separate them, but nickel extraction is still slow, though complete, with the higher alkyl bipyridines from dilute acid.

Unfortunately, a commercial extractant for Ni(II) has not been found. The Ni-bipyridine complex's favourable high stability over Cu(II), Co(II), Fe(II) and Fe(III) complexes has been shown to make it a selective extractant for Ni(II) when the complex formation can occur in the aqueous phase, but the slow rate of extraction with the larger potential extractants precludes its use in commercial fields. Copper becomes the selected metal extracted by the higher alkyl bipyridines. This selective extraction of Cu(II) from acid sulphate solutions over a wide range of acidity is of particular importance. This property is of possible commercial interest in situations such as the treatment of bleed streams from copper tankhouses.

The alkyl bipyridine reagents can extract Ni(II), Co(II) and Cu(II) from iron solutions in acid.

The project has shown the value of research into design of an extraction reagent. Extraction properties and selectivity of a ligand can be related to its physico-chemical structure. Calculated changes to the molecule and conditions of extraction contribute to the design of completely new systems.

6. EXPERIMENTAL PROCEDURE

6.1. Measurement of Physical Properties

Details of the measurement of those physical properties used as criteria of structure and/or purity of the organic compounds synthesized are given below, together with details of the instruments used in various physical measurements and procedures in the solvent extraction tests.

Melting points of solid products were determined using samples in capillary tubes in a Gallenkamp electrically heated block melting point apparatus, type MF370. Melting points are uncorrected.

Infrared spectra were obtained using a Perkin Elmer Grating Infrared Spectrophotometer 577. The wavelength scale was calibrated to the strong absorption bands of a 0.05mm polystyrene film, at 3027, 1944 and 1601cm^{-1}. Samples for measurement were prepared in one of four ways:

a. Pure liquid sample thin film between 5mm sodium chloride discs,

b. Finely ground solid samples in a liquid paraffin mull between 5mm sodium chloride discs,

c. Finely ground solid sample incorporated into a pressed potassium bromide disc (prepared with a Specadie 3550 minipress),

d. Solution of the sample in chloroform or carbon tetrachloride in sodium chloride cells of various fixed path lengths.

Details of frequencies (ν) of absorptions in the infrared spectra of individual samples are listed in the text with the following qualifications in abbreviation: strong (s), medium (m), weak (w). Absorptions masked by the absorption by liquid paraffin are shown in brackets.

Nuclear Magnetic Resonance Spectra were obtained using a Varian EM 360 A 60MHz instrument. Most samples were dissolved in deuterochloroform containing tetramethylsilane as a reference for 0ppm. Details of NMR spectra of individual compounds are listed as a series of chemical shifts in ppm Gauss (δ). The splitting of each absorption is denoted as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). The ratios in brackets represent the integration ratios of the listed absorptions.

Visible-ultraviolet absorption data were obtained from a Unicam SP 800 Ultraviolet Spectrophotometer. A matched pair of 5mm quartz cells was used for all measurements. Water was used as a reference for aqueous solutions and the appropriate diluent for organic solutions.

Three chromatographic techniques were used to separate compounds in mixtures:

a. Gas-liquid chromatography was used analytically. A Pye Series 104 Katharometer Isothermal Chromatograph (Model 34) was the instrument in use. A 1.5m glass column with a packing of methyl silicone gum (E30) on a solid support medium, usually heated to 200°, was used for all bipyridine studies. The carrier gas was nitrogen.

b. Column chromatography was performed in a 20mm diameter, 40cm glass column fitted with a sintered glass disc and tap. The packing was Brockmann Grade 1 neutral alumina. The eluting solvents were used in the eleotropic series of increase in polarity from petroleum ether through to ethanol, to elute selectively each component of a mixture.

c. Small scale qualitative Thin Layer Chromatography plates were made by coating microscope slides with a thin layer of silica gel G (type 60) (Merck). Iodine vapour was used for spot development.

A Buchi Rotavapor R110 was used to evaporate large volumes of volatile solvent from solutions of organic compounds.

Metal ion concentrations in solution were measured by atomic absorption. A Perkin Elmer 306 Atomic Absorption Spectrophotometer or a Perkin Elmer 272 Atomic Absorption Spectrophotometer was used with Perkin Elmer Intensitron lamps. Standard conditions were used [165]. A Variable Diluter by Hook and Tucker Instruments Ltd was used for most dilutions of extraction solutions.

Solution pH values were measured using a Pye Unicam PW 9409 digital pH meter incorporating a Russell pH electrode, type CTW 72. Buffers used to calibrate the electrode were sodium/potassium dihydrogen phosphate for pH 7.00 (20^o) and 0.05M potassium tetroxalate for pH 1.68 (20^o).

Extraction mixtures were shaken on a Griffin flask shaker.

Microanalyses were performed by the Imperial College Chemistry Department Microanalytical Section.

All temperatures are given in degrees Centigrade.

6.2. Syntheses of Reagents

6.2.1. By Raney Nickel catalysed condensations

Raney Nickel Catalyst

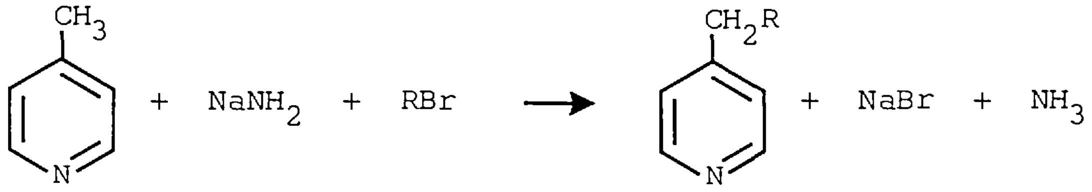
The method of Badger and Sasse [137], used to prepare W7-J Raney Nickel, was slightly modified for use in the preparation of a suitable catalyst to condense alkyl bipyridines to dialkyl bipyridines.

