To my Mother, Brother

and

memory of my Father

GEOCHEMICAL ASPECTS OF
WASTE DISPOSAL

A thesis submitted for the degree of

Doctor of Philosophy

by

Parisa Monsef-Mirzai

at

The University of Aston in Birmingham

September 1980

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Summary

The work began with an investigation of methods of determination of phenol in solution and was extended to investigate ways of rendering phenol harmless using chemical means applicable to conditions encountered at a waste disposal site. In addition the possibility of finding a catalyst which may promote chemical reactions of phenol to afford less environmentally problematic compounds was investigated. Attention was devoted to catalysts which may be supported on clays, such as montmorillonite and decompose phenol. Hence certain copper(II) complexes which could catalyse ring opening reactions of phenols under homogenous conditions were considered. The preparation of these copper(II) complexes and their characterisation are reported in this work. Phase-transfer catalysis is used to convert phenols to ethers in the presence of montmorillonite. Extension of this method to other systems of chemical interest are described.

The interaction of different copper(II) compounds with montmorillonite was studied by means of electron spin resonance spectroscopy and X-ray powder diffraction. A significant effect was observed on the exchange-absorption of the copper(II) ions by clay with different anions. The results indicate that some of the metal taken up by the clay is very labile and could well be remobilised by aqueous media. Also the influence of a high concentration of anion showed that the complex formation between the anion and metal, can result in a lower absorption of the metal from solution.

Electron spin resonance and Mössbauer spectroscopies were used to investigate the nature of kaolinite. The results indicate some iron surface contamination and ferric ion substiution for aluminium in the octahedral layer. An investigation of cation exchange on kaolinite surface was carried out using electron spin resonance spectroscopy as the major analytical tool. Two distinct exchange sites were identified.

Key Words :

Montmorillonite
Phase-transfer catalysis
Kaolinite
Waste-disposal

The work described in this thesis was carried out between 1976 and 1979 at the University of Aston in Birmingham. It has been carried out independently and has not been submitted for any other degree.

Monsef

Parisa Monsef-Mirzai

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In this thesis SI units have been used unless convention decreed otherwise. Appropriate conversion factors are :

	SI	
1 Å	100 pm	
1 Gauss	10^{-4} Tesla	
meq. $100g^{-1}$	$\frac{\text{mmol.}}{10n}\ \text{kg}^{-1}$	(n is charge on cation)

CHAPTER ONE

GENERAL INTRODUCTION

1.1 Background

During the last century it was recognized that chemical or bacterial impurities in water were a major cause of sickness and epidemics. For a short time water requirements could be developed within the immediate vicinity of the user but as demand increased it was found that a sufficient quantity could not be obtained in all locations. The need for water supply schemes became necessary but plans commonly conficted with building schemes of many different kinds.

To meet the increasing demand with good quality drinking water the available supplies have to be protected from impurities of every kind.

1.2 Groundwater Pollution [1,2]

More than 170 documented case histories of groundwater contamination or pollution were studied to develop an understanding of the status of groundwater pollution research. The case histories indicate that once groundwater is contaminated, remedial action is both time consuming and expensive, therefore protection of groundwater from contamination is essential. For this reason, extensive research in recent years has focussed on the movement and attenuation of contaminants in various hydrogeologic settings.

We have come a long way in understanding the behaviour of contaminants in the subsurface, and in understanding the suitability of waste disposal in various geologic environments. We now have a basis for preparing guidelines that will protect groundwater from the effects of waste disposal activities.

Contaminants may reach groundwater from a variety of sources. Some wastes may reach the subsurface; examples include septic systems, spray irrigation, and land disposal of sludge. Other wastes may reach groundwater unintentionally. Wastes may migrate to groundwater from impoundments, landfills, animal feedlots, leaky sewer lines, and other sources. Not only wastes may affect groundwater, for petroleum products may enter the groundwater flow system from a leak in a pipeline or storage tank.

Over the past three years, 173 case histories of subsurface contamination or pollution were studied. It has been suggested that the extent of groundwater contamination is determined by(1) the hydrogeologic setting,(2) the nature of the contaminant, and(3) the effectiveness of regulatory action.

The most common category of contaminant was industrial wastes. This category includes a wide variety of wastes from all types of industries, such as acids, various solvents, and plating wastes. Most, but not all, of the groundwater contaminants reported were waste products. Various chemicals were discharged to the subsurface from accidental spills. Industrial wastes reach groundwater from impoundments or lagoons, spills, pipeline breaks, land disposal of wastes, and improper disposal.

Landfill leachate was the second most common contaminant. About 15 percent of the landfills that were studied produced well pollution, this apparently suggests that landfills are a less serious hazard than other sources of contamination, but the proximity of sites to wells is an important factor. Many of the case studies were research investigations concerned with the migration of leachate from landfills. In most cases the extent of groundwater contamination was limited to the site itself or to a small area adjacent to it. The geological materials have generally been able to attenuate the contaminants particularly if a zone of unsaturated rock is beneath the site or if leachate concentrations are reduced by dilution in the groundwater flow system.

Sites on rocks which are fine-grained and homogenous appear to be the most suitable for landfill siting. Clay minerals limit the rate of leachate migration and remove some chemical constituents by cation exchange, thereby providing a natural renovation of the leachate. Cations in solution replace calcium and magnesium on the clay structure and increase their concentration in the leachate.[1]

Most contaminants are detected some time after entering the subsurface. Weeks, months, or years may pass before a problem is noticed. The contaminant may travel a great distance and may affect a large portion of an aquifer before pollution is recognized. Even if the source is identified and removed, and no further contaminants enter the groundwater flow system, contaminants can continue to adversely affect groundwater for a long time.