Nickel-aluminium alloy (50:50 Ni:Al, 177μ, supplied by Koch-Light) (37.5g) was carefully added in small portions, over 10 minutes, to a sodium hydroxide solution (48g /180ml H_2O) which was contained in a large vessel and was vigorously stirred to control frothing. The temperature increased rapidly. The mixture was then stirred for 6 hours at 100^o. After standing at room temperature overnight, the supernatant liquid was decanted and the finely dispersed nickel was washed by decantation with water (8 x 100ml). The wet catalyst was then transferred to a 3-necked flask fitted with a condenser (closed at the top with a stopper), a dropping funnel and a connection to a water pump (with a large volume (2 l) trap to allow for possible sudden releases of hydrogen from the reactive catalyst). The flask was slowly evacuated and warmed on a water bath, care being taken to avoid losses of catalyst by vigorous boiling. After being kept at $100^o/_{15\text{-}20mmHg}$ for 2 hours the catalyst was ready for use. The pyridine (or heterocyclic derivative) was added, via the dropping funnel, to the evacuated flask. (Care must be taken to avoid access of air until the catalyst has been thoroughly wetted.)

Preparation of Alkyl Pyridines

4-Methyl pyridine, 3-methyl pyridine, 3-ethyl-4-methyl pyridine and 4-(1,1-dimethylethyl) pyridine were obtained from commercial suppliers. Old samples were purified by refluxing over potassium hydroxide for 2 hours then fractional distillation.

4-Propyl pyridine, 4-butyl pyridine, 4-pentyl pyridine and 4-nonyl pyridine were prepared by the method proposed by Tschitschibabin [152] and developed by Knight and Shaw [153] and described by Bergstrom [154].



Finely ground sodamide (1.2 moles) was added to cold 4-methyl pyridine (1.0mol) in a 2-necked flask fitted with a dropping funnel and a calcium chloride guard tube. The mixture was stirred at 0° for 1 hour, in which time the liquid colour darkened to black. The appropriate alkyl bromide was added dropwise over 2 hours at 0° via the dropping funnel. (Heat was evolved.) The mixture lost most of its colour and a white precipitate formed before all of the alkyl bromide had been added. The mixture was stirred overnight to complete the reaction, then water was added carefully to dissolve remaining sodamide and the precipitated salts. Diethyl ether was added and the two phases were separated. The ether solution was washed with water, then the ether was evaporated. The residue was steam distilled to remove 4-methyl pyridine, then the remainder was distilled to give the alkyl pyridine. Each alkyl pyridine was redistilled before use.

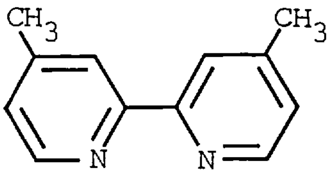
4-Propyl pyridine	b.p. $189^{o}/_{760\text{mm Hg}}$
4-Butyl pyridine	b.p. $208^{o}/_{760\text{mm Hg}}$
4-Pentyl pyridine	b.p. $110^{o}/_{15\text{mm Hg}}$
4-Nonyl pyridine	b.p. $160^{o}/_{15\text{mm Hg}}$

Dialkyl Bipyridines

This general procedure followed the degassed Raney Nickel preparation. Details for each case follow.

The alkyl pyridine (75ml) was admitted to the evacuated flask containing the Raney Nickel catalyst. When the catalyst was thoroughly wetted air was admitted and the mixture was then refluxed at atmospheric pressure or under reduced pressure (20mm Hg) for those with very high boiling points. The time of reflux varied from 4 to 60 hours, as listed below for individual cases. After the appropriate reflux time the mixture was cooled slightly then filtered with care as the catalyst is pyrophoric. The catalyst was washed several times with hot ethanol then stored under water. The combined filtrates were cooled and the crystals of dialkyl bipyridine that formed, in the case of solid products, were filtered off. The filtrates were reduced, precipitating more crystals, then the rest of the filtrate was distilled to reclaim unused alkyl pyridine. The distillation residue was chromatographed on alumina. The chromatographed product contained alkyl pyridine, the required dialkyl bipyridine, some tripyridines and some bipyridines from pyridine base impurities in the starting material alkyl pyridine. Small amounts of pyrroles and nickel complexes were separated in the purification processes. Crystalline dialkyl bipyridines were recrystallized from ethanol. Liquid products were fractionally distilled after the distillation of alkyl pyridine.

4,4'-Dimethyl-2,2'-bipyridine



M.W. 184

Colourless plates, m.p. 170.5 - 171° (lit. 171 - 172°)

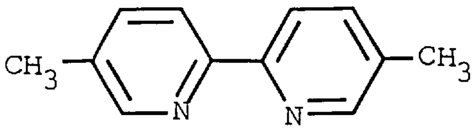
ν(cm^{-1})=(2930), 1590s, 1560w, 1550w, (1458,1367), 1250w, 990w, 827m.

δ(ppm)= 2.4s, 7.0d, 8.2s,8.5d, (3:1:1:1)

Preparation: 4-Methyl pyridine was refluxed at $145^{\circ}/_{760\mathrm{mmHg}}$ for 24 hours over degassed Raney Nickel.

Yield 20% based on pyridine.

5,5'-Dimethyl-2,2'-bipyridine



M.W. 184

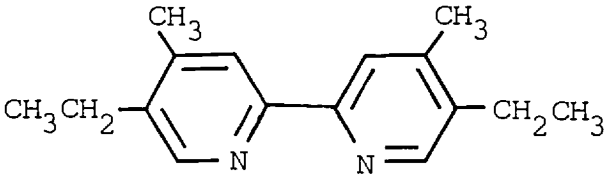
Colourless crystals, m.p. 112-3° (lit.[143] 114.5 - 115°)

ν(cm^{-1})=(2920), 1597w, 1550m, (1464, 1370), 1271, 1243w, 1220m, 1129m, 1155w, 1031m, 971w, 828s, 794w, 738s, 651m.

δ(ppm)= 2.3s, 7.5d, 8.1d, 8.4s, (3:1:1:1)

Preparation: 3-Methyl pyridine was refluxed over degassed Raney Nickel at $144^{o}/_{760mmHg}$ for 7 hours. A low yield was obtained. (3%).

5,5'- Diethyl -4,4'-dimethyl-2,2'-bipyridine



M.W. 240

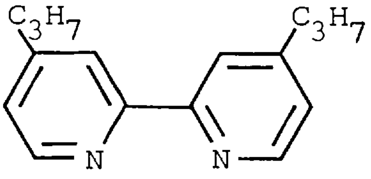
Colourless crystals, m.p. 142°

ν(cm^{-1})=(2930), 1592s, 1550m, (1464, 1370), 1346w, 1316m, 1059m, 951w, 888m, 850m.

δ(ppm)= 1.3t, 2.4s, 2.7q, 8.1s, 8.3s, (3:3:2:1:1)

Preparation: 3-Ethyl-4-methyl pyridine was refluxed at $198^{o}/_{760mmHg}$ for 4 hours over degassed Raney Nickel. A yield of 20g/75ml pyridine base was obtained. (27%).

4,4'-Dipropyl 2,2'-bipyridine



M.W. 240

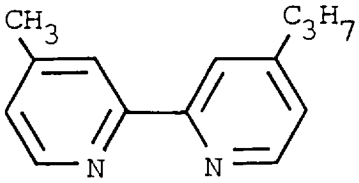
Yellow liquid, b.p. $\sim 210^{o}/_{15mmHg}$

ν(cm^{-1})= 2960m, 2930m, 2871m, 1593s, 1550m, 1459m, 1379m, 1109w, 990w, 819w.

Preparation: 4-Propyl pyridine was refluxed at $189^{o}/_{760mmHg}$ for 60 hours over degassed Raney Nickel. Crystals of 4,4'-

dimethyl-2,2'-bipyridine first separated from the filtrates. During the distillation of the filtrate under reduced pressure (20mm Hg), 4-methyl pyridine and 4-propyl pyridine distilled. Then 4,4'-dimethyl-2,2'-bipyridine precipitated in the condenser. (The methylated products formed due to contamination and decomposition of the 4-propyl pyridine.) The distillation was continued and a yellow liquid distilled. White crystals separated from this liquid on cooling and these were identified as 4-methyl-4'-propyl-2,2'-bipyridine. The yellow liquid was purified by passage through an alumina column and the product proved to be 4,4'-dipropyl-2,2'-bipyridine. Yield 18%.

4-Methyl-4'-propyl-2,2'-bipyridine



M.W. 212

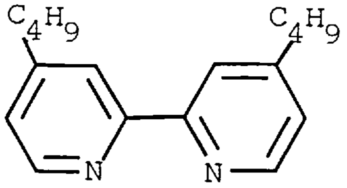
White crystals, m.p. 56-7^{o}

ν(cm^{-1})=(2930), 1592s, 1547m, (1460, 1375), 1113w, 990w, 840w, 828m, 818m.

δ(ppm)= 1.0t, 1.7m, 2.3s, 2.6t, 7.0d, 8.0s, 8.4s, (3:2:3:2:2:2:2)

Preparation: This product was a side product from the preparation of 4,4'-dipropyl-2,2'-bipyridine described above. Yield 15%.

4,4'-Dibutyl-2,2'-bipyridine



M.W. 244

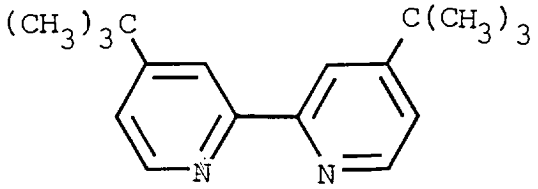
Yellow oil, b.p. $220^o/_{20mm\ Hg}$

ν(cm^{-1})= 2958s, 2928s, 2870s, 1592s, 1550s, 1460s, 1413w, 1379s, 1105w, 990m, 902w, 834s, 730m, 670w.

δ(ppm)= 1.5m, 2.6t, 7.0d, 8.1s, 8.5d, (7:2:1:1:1)

Preparation: 4-Butyl pyridine was refluxed at $208^o/_{760mmHg}$ for 45 hours over degassed Raney Nickel. The product was distilled from the filtrate, and was washed with 0.1M H_2SO_4 to remove 4-butyl pyridine which contaminated the distillate. Yield 20%.

4,4'-Di(1,1-dimethylethyl)-2,2'-bipyridine



M.W. 268

Pale blue needles and colourless plates, m.p. 158-9^o These appeared to be cis and trans forms as melting points, mixed melting points, NMR and IR spectra, thin layer chromatography plates for each were the same. A recrystallization gave homogeneous blue needles.

Analysis: C 80.63, H 9.16, N 10.43

C 80.55, H 9.01, N 10.44, calculated for $C_{18}H_{24}N_2$

ν(cm^{-1})=(2930), 1592s, 1583s,1543s,(1460, 1372), 1268m, 1201w, 1135m, 1113m, 1076w, 993w, 902m, 849m, 840s, 730m, 670m, 606m.

δ(ppm)= 1.4s, 7.3d, 8.3s, 8.6d, (9:1:1:1)

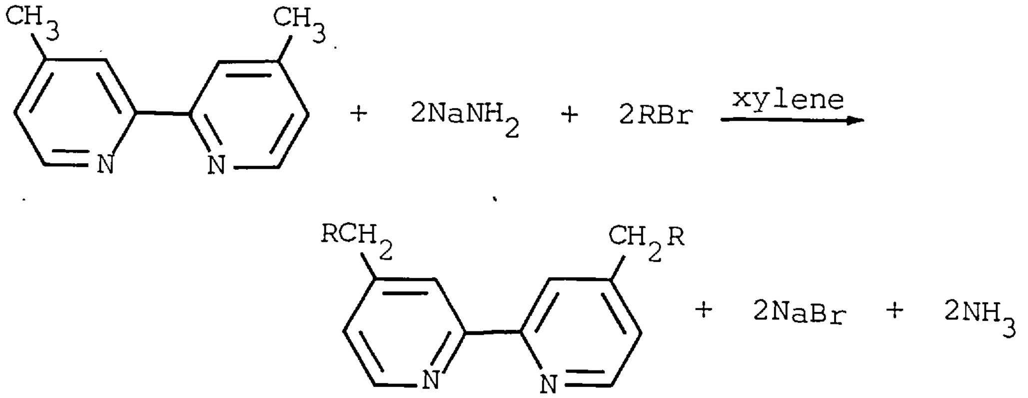
Preparation: 4-(1,1-dimethylethyl) pyridine was refluxed at $196^{\circ}/_{760mmHg}$ for 48 hours over degassed Raney Nickel. Yield 36%.