Groundwater pollution may lead to problems of inconvenience, such as taste, odour, colour, hardness, or foaming, but some cases are far more serious when pathogenic organisms, flammable or explosive substances or toxic chemicals or their products are concerned, particularly when long-term health effects are unknown.

The best way to minimize groundwater contamination is to prevent it. Therefore, the regulation of waste disposal to protect groundwater is especially important. To effectively regulate potential sources of contamination, we must understand the behaviour of contaminants in the subsurface.

Groundwater contamination or pollution can be reduced, but can not be totally eliminated. Accidental spills and unlawful dumping will continue. Because of the impossibility of monitoring all pipelines and storage facilities of the oil industry, petroleum products will continue to be a significant source of groundwater contamination.

Increased land disposal of wastes will require effective regulation to minimize enviromental degradation.

Finally it has been pointed out once polluted, an aquifer may remain in an unusable or even hazardous condition for decades or even centuries.

1.3 Domestic and Industrial Wastes [3,4]

Solid wastes differ from air and water pollutants, because they remain at the point of origin when a decision is made to dispose of them. The disposal problem, thus, is one of the most economic means that is consistent with plant operations and government regulations. The problem is clearly related to the amount of industrial and domestic wastes which will continue to be generated, the composition of the waste, the location and hydrogeological setting of the sites, and the degree of control employed during site operation.

Industry is a relatively small contributor to the nation's solid waste burden (about 6% of the total), but still generates over 500,000 kilo.day^{-1}. Of this roughly one third comes from the chemical process industries in the form of off-specification products, unsalable byproducts, tank bottoms, filter cakes, spent catalysts, and wastes from plant upsets and spills. Many of them are hazardous and include tar residues, organic solvents, alcohol wastes, chlorinated hydrocarbons, cyanide wastes, plating acids, and toxic metals. Beyond knowledge of the main toxic contaminants, the exact composition of wastes is rarely known and wastes from several processes are commonly mixed for transportation.

1.4 Treatment of Wastes before Disposal[5]

Primary conditioning is a factor often overlooked in waste handling. For example specific chemicals may be recovered by processes such as stripping, distillation, sorption, extraction. Solids such as metals, glass and plastics can be removed by hand picking, magnets and jigging. Sizing by crushing, grinding or pulverizing, and in some instances pelletizing, makes some solid wastes easier to handle. Generally, size reduction eliminates incineration problems, and is necessary for composting. It is also generally the first step in physical separations.

Mixing and blending make wastes more uniform, and in some instances neutralization is necessary before incineration. Drying is a common conditioning step with sludges, as well as scrap metals, which if wet may explode when they contact hot materials in a furnace.

1.5 Disposal Techniques

There are three main solid-waste disposal methods in use today.

They are sanitary landfilling, central incineration and composting.

The United States Environmental Protection Agency reports[6] disposal costs ranging from \$ 1 to \$ 420/tonne (1971 prices). The lower figure probably represents material piled on a barge inplant and dumped at sea. Sanitary landfill runs at \$ 4 to \$ 5/tonne, and average incineration costs are in the range of \$ 25 to \$ 30/tonne. These figures do not include inplant collection and storage, which amount to as much as 60% of total disposal charges.

1.6 Disposal in Sanitary Landfills[7,8]

Sanitary landfilling is basically a simple technique that involves spreading and compacting wastes that are covered each day with earth. Wastes should be either inert to begin with, or capable of being degraded by microbial attack to harmless compounds.

The main problems in landfill are production of leachate,[9] that may contaminate groundwater, and accumulation of gases, that may catch fire or explode. The nature of such pollution will depend on whether the decomposition process takes place in the presence of atmospheric oxygen or soil air (aerobic) or in the absence of oxygen (anaerobic). Aerobic decay produces stable end products such as CO_2, NO_3^-, SO_4^{2-}, H_2O, and a relatively inert residue. Anaerobic decay produces CO_2, methane, ammonia, hydrogen gas, alcohols and organic acids, and other partially oxidized organic species which exert a high BOD (biochemical oxygen demand).

The most common industrial use of landspreading is for disposal of petroleum refinery wastes. Aliphatic hydrocarbons such as gasoline and tars rapidly decompose in soil. Unsaturated, branched-chain componds are generally less susceptible to decomposition. Aromatic rings can be cleaved by soil organisms such as Xanthomonas and the resulting straight-chain compounds are readily oxidized to carbon dioxide and water.

1.7 Incineration

Incineration is a controlled process for oxidizing solid, liquid or gaseous combustible wastes to carbon dioxide, water and ash. Sulphur and nitrogen-containing compounds will produce their corresponding oxides and should not be incinerated without considering their effect on air quality. Halogenated hydrocarbons not only affect air quality, but may corrode the incinerator.

Incineration has certain advantages, particularly where land disposal sites are not available or are too remote for economic hauling. It has the disadvantages of high air pollution potential, high capital investment, and high operating cost because relatively skillful operators are needed. It also produces a residue which must ultimately be disposed of.

For general application in industrial waste disposal, rotary Kilns and multiple-hearth furnaces are the most useful. A rotary Kiln at Dow Chemical[10] disposes of low ash liquid residues and solid wastes such as plastic trimmings, Styrofoam, paper, wood and other solids with varying heat values. This design is also used in municipal installations. Refractory maintenance is a high-cost item with rotary Kilns since it must be replaced about once a year.