The Raney Nickel reaction was attempted with 4-pentyl pyridine (reflux at $221^{\circ}/_{760mmHg}$ for 60 hours and at $110^{\circ}/_{15mmHg}$ for 24 hours and 40 hours over degassed Raney Nickel) but no bipyridine product could be detected or isolated. Similarly 4-nonyl pyridine was refluxed at $160^{\circ}/_{15mmHg}$ for 24 hours and heated at $160^{\circ}/_{760mmHg}$ for 48 hours, but no bipyridine was formed.

6.2.2. By Tschitschibabin Method

A modified form of the Tschitschibabin [152] method of adding alkyl chains to a methyl group on pyridine via a sodamide metallation of the methyl group was used to prepare the longer chain dialkyl bipyridines from 4,4'-dimethyl-2,2'-bipyridine. Xylene proved to be a good solvent for the dissolution of 4,4'-dimethyl-2,2'-bipyridine for contact with solid sodamide.

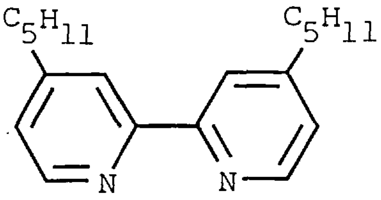
The reaction proceeds thus:



4,4'-Dimethyl-2,2'-bipyridine (9.2g, 0.05mol) was dissolved in hot xylene (20ml) and ground sodamide (6.0g, 0.13mol) was added slowly. The mixture was stirred at 100° for 1 hour in which time the solution went black. The appropriate alkyl bromide (0.1mol) was added dropwise over 2 hours with constant stirring and the temperature maintained at 100°. The mixture lost most of its colour and a white precipitate formed before the addition of the last of the alkyl bromide. It was stirred at 100° for a further 2 hours, then water was added carefully to decompose any remaining sodamide and the precipitated salts. The xylene layer was separated from the aqueous phase and washed with water. The xylene and remaining alkyl bromide were distilled off and then the residue was steam distilled to remove the last traces of xylene. Petroleum ether (b.p. 60 -80°) was added to the residue and the petroleum ether solution cooled to precipitate residual starting material, 4,4'-dimethyl-2,2'-bipyridine. The filtrate contained the higher dialkyl bipyridine as the major product. Some mono-substituted and more highly substituted products could be separated by acid washing, distillation and column chromatography. The final product was distilled under reduced pressure (0.1mm Hg) but was usually still slightly contaminated by more highly substituted bipyridines.

The following 4,4'-dialkyl-2,2'-bipyridines were prepared by this general method. Relevant details have been added.

4,4'-Dipentyl-2,2'-bipyridine



M.W. 296

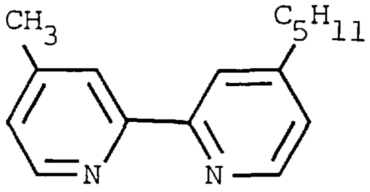
Yellow oil, b.p. $160^{o}/_{1mmHg}$

$\nu(cm^{-1})$= 2955s, 2927s, 2859s, 1593s, 1550m, 1457s, 1377m, 990w, 900w, 823m.

δ(ppm)= 1.3m, 2.6t, 7.0d, 8.2s, 8.5d, (9:2:1:1:1)

1-Bromo butane, b.p. 101^{o}, used in this preparation was obtained commercially. An efficient condenser was fitted to the reaction vessel to allow for its reflux at the reaction temperature. Yield 50% based on 4,4'-dimethyl-2,2'-bipyridine.

4-Methyl-4'-pentyl-2,2'-bipyridine



M.W. 240

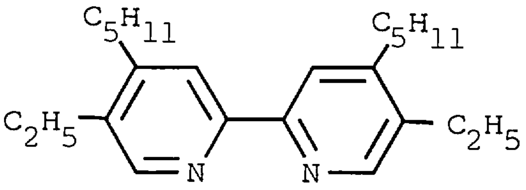
Orange oil, b.p.~$140^{o}/_{1mmHg}$

$\nu(cm^{-1})$= 2956s, 2930s, 2857s, 1594s, 1550s, 1460s, 1375s, 1108w, 990m, 900w, 822s, 710m, 670w.

δ(ppm)= 1.4m, 2.4s, 2.7t, 7.0d, 8.2s, 8.5d, (9:3:2:2:2:2)

This compound was a side product in the preparation of 4,4'-dipentyl-2,2'-bipyridine. It was isolated from the major product in an acid wash (0.5M H_2SO_4) of the crude product. The acid soluble fraction was treated with solid sodium hydroxide and the base which separated was taken up in petroleum ether, washed with water and proved to be pure 4-methyl-4'-pentyl-2,2'-bipyridine. Yield 20%.

5,5'-Diethyl-4,4'-dipentyl-2,2'-bipyridine



M.W. 352

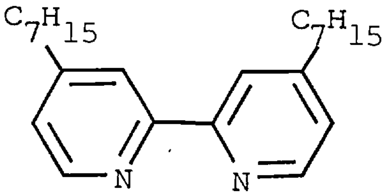
Orange oil,

$\nu(cm^{-1})$= 2960s, 2930s, 2870s, 1591s, 1543m, 1466s,1373w, 1343w, 1315w, 1057w, 889m, 849w.

δ(ppm)= 1.3m, 2.7q, 8.2s, 8.4s, (14:2:1:1)

This product was prepared from the reaction of 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine with sodamide and 1-bromo-butane. The yield was low (10%). It was purified by passage through an alumina column.

4,4'-Diheptyl-2,2'-bipyridine



M.W. 352

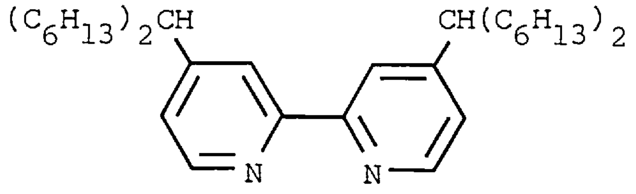
Orange oil, b.p. $170^{0}/_{\sim 1\,mmHg}$

$\nu(cm^{-1})$= 2952s, 2926s, 2855s, 1595s, 1554m, 1459m, 1375m, 990w, 824m,

δ(ppm)= 1.3m, 2.5t, 7.0d, 8.2s, 8.5d, (13:2:1:1:1)

1-Bromo hexane, b.p. $155^{o}/_{760mmHg}$, was the alkylating agent used. The product was insoluble in petroleum ether so the crude product was dissolved in chloroform for the acid washes. It was purified by passage through an alumina column. Yield 30%.