1.8 Composting

Composting is not widely practiced because of the cost of repeated handling of the wastes and the need to separate undecomposable residues which may amount for as much as 30 percent of the total waste. The end product from composting is a desirable soil conditioner.

1.9 Site Selection[11]

Selection of a landfill site for a particular waste or mixture of wastes necessitates consideration of a variety of factors. The most important of these factors concerns the hydrogeology of the site, particularly the permeability of the strata and the elevation and gradient of the water table. Clays and shales have permeabilities in the range 10^{-7} - 10^{-9} cm s^{-1} and afford the maximum protection to underlying groundwater supplies. The least protection is offered by rocks in which water movement is via fissures or solution cavities. Strata in which groundwater movement is intergranular, such as sands and gravels, generally have lower permeabilities than fissured materials and leachates will travel less rapidly and have a greater chance of being rendered innocuous through chemical and physical processes. The pH of acidic wastes will be increased through contact with limestones and many clay minerals are strongly adsorbent to various elements.

There are two basic techniques of leachate management: The "concentrate and contain" technique and the "dilute and disperse" method.

Concentrate and contain: Three or four years ago the view then prevalent was that the ideal landfill was one surrounded by impermeable material which would effectively contain the leachate that was formed. Undoubtedly such a site provides a measure of security against groundwater contamination, but operational experience in managing these "concentrate and contain" sites has shown that this benefit is more than outweighed by considerable risks of surface water pollution and practical problems in site management.

The reason is simple, strong leachate accumulates in the site, rising in level until sooner or later it breaks out in seepage zones around the edge of the landfill. When this happens (and it may be some years after waste disposal operations cease) pollution of surface water will be threatened and the remedial measures to prevent it are both difficult and expensive.

Dilute and disperse: "dilute and disperse" sites are those in which leachate is free to move slowly through the (permeable) strata that lie beneath them. Earlier intuitive beliefs held that such sites must be intrinsically unsafe because of the threat of direct contamination to groundwater aquifers.

1.10 Mitco Site

This is a typical example of an old brick clay quarry used for waste disposal. The problem with this sort of site is that it is watertight as the surrounding rocks have a low permeability. Consequently any rain water entering is unable to escape therefore there is a risk of flooding causing possible pollution of surface water.

The Mitco site received phenol bearing lime sludges as well as solid wastes early in its filling history causing contamination. During the period 1975 to 1978 the site was taken over by Effluent Disposal Limited, and used for the disposal and treatment by neutralization of large quantities of contaminated acids from the steel processing industry. The acids were neutralized with calcium carbonate and because of the high concentration of sulphuric acid the site began to fill up with calcium sulphate sludges. The neutralized liquid was decanted and taken by tanker for disposal at sea. More recently this liquid has been disposed of underground in an old coal mine via a borehole on the Mitco site.

1.11 Role of Clays

To investigate the reactions likely to occur in disposal sites, the properties of the rocks composing the site must be understood. In the particular case of the removal of phenols, it is the properties of the clay minerals in the rocks which are important, because their structural characteristics facilitate the absorption of polar organic molecules.[12]

Clay minerals commonly found in sedimentary rocks include Kaolinite, Illite, Chlorite, Montmorillonite, and mixed layer clays. Montmorillonite and kaolinite were used in this work as they were readily available in large quantities in their pure form.

1.12 Structural Principles of Clays[13,14,15]

The principal building elements of the clay minerals are two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminium or magnesium-oxygen-hydroxyl octahedra. In the silicon-oxygen sheets, the silicon atoms are coordinated with four oxygen atoms. The oxygen atoms are located on the four corners of a regular tetrahedron with the silicon atom in the centre. (Fig 1a) In the sheet, three of the four oxygen atoms of each tetrahedron are shared by three neighbouring tetrahedra. The fourth (terminal) oxygen atom of each tetrahedron points upward in the sketched arrangement. (Fig 1b) The silicon-oxygen sheet is called the tetrahedral sheet or silica sheet.

In the aluminium or magnesium-oxygen-hydroxyl sheets, the aluminium or magnesium atoms are coordinated with six oxygen atoms or hydroxyl groups which are located around the aluminium or magnesium atom with their centres on the six corners of a regular octahedron. (Fig 2a) The sharing of oxygen atoms by neighboring octahedra results in a sheet such as that shown in (Fig 2b). The oxygen atoms and hydroxyl groups lie in two parallel planes with aluminium or magnesium atoms between these planes. This sheet is called the octahedral sheet or the alumina or magnesia sheet, also called gibbsite $Al(OH)_3$ layer or brucite $Mg(OH)_2$ layer respectively.

The analogous symmetry and the almost identical dimensions in the tetrahedral and the octahedral sheets allow the sharing of oxygen atoms between these sheets. The fourth oxygen atom protruding from the tetrahedral sheet is shared by the octahedral sheet. This sharing of atoms may occur between one silica and one alumina or magnesia sheet, to form two-layer minerals. If one alumina or magnesia sheet shares oxygen atoms with two silica sheets, then this is a three-layer minerals. The

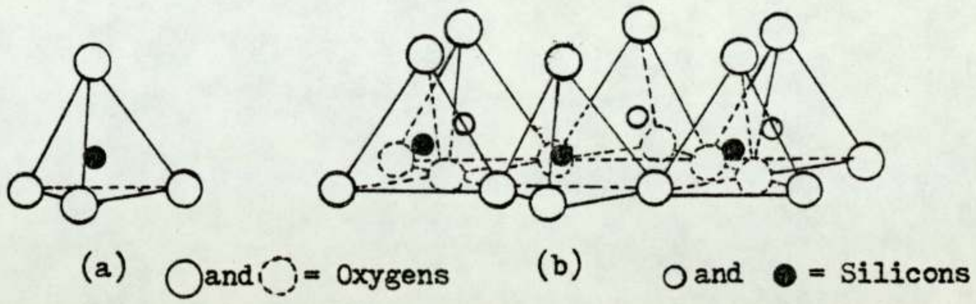


Fig. 1. Diagrammatic sketch showing (a) single tetrahedron and (b) sheet structure of silica tetrahedrons arranged in a hexagonal network.

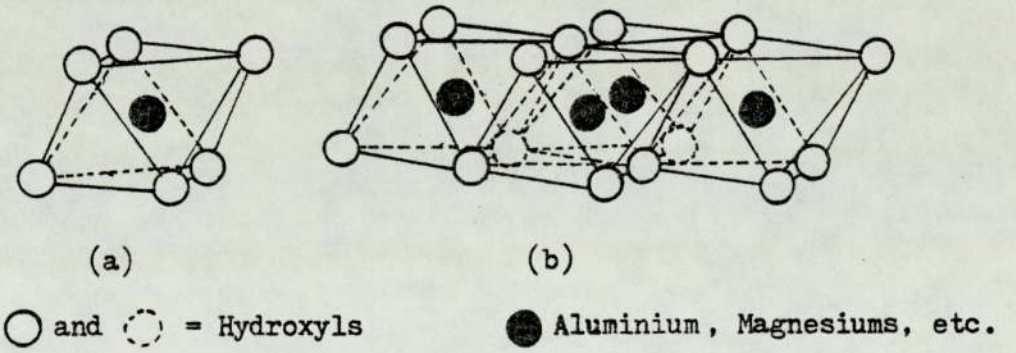


Fig. 2. Diagrammatic sketch showing (a) single octahedral unit and (b) the sheet structure of the octahedral units.

combination of an octahedral sheet with one or two tetrahedral sheets is called a unit layer. The distance between a certain plane in the unit layer and the corresponding plane in the next unit layer is called the 001, basal or c spacing. Its determination from X-ray diffraction patterns immediately enables one to distinguish between two-layer clays with a c spacing of about 7.1 - 7.2 Å and three-layer clays with a c spacing of at least 9.2 Å.

Kaolinite is a two-layer clay mineral consisting of one tetrahedral sheet and one octahedral sheet. (Fig 3) The mineral is not expansible as the sheets are firmly held together by the electrostatic attraction of the oxygen atoms and hydroxyl groups between the two layer units. For this reason, penetration of the kaolinite interlayers by organic compounds is difficult to achieve and adsorption is generally confined to the external crystal surfaces.

The cation exchange capacity of the kaolinite minerals is low most commonly between 1 to 10 meq per 100 g. It has been suggested that the exchangeable ions are located on the broken edges of the kaolinite plates, where they would compensate for charge deficiencies owing to broken bonds.[13] However it is not likely that the broken edges have cation exchange sites. It is more reasonable to assume that, as in montmorillonite, the exchangeable cations are located on the flat-layer surface and compensate a net negative lattice charge resulting from a small degree of isomorphous substitution. Since the basal spacing of kaolinite does not leave room for interlayer cations, all the charge compensating cations must be adsorbed on the exterior surface of the stack of unit layers which constitute a particle.

Montmorillonite is a three-layer clay mineral consisting of

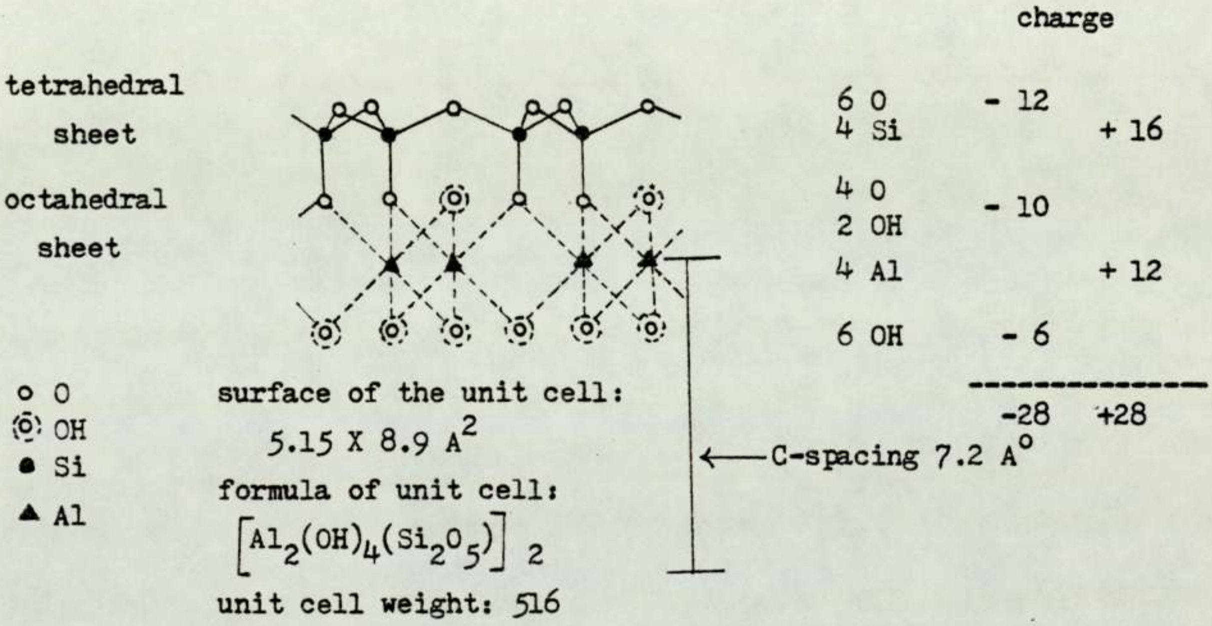
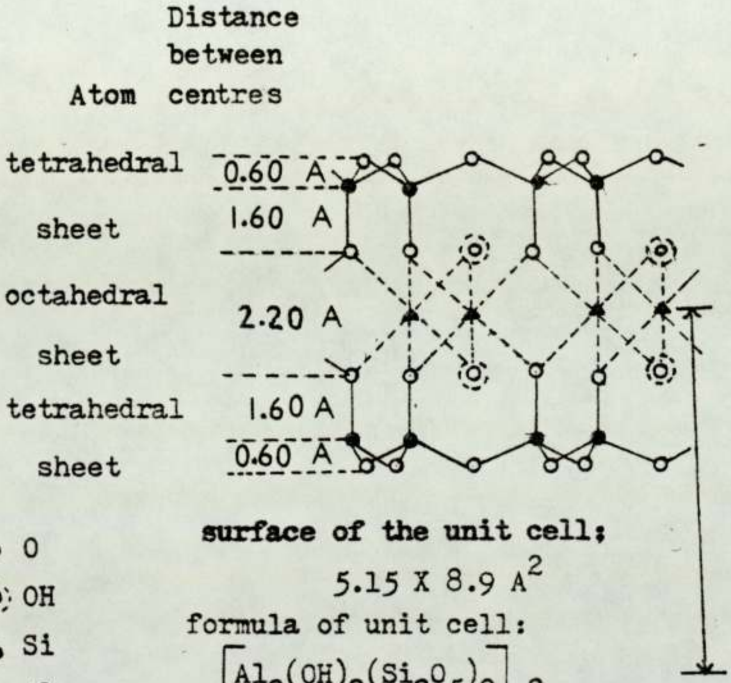