4,4'-Di(1-hexylheptyl)-2,2'-bipyridine



M.W. 510

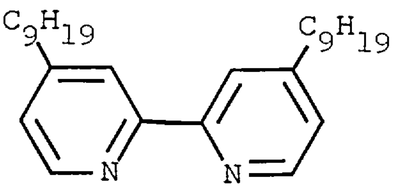
Orange oil, b.p. $>250^{o}/_{1mmHg}$

ν(cm^{-1})= 2952s, 2925s, 2852s, 1592s, 1550m, 1460m, 1375m, 990w, 825m.

δ(ppm)= 1.3m, 7.0d, 8.2s, 8.5d, (~30:1:1:1)

A small amount of this product was isolated from the petroleum ether soluble fraction in the 4,4'-diheptyl-2,2'-bipyridine preparation. It is probably a mixture of the triple and quatro substituted products. Yield 30%.

4,4'-Dinonyl-2,2'-bipyridine



M.W. 408

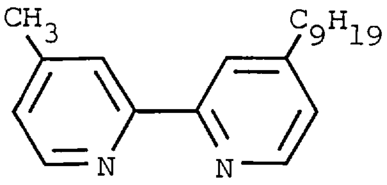
Brown oil, b.p. $236^{o}/_{15mmHg}$

ν(cm^{-1})= 2955s, 2921s, 2855s, 1591s, 1550m, 1458s, 1376m, 990w, 903w, 836m, 720w.

δ(ppm)= 0.9m, 1.2m, 2.6t, 7.1d, 8.3s, 8.6d, (3:14:2:1:1:1)

1-Bromo octane was used as the alkylating agent. The product was isolated by distillation and column chromatography. Yield 30%.

4-Methyl-4'-nonyl-2,2'-bipyridine



M.W. 296

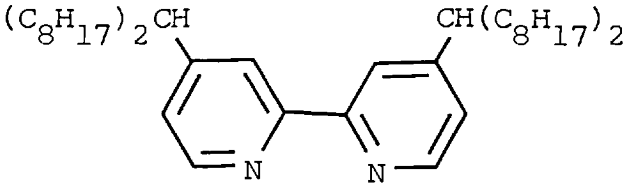
White wax, picrate m.p. 70° (picrate of 4,4'-dimethyl-2,2'-bipyridine m.p.= 138°).

ν(cm^{-1})= 3025w, 2950s, 2921s, 2852s, 1592s, 1550m, 1457s, 1374m, 1106w, 990w, 850w, 822m, 720w, 670w.

δ(ppm)= 0.8m, 1.2m, 2.4s, 2.6t, 7.0d, 8.2s, 8.5d, (3:14:3:2:2:2:2)

This product was a side product in the preparation of 4,4'-dinonyl-2,2'-bipyridine. It was isolated by column chromatography.

4,4'-Di(1-octylnonyl)-2,2'-bipyridine



M.W. 632

Brown oil, b.p. >250°/1 mmHg

ν(cm^{-1})= 2952s, 2921s, 2853s, 1591s, 1550m, 1457s, 1385m, 990w, 903w, 835m, 720w.

δ(ppm)= 1.3m, 7.1d, 8.2s, 8.5d, (~35:1:1:1)

This product was obtained from the distillation residue in the isolation of 4,4'-dinonyl-2,2'-bipyridine. The residue was passed through an alumina column to give the triple and quatro substituted products. Yield 30%.

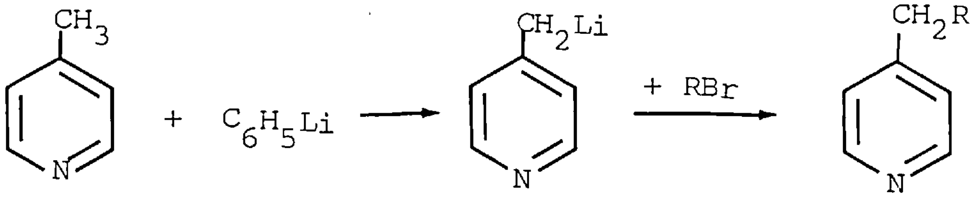
6.2.3. Via Organolithium Reagents

Organolithium reagents such as phenyl lithium and methyl lithium have been reported to metallate the methyl group of a methyl pyridine molecule in the same way that sodamide does [158,160,161]. This method was used here to attempt to alkylate the methyl groups of 4,4'-dimethyl-2,2'-bipyridine. However, in each reaction, substitution by phenyl or methyl occurred in the 6 and/or 6' positions as well as, or instead of, alkylation at the methyl groups.

a. Reaction of 4,4'-dimethyl-2,2'-bipyridine with phenyl lithium and 1-bromo octane

The method of Wibaut and Hey [160] was followed using 4,4'-dimethyl-2,2'-bipyridine as the pyridine base and 1-bromo octane as the alkylating agent.

$$C_6H_5Br \quad + \quad Li \quad \xrightarrow{\text{ether}} \quad C_6H_5Li$$



Phenyl lithium was prepared by adding bromobenzene (3.14g,0.02mol) dropwise to a stirred mixture of finely cut pieces of lithium (0.28g,0.04mol) in diethyl ether (15ml) at such a rate that the ether refluxed gently. The mixture was refluxed for 1 hour in which time most of the lithium had dissolved. The solution was then transferred to a dropping funnel and added slowly to a stirred mixture of 4,4'-dimethyl-2,2'-bipyridine (1.84g,0.01mol) in ether (10ml). (The bipyridine was not all dissolved.) The resulting deep red mixture was stirred for a further 30 minutes at room temperature. 1-Bromo octane (3.86g,0.02mol) was added dropwise over 10 minutes and the mixture was stirred for 3 hours. The colour of the mixture went through blue to green-yellow. 1,2-Dichloroethane was added to the ether solution to dissolve the 4,4'-dimethyl-2,2'-bipyridine remaining. Water was added and then the aqueous phase was discarded. Hydrochloric acid (38%) was shaken with the organic solution to form and separate the short chain alkyl bipyridine hydrochlorides. (The longer chain alkyl bipyridines do not form acid soluble hydrochlorides.) The acid soluble fraction, after treatment with sodium hydroxide, produced white crystals of 4,4'-dimethyl-6-phenyl-2,2'-bipyridine, m.p. 130^{o}.