Fig. 3 . Atom arrangement in the unit cell of a two-layer mineral

(schematic)

an octahedral layer between two tetrahedral layers. (Fig 4) Bonds between the sheets are weak, allowing polar molecules to enter and expand the structure. In the tetrahedral sheet, tetravalent silicon may be partly replaced by trivalent aluminium. In the octahedral sheet, there may be replacement of trivalent aluminium by divalent magnesium without complete filling of the third vacant octahedral position. Aluminium may also be replaced by iron, chromium, zinc,[16] copper,[17] and other atoms.[18] The small size of these atoms permits them to replace the small silicon and aluminium atoms, therefore this replacement is called isomorphous substitution. In many minerals an atom with lower positive oxidation state replaces one of higher oxidation state, resulting in an excess of negative charge. This excess of negative lattice charge may be compensated by the adsorption on the layer surfaces of cations which are too large to be accommodated in the interior of the lattice.

In the presence of water the compensating cations on the surface may be readily exchanged with other cations in solution, hence they are called "exchangeable cations". The total amount of these cations may be determined analytically and when expressed in milliequivalents per 100 grams of dry clay, is called the cation exchange capacity (CEC) or the base exchange capacity (BEC) of the clay. The exchangeable cations are located on each side of each unit layer in the stack, hence, they are present not only on the external surfaces of the particle but also in between the unit layers. Their presence causes a slight increase of the basal spacing as compared with that of pyrophyllite from about 9.13 Å to at least 9.6 Å (for the dry clay) or slightly higher when the compensating cations are larger. The difference between the basal spacing of pyrophyllite and that of a montmorillonite



	charge	
6 O	- 12	
4 Si		+ 16
4 O 2 OH	- 10	
4 Al		+12
2 OH 4 O	- 10	
4 Si		+16
6 O	- 12	
	-44	+44

C- spacing 9.2 A°

o O
(ȯ) OH
● Si
▲ Al

surface of the unit cell;

$5.15 \times 8.9\ A^2$

formula of unit cell:

$\left[Al_2(OH)_2(Si_2O_5)_2\right]_2$

unit cell weight : 720

Hydroxyl water : 5 %

Fig.4 . Atom arrangement in the unit cell of a three-layer mineral (schematic).

is much less than the diameter of the compensating cations. Apparently, these cations are partly sunk in the holes of the tetrahedral sheet. When montmorillonite clays are contacted with water or with water vapour, the water molecules penetrate between the unit layers.[19] This so-called interlayer swelling, or (intra-) crystalline swelling, of montmorillonites is evident from an increase of the basal spacing of the clays to definite values of the order of 12.5-20 Å, depending on the type of clay and the type of cation.

Montmorillonite also admits organic compounds of a polar or ionic character between the unit layers,[12,20,21] The adsorption of the organic compounds leads to organo-complexes of montmorillonite.[22,23] The basal spacing of these complexes depend on the size and the packing of the organic molecules.

1.13 Previous Work

Carter[24] investigated the inorganic chemistry of clay minerals associated with various acid wastes to determine the ion exchange phenomena under practical conditions in waste disposal. Experiments were set up to determine whether the geological materials at the sites would react with wastes to remove the toxic components. The interaction of the metal ions, Fe^{3+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, and Cd^{2+}, in concentrations representative of those found in typical acid effluents, with clay minerals was investigated. The adsorption of heavy metal ions in solution by clays was investigated both with single metal ion solutions and with solutions containing a number of different ions. It was found that adsorption is dependent on the nature of the adsorbing ion, the nature of the clay minerals, and the environment. It was shown that the amount of metal ions sorbed by clay is determined by the pH of the solution. In relatively strongly acidic solutions, clays are positively charged giving rise to positive sites which will undergo anionic exchange. At pH 3 and above clays are negatively charged and undergo cationic exchange.

In Carter's work the electron spin resonance (e.s.r) technique was used as a useful method to detect the adsorption of paramagnetic metals by clay minerals. Two aspects of her work will be followed up in this thesis:

i) the sorption of chromium species by kaolinite.

ii) the use of electron spin resonance to determine how the paramagnetic metals interact with clays.

i) Carter reported that when chromium (III) was taken up by kaolinite after several days some of the metal was returned to the solution. This was attributed to hydrolysis of $\left[Cr(H_2O)_6\right]^{3+}$on the clay, producing new ionic species of lower charge which sets up a new equilibria with the solution. It is intended, in this work, to investigate this observation further.

ii) electron spin resonance was a good technique to identify the paramagnetic metals adsorbed on the clay (e.g Cu^{2+}). However it is possible that Carter has mis-interpreted her data for copper (II) on kaolinite, since kaolinite itself gives strong e.s.r signals which are similar to those attributed by Carter to axially distorted copper (II) ions.

Angel et.al[25,26,27] reported that the e.s.r spectrum of kaolinite contains two main groups of resonance lines centred at about

$g = 2.0$ and $g = 4.0$ respectively. They suggested that a 3-line resonance centred at $g = 4.0$ be attributed to iron(III) replacing silicon(IV) in distorted tetrahedral sites; and the asymmetric 2-line resonance at $g = 2.0$ appears characteristic of an $S = 1/2$ system.

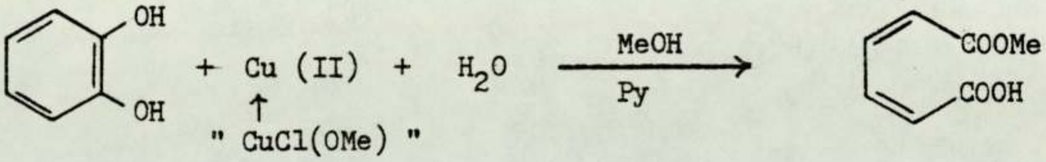
In particular[28], it has been suggested that the production of a stable paramagnetic centre (such as that which might account for the $g = 2.0$ signal in kaolinite) generally requires the presence of some sort of "pre-centre" which, when irradiated, subsequently traps a hole or an electron. The "pre-centre" often takes the form of a foreign ion substituting within the crystal structure and requiring charge compensation, in kaolinite divalent magnesium or divalent iron substituting for trivalent aluminium may provide the necessary pre-centre for the production of a stable defect.[28] These results suggested that divalent iron might be able to perform the same function as divalent magnesium, hence when a synthetic kaolinite was doped with iron(II), the same $g = 2.0$ was seen.[29] Thus there seems to be reasonable evidence for the defect theory. It will therefore be of interest to take this work further because an understanding of the e.s.r spectrum of the clay is needed before the e.s.r spectrum of adsorbed ions can be interpreted.

1.14 Phenols in Waste

Phenol and substituted phenolic materials[30] are common in nature but relatively little is known about the kinetics or thermodynamics of their sorption on to clays, however it is known that phenolic-clay complexes may affect plant growth when present in soils. Another problem is that phenols may be detected orally when present in drinking water[31], consequently prevention of contamination of potable groundwater by phenol is to be avoided. Thus removal of phenols from waste is a desirable objective.

For this purpose two ideas were considered :

a) the possible use of complexes to decompose phenol. For example it is known that copper (II) methoxo-complexes coordinated with pyridine will ring open phenols.[32,33]



In this work it was decided to characterise the active complex, to attempt to synthesise the complex on montmorillonite and to explore the possible use of related complexes supported on clays for the removal of phenol by chemical means.

The final objective is to see if phenol can be decomposed chemically in an environment simulating waste disposal of the concentrate and contain type.

The idea to be evaluated receives support from two recent pieces of work. The isolation of the first unsubstituted diphenoxo-complexes of copper(II) stabilised by coordination with (1) 2,2'-bipyridyl, (bipy) and (2) ethylenediamine (en) has been reported.[34] These compounds constitute a further example of " Cu(II)-OR " systems which may be active for our purpose.

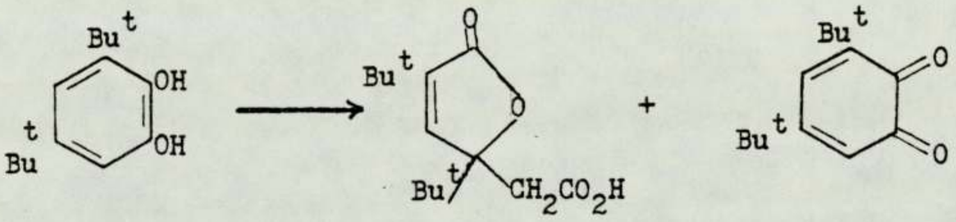
$$[\mathrm{CuCl_2(bipy)}] + 2\mathrm{Na}[\mathrm{OPh}] \xrightarrow{\mathrm{thf}} 2\mathrm{NaCl} + [\mathrm{Cu(OPh)_2(bipy)}] \qquad (1)$$

$$\left[\mathrm{CuCl_2(en)}\right] + 2\mathrm{Na}\left[\mathrm{OPh}\right] . \mathrm{PhOH} \xrightarrow{\mathrm{thf}} 2\mathrm{NaCl} + \mathrm{PhOH} + \left[\mathrm{Cu(OPh)_2(en)}\right] . \mathrm{PhOH}$$

(2)

(thf = tetrahydrofuran)

Another recent paper related to the theme developed here describes the oxidative aromatic ring cleavage by molecular oxygen of 3,5-di-t-butylcatechol (3) to give a lactone (4).[35] The reaction is catalysed by a non-enzymatic iron(II) complex coordinated by 2,2'-bipyridine and pyridine.