ν(cm^{-1})= (2925), 1597s, 1550m, (1455, 1374), 1255w, 1213w, 1077w, 1029w, 990w, 870m, 825m, 792w, 776m, 734w, 690m.

δ(ppm)= 2.5s, 7.1m, 7.5m, 8.1m, 8.5m, (6:1:5:2:2)

The acid insoluble fraction consisted of various substitution products, with phenyl substitution in the 6-position and alkylation at the 4- and/or 4'-positions, i.e. 4-methyl-4'-nonyl-6(or 6')-phenyl-2,2'-bipyridine and

4,4'-dinonyl-6-phenyl-2,2'-bipyridine. NMR showed that only one ring was phenyl substituted.

b. Reaction of 4,4'-dimethyl-2,2'-bipyridine with methyl lithium and 1-bromo octane

It has been reported [158] that methyl lithium does not substitute into the pyridine ring as phenyl lithium does, but only onto the acidic methyl group of the methyl pyridines. The previous reaction was repeated using methyl lithium prepared from methyl iodide and lithium in ether, instead of phenyl lithium. Very little product was isolated and NMR suggested that the starting material was only partially alkylated, with one octyl chain and methyl substitution in the ring. The product was unstable in air.

c. Reaction of 4,4'-dimethyl-2,2'-bipyridine with methyl lithium and 1-bromo octane in tetrahydrofuran

Tetrahydrofuran is known to promote anion formation and 4,4'-dimethyl-2,2'-bipyridine is more soluble in this solvent so the previous reactions were repeated in tetrahydrofuran. Methyl lithium cannot be prepared from methyl iodide in tetrahydrofuran as the solvent promotes a coupling reaction in methyl iodide [166]. Methyl lithium was therefore prepared in ether and added to 4,4'-dimethyl-2,2'-bipyridine in tetrahydrofuran. Again there was a colour reaction but very little product could be isolated.

6.2.4. By the Ullmann Reaction

The coupling of two pyridine rings to form a bipyridine can be effected by an application of the Ullmann reaction, which involves treatment of a bromo pyridine with copper powder [167].

$$2\ ArX + Cu \longrightarrow Ar\text{-}Ar + CuX_2$$

Two other references [168,169] suggested the use of dimethylformamide, tetralin, decalin, pseudo-cumene, decane or diphenyl as solvents for the reaction.

The Ullmann reaction requires a bromo aryl base. 4-Alkyl-2-bromo-pyridines can be prepared by the diazotization of the 4-alkyl-2-amino-pyridine by the Craig method [170]. Case [145], Case and Kasper [171] and Solomon [172] have described the bromination of 4-methyl-, 4-ethyl- and 4-propyl-pyridine. Their methods have been followed to prepare 2-bromo-4-pentylpyridine.

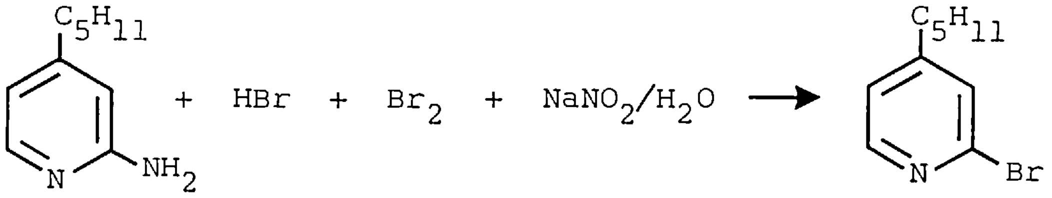
2-Amino-4-pentyl pyridine [172,173]

Finely ground sodamide (4.8g,0.12mol) was added to 4-pentyl pyridine (14.9g,0.1mol) in dry xylene (15ml). The stirred mixture was heated to 100°. Hydrogen, ammonia and heat were evolved. The reaction temperature was maintained at 115° for 10 hours at the end of which time, very little hydrogen was being evolved. The mixture was cooled, diethyl ether was added, then it was poured onto ice. The liquid was acidified with hydrochloric acid and the ethereal layer re-extracted with acid. The combined acid extracts were made alkaline with sodium hydroxide and the precipitated base was taken into diethyl ether. Distillation gave unreacted 4-pentyl pyridine, then 2-amino-4-pentyl pyridine crystallized in the condenser (b.p. $160^{o}/_{25mmHg}$).

$\nu(cm^{-1})$= 3420s, 3294m, 3150m, 1910w, 1620s, 1545s, 1490m, 1450s, 1373m, 1303m, 1270w, 1173w, 997m, 866m, 790m.

δ(ppm)= 1.3m, 2.4t, 4.4s, 6.2s, 6.4d, 7.8d, (9:2:2:1:1:1)

2-Bromo-4-pentyl pyridine



To a solution of 2-amino-4-pentyl pyridine (2.6g,0.016mol) in 48% hydrobromic acid (10ml), cooled to -17° and stirred, bromine (3ml,0.06mol), previously cooled to 0°, was added dropwise over 10 minutes. A red, oily mixture resulted but became more uniform with stirring. A solution of sodium nitrite (3.3g,0.05mol) in water (5ml) at 0°, was then added slowly. The mixture was stirred for 1 hour, with the temperature kept below 0°. The mixture was made alkaline with ice-cold 25% sodium hydroxide solution (20ml), added slowly to keep the temperature below 20°. The mixture went red, then yellow and an oil separated. The oil was extracted into diethyl ether. The ether solution was washed with water, dried, and the ether was evaporated to leave 2-bromo-4-pentyl pyridine.

$\nu(cm^{-1})$= 2955s, 2926s, 2859s, 1587s, 1536m, 1460s, 1379s, 1215w, 1121m, 1079s, 988m, 855w, 823w, 731w, 702m.