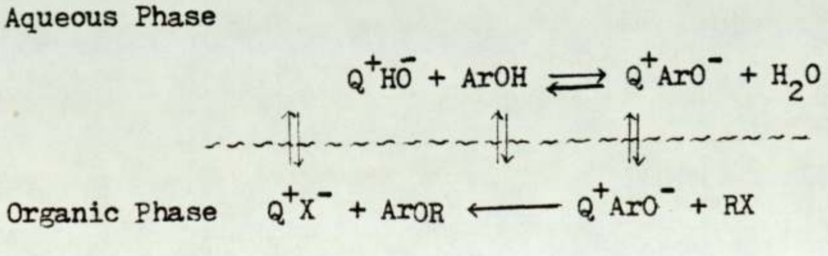
(3) (4)

b) the use of phase-transfer catalysis (PTC) for the synthesis of phenol ethers was also considered as an additional approach to the problem of inducing chemical reaction of phenols in waste. Thus we might develop a clay supported PTC which could for example, catalyse the esterification of phenols.

1.15 The Principle of Phase Transfer Catalysis[36]

Phase transfer catalysis uses either a quaternary ammonium or phosphonium salt as a catalyst. In general, there are two immisicble phases. One of these phases (generally aqueous) contains a reservoir of the salt expected to function either as base or nucleophile. The second phase is organic and contains the substrate which is expected to react with the salt. Since the salt containing phase is insoluble in the substrate containing phase, there will be no reaction observed in the absence of interfacial phenomena. A phase transfer catalyst is added to the mixture. This is ordinarily a quaternary ammonium or phosphonium halide or bisulphate which contains a lipophilic cation. The lipophilic cation is soluble in both aqueous and organic phases and when in contact with the aqueous reservoir of salt, exchanges anions with the excess of anion in the salt solution.

The phase transfer method has been used in the preparation of a variety of phenolic ethers.[37] Based on the principle of phase-transfer catalysis, the method involves alkylation of the phenoxide ion with an alkyl halide or sulphate ester in a methylene chloride-water system at room temperature, using a quaternary ammonium salt as the effective reagent for transport of the phenoxide ion between the two phases.



Q = quaternary

Thus, in this work it is proposed to investigate the possible use of clay supported PTC since, if montmorillonite is selected, it may be that the water associated with the exchangeable cations could function as the "aqueous phase" in the presence of an organic medium. In relation to the problems of waste disposal, this idea relates more to possible pre-treatment of waste. However, if the idea could be shown to be valid, extensions to more conventional areas of synthetic chemistry should be possible.

Clay minerals have been shown to be catalysts for many reactions, for example monoalkylphenols have been made by passing a mixture of phenol and an olefin of 8-18 carbon atoms through a catalyst bed at 250°- 350°F (approximately 120-177°C). The catalyst is a granular activated clay, such as acid treated bentonite and montmorillonite.[38]

CHAPTER TWO

PHYSICAL TECHNIQUES

PHYSICAL TECHNIQUES

2.1 Electron Spin Resonance Spectroscopy

2.1.1 The Spectrometer

The e.s.r spectra shown here were recorded on a Japan Electron Optics Limited (JEOL) PE-1X type spectrometer operating in the X-band microwave region. On this machine, spectra may be recorded at one of two modulation frequencies, 100 kHz for normal high sensitivity measurements, and 80 MHZ for measurements at reduced temperature. In this case all spectra were obtained at 100 kHz modulation frequency.

Automatic frequency control is an incorporated feature of the machine, allowing the Klystron frequency to be locked to the resonant frequency at the sample cavity.

The spectrometer sample cavity is a high (Q) cylindrical reflection cavity operating in the TE_{011} mode. Various facilities are incorporated into the cavity to enable a number of operations to be easily carried out. A port in the side of the cavity enables the insertion of a standard sample, in this case, a manganese(II) salt. An inlet and outlet system allows a stream of nitrogen (for heating and cooling purposes) to be passed and a removable cover exposes a window for U.V. irradiation.

The recording system incorporated into the spectrometer is a digital DYT recorder, with three operational modes: firstly, in the DY mode, the chart roll is fixed and the pen-bar scans the spectrum through the predetermined field sweep (ranges from ± 0.25 G to ± 2500 G);

in the DYT mode, the pen-bar scans the spectrum as before, but the chart roll is also moved, in the opposite direction, enabling the spectrum to be magnified 1.5 ,2 or 3 times the original size; finally, operation in the YT mode fixes the pen-bar while moving the chart roll, thus enabling the measuement of reaction rates and kinetic studies by setting the pen-bar at some point in the spectrum and following the rate of increase or decrease in intensity of a particular line in the spectrum.

2.1.2 Selection of Sample tube

The sample tube should not contain transition metals such as iron, cobalt, manganese, chromium, vanadium, and copper or any of their compounds.