δ(ppm)= 1.4m, 2.6t, 7.0d, 7.2s, 8.2d, (9:2:1:1:1)

Attempted condensation of two 2-bromo-4-pentyl pyridine molecules by the Ullmann reaction

Dimethylformamide (7ml) and copper powder (1.92g,0.03mol) were heated to reflux. 2-Bromo-4-pentyl pyridine (3g,0.012mol) was added dropwise over 30 minutes then the mixture was refluxed for 2 hours (in which time it went black) then cooled. Dimethylformamide was distilled then the distillation residue was washed well with water. Concentrated sodium hydroxide solution was added to hydrolyse the copper complex and organic materials were extracted into chloroform. The black chloroform solution was passed through an alumina column but no bipyridine product could be detected or isolated. The small scale and impurity of the intermediates may have been the cause of the failure of this reaction.

6.2.5. Oxidation Products of Bipyridines and Pyridines

An attempt was made to synthesize a carboxylated bipyridine.

Oxidation of 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine

The procedure for the oxidation of 4-methyl pyridine to 4-pyridine carboxylic acid by potassium permanganate was followed [174,175].

Potassium permanganate (3.3g,0.02mol) was added to 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine (2.4g,0.01mol) in water (25ml). The mixture was refluxed until the permanganate colour had disappeared. Another portion of potassium permanganate (3.3g, total 0.04mol) in water (10ml) was added and the mixture refluxed until the colour had disappeared again. The mixture was filtered and the filtrate was acidified with hydrochloric acid and left overnight. A small amount of yellow product precipitated. This was a carboxylic acid. The filtered solids contained a lot of unreacted 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine, so the whole procedure of addition of potassium permanganate until the colour disappeared (0.09 moles in total) was repeated on this reclaimed starting material. This mixture was filtered and still a little 5,5'-diethyl-4,4'-dimethyl-2,2'-bipyridine was reclaimed. (Thus the reaction had used over 8 moles of permanganate to 1 mole of bipyridine.) The filtrate was reduced and acidified to pH 2. A precipitate, highly contaminated with potassium chloride, formed. Its high water solubility and the stoichiometric amount of potassium permanganate used suggested that this impure product was 2,2'-bipyridine-4,4',5,5'-quatro carboxylic acid.

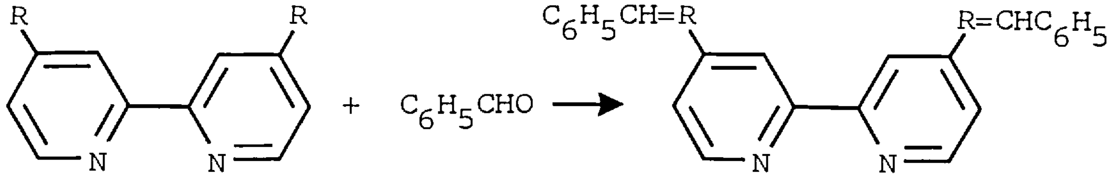
Oxidation of 3-ethyl-4-methyl pyridine

Potassium permanganate (6.6g, 0.04mol) was added to 3-ethyl-4-methyl pyridine (2.4g, 0.02mol) in water (50ml) and the mixture was refluxed until all permanganate colour had disappeared (1 hour). Manganese dioxide was filtered off. The filtrate was steam distilled to remove remaining 3-ethyl-4-methyl pyridine. The residue was reduced (15ml), hydrochloric acid was added to make the pH 2 and the solution was left to stand overnight. The precipitate that formed was contaminated with potassium chloride which was then washed from the product with water. The only product was pyridine-

3,4-dicarboxylic acid, m.p. 260° (lit. 260°). Both the 3 and 4 positions had been oxidized.

6.2.6. Condensation of bipyridines and pyridines with aldehydes

Sasse and Whittle [143] used the Stanek and Horak method[162] to condense substituted bipyridines with benzaldehyde.



This method was used here to make 5,5'-diethyl-4,4'-di(2-phenylethenyl)-2,2'-bipyridine and 4,4'-di(2-phenylethenyl)-2,2'-bipyridine.

5,5'-Diethyl-4,4'-di(2-phenylethenyl)-2,2'-bipyridine

5,5'-Diethyl-4,4'-dimethyl-2,2'-bipyridine (2.5g,0.01mol), benzaldehyde (3.0g,0.03mol), acetic anhydride (2.0g, 0.02mol) potassium acetate (2.0g,0.02mol) and a crystal of iodine were refluxed together for 30 hours. Water was added and the mixture was steam distilled to remove unreacted benzaldehyde. Water and chloroform were added to the residue, the mixture was shaken and then the phases were separated. The organic phase was reduced in volume and a white solid separated from the brown tarry residue. Ethanol was added and the white solid was filtered off, washed and recrystallized from ethanol/chloroform. This was 5,5'-diethyl-4,4'-di(2-phenylethenyl)-2,2'-bipyridine, m.p. 177° (lit. 182°).

4,4'-Di(2-phenylethenyl)-2,2'-bipyridine

This compound was prepared in the same way as the previous one, from 4,4'-dimethyl-2,2'-bipyridine. The mixture was refluxed for 70 hours, and on cooling a white solid precipitated from the reaction mixture. It was washed with chloroform, water and acetone, but was found to be insoluble in all common solvents, therefore it could not be recrystallized. The product is 4,4'-di(2-phenylethenyl)-2,2'-bipyridine, m.p. 265^{o} (lit. 268.5 - 269.5^{o}).

Reaction of 4,4'-dimethyl-2,2'-bipyridine with an aliphatic aldehyde

The preceding reaction was repeated using an aliphatic aldehyde, 2-ethyl-butyraldehyde.

4,4'-Dimethyl-2,2'-bipyridine (1.84g,0.01mol), 2-ethyl-butyraldehyde (3.0g,0.03mol), acetic anhydride (2.0g, 0.02mol), potassium acetate (2.0g,0.02mol) and a crystal of iodine were refluxed together for 50 hours. 4,4'-Dimethyl-2,2'-bipyridine (1.5g) was recovered and no condensation products could be detected.

Reaction of 4-methyl pyridine with an aliphatic aldehyde

There are references [176-8] to the reaction of methyl pyridines with aromatic aldehydes in acetic anhydride and piperidine. The reaction was tried here with an aliphatic aldehyde, 2-ethyl butyraldehyde.

4-Methyl pyridine (9.3g,0.1mol), 2-ethyl butyraldehyde (10.0g,0.1mol), piperidine (1ml) and acetic anhydride (50ml) were refluxed together for 24 hours. The solution went black after 30 minutes. The mixture was distilled and the fraction boiling over 145° (the boiling point of 4-methyl pyridine) was collected. There was still contamination by other reactants in this fraction and no condensation product could be isolated.

6.2.7. Reactions of 4,4'-dimethyl-2,2'-bipyridine-1,1'-dioxide

4,4'-Dimethyl-2,2'-bipyridine-1,1'-dioxide

The method of Jojo Haginiwa [149] and Maerker and Case [150] was used to prepare the N,N-dioxide from the bipyridine.

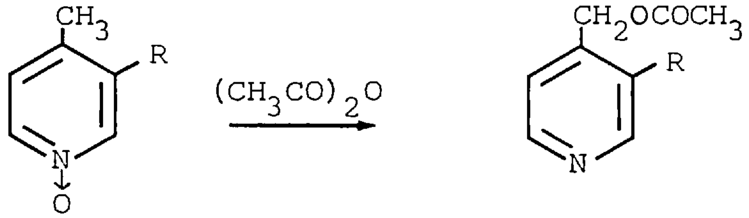
4,4'-Dimethyl-2,2'-bipyridine (5.5g,0.03mol) in glacial acetic acid (25ml) was heated to 70 - 80°. 30% Hydrogen peroxide (5ml) was added initially and another portion of hydrogen peroxide (5ml) was added after 4 hours. The reaction mixture was heated for a total of 8 hours. The mixture was made alkaline with potassium hydroxide and the N,N-dioxide precipitated. It was washed with a little aqueous ammonia. The mother liquor and washings were reduced in volume to near dryness and extracted with hot chloroform. The small aqueous fraction was separated from the organic by filtration through phase separatory paper and the dioxide was reprecipitated by addition of diethyl ether to the chloroform solution.

Reaction of 4,4'-dimethyl-2,2'-bipyridine-1,1'-dioxide with sodamide and 1-bromo octane

Finely ground sodamide (1.0g,0.03mol) was added to a solution of 4,4'-dimethyl-2,2'-bipyridine-1,1'-dioxide (2.16g, 0.01mol) in chloroform (5ml) and stirred for 2 hours at 20°. There was no visible change in the mixture. 1-Bromo octane (3.86g, 0.02mol) was added dropwise over 1 hour, and the reaction mixture was stirred overnight. The mixture went slightly brown. Water was added carefully and the two phases were separated. The organic phase produced only starting materials on addition of diethyl ether and distillation. The aqueous phase was evaporated to near dryness and then extracted with hot chloroform. When treated with diethyl ether, this produced starting material only.

Reaction of 4,4'-dimethyl-2,2'-bipyridine-1,1'-dioxide with acetic anhydride

Many methyl pyridine N-oxides can be reacted with acetic anhydride to produce acetates [163,164].



The esterification of 4,4'-dimethyl-2,2'-bipyridine was attempted by this method.

4,4'-Dimethyl-2,2'-bipyridine-1,1'-dioxide (1.08g, 0.005mol) was heated with acetic anhydride (10ml). Heat was evolved and the N-oxide dissolved. The solution was refluxed for 4 hours. Acetic anhydride was removed by distillation. Some of the residue dissolved in diethyl ether and water, but there was some material which was insoluble in both phases. The ether fraction gave a red colour reaction to ferrous ions, so it was supposed that a bipyridine was present. The ether fraction was washed with potassium carbonate, then water, to remove acetic acid and any N-oxide remaining. A small amount of product was consistent with the diacetate of 4,4'-dimethyl-2,2'-bipyridine structure.

6.3. Solvent Extraction Tests

Aqueous Solutions

Standard metal salt solutions were made up from commercial Analar compounds, in distilled water or the appropriate acid. Perchlorate, chloride and sulphate salts of the various transition metals whose complexes were under investigation were used to make up the solutions where the participation of those particular anions in the extraction was being questioned. When higher anion concentrations than those supplied by the metal salt were required, the background sodium anion salt was used. The appropriate acid, perchloric, hydrochloric or sulphuric, was used relevant to the anion in use for the test. Thus for studies of nickel solutions in sulphate medium, nickel sulphate in sulphuric acid and in some cases sodium sulphate background, was used, its metal concentration being defined by the concentration of nickel required in ppm.

Organic Solutions

Most tests were done using a solution of alkyl bipyridine of known concentration in 1,2-dichloroethane. Other diluents were used as detailed.

Extraction Tests

For each test, equal volumes (2, 5 or 10 ml) of aqueous and organic solutions were shaken together under the same conditions, for standard times in kinetic studies or for set times where the time taken to reach equilibrium was known, for equilibrated distributions. Two minutes were allowed for phase separation in kinetic studies and a longer time for equilibrated mixtures. Aliquots of the aqueous phase were then taken for pH measurement and dilution and determination of metal concentration by atomic absorption measurements. The metal distribution was determined by comparing the metal concentration in a sample of the initial aqueous solution with the metal concentration in the aqueous phase after extraction (both suitably diluted before atomic absorption measurement). The organic metal concentration was obtained by the difference between these values.

Stripping

Equal volumes of the metal complex loaded organic solution and the aqueous stripping agent (H_2O, 8M NH_3, 1M NaOH etc.) were shaken together for 1 hour or as detailed. After phase separation organic and aqueous phase samples were diluted with ethanol or water respectively for measurement of metal concentration by atomic absorption, against standard solutions.

Bulk reduced organic residues containing free reagent and metal complexed reagent were stripped of metal by five contacts with large volumes of ammonia solution for 8 hours each. The organic solution was then washed with water, dried over sodium sulphate, filtered and the solvent evaporated to leave pure bipyridine reagent. Its purity was checked by gas liquid chromatography comparing it to the freshly prepared reagent.

7. REFERENCES

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