The sample tube used in the e.s.r measurements was a standard JEOL quartz tube. But usually when the signal intensity was high, samples were placed in a glass melting point tube, and then spectra were obtained by placing this tube in the quarz tube. It was noticed that glass itself gave an e.s.r signal at 1500 Gauss. The quartz sample tube itself was used when the signal intensity was low.

2.1.3 Measurement of g-Values

The standard sample is a manganese (II) salt, diluted with magnesium oxide, enclosed in a holder which may be inserted into the sample cavity through a port provided for this purpose.

Manganese has a nuclear spin of $(I = 5/2)$ and the e.s.r spectrum has $(2I + 1) = 6$ sharp lines. The central two lines are separated by 86.9 G (Fig 5), and the fourth line has g-value of 1.981, therefore this enables the g-value of an unknown sample to be calculated using the following equation :

$$g = \frac{g_1 \; H_1}{H + \Delta H}$$

where : g is the g-value of the unknown sample.

g_1 is the g-value of standard peak.

H is the value of the field at the unknown peak.

H_1 is the value of the field at the standard peak.

ΔH is the difference in field position between the unknown and standard peaks.

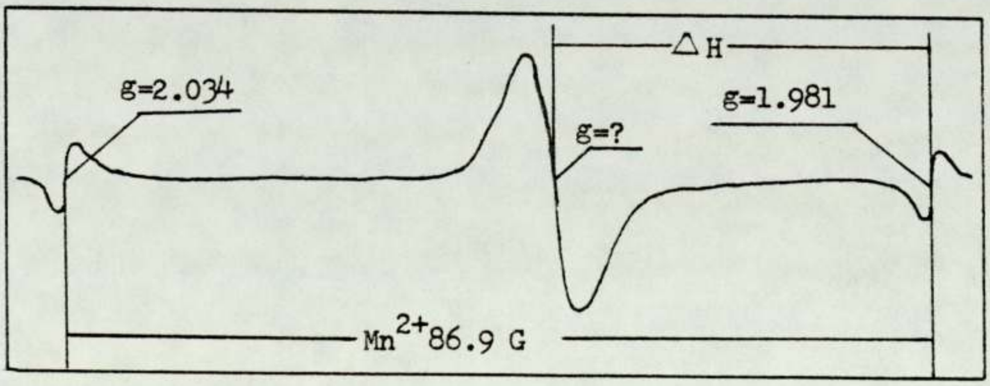


Fig 5

2.2 X-Ray Powder Diffraction

X-ray powder diffraction data were obtained as a standard analytical service within the geology department of Aston University using Co Kα radiation, wavelength 1.79 Å, with iron filters. The identification of peaks was achieved through comparison with X-ray powder diffraction spectra of natural clay minerals.

2.3 Infrared Spectroscopy

The infrared spectra were recorded using Perkin Elmer 457 (4000-250 cm^{-1}) and 225 (400-200 cm^{-1}) spectrophotometers. Solid state specimens were prepared as Nujol mulls supported between KBr plates, CsI plates or polythene plates, or examined as KBr discs, prepared by pressing a mixture of sample and powdered KBr.

2.4 Magnetic Susceptibility Measurements

Paramagnetic susceptibilities were measured by the Gouy method at room temperature. A semi-micro Stanton Instrument balance was used in conjunction with an electromagnet operating at a current of 10 amps. Gouy tube constants were determined using $Hg[Co(NCS)_4]$ as a standard with a known gram susceptibility of 16.44×10^{-6} c.g.s units at 20 °C. Magnetic susceptibilities were calculated using the following equation :

$$10^6 \chi = \frac{\alpha + \beta F}{W}$$

where : F is the force on the sample

W is the sample weight

α is the correction due to the paramagnetism of air (O_2)

β is a constant for the tube, determined with the standard

2.5 Gas Liquid Chromatography

2.5.1 : Gas liquid chromatography was used for determination and identification of the reaction products. Gas liquid chromatograph analysis were carried out using Pye Unicam Ltd G C D Gas Chromatograph

Specifications

Column = Stainless steel
Length of the column = 2m
Diameter of the column = 0.6 cm
Packing of the column = 25% silicon grease on phase prep A
Carrier gas = Nitrogen (N_2)
Rate of flow = 30 ml min^{-1}
Temperature of the column = 150°C
Detector = Flame ionisation

2.5.2 : Phenol was identified and determined using a Pye series 104 gas liquid chromatograph.

Specifications

Column = Stainless steel

Length of the column = 2m

Diameter of the column = 0.3 cm

Packing of the column = 5% Di-(3,3,5 trimethyl cyclo hexyl)O-phthalate-4 chromasorb on G.AW.DMCS 80-100 mesh

Carrier gas = Nitrogen (N_2)

Rate of flow = 25 ml min^{-1}

Temperature of the column = 130°C

Detector = Flame ionisation

2.6 Chemicals

All chemicals were obtained from commercial sources. The pure minerals montmorillonite and kaolinite were obtained from Berk Limited, and English China Clays Sales Co Ltd, respectively.

Analyses supplied by the companies gave the following specifications for the clays.

Chemical analysis	Montmorillonite	Kaolinite
	%	%
SiO_2	52.2	46.2
Al_2O_3	12.8	38.7
Fe_2O_3	10.2	0.56
TiO_2	0.6	0.09
MgO	2.5	0.2
CaO	2.2	0.2
K_2O	0.4	1.01
Na_2O	0.1	0.07
H_2O (-105°C)	12.3	–
H_2O (+105°C)	6.6	–
Loss on ignition	–	13.14
pH	6.5-7	5.0 ± 0.5
Cation exchange capacity	80-85 meq per 100g	–
Particle size		
% below 53 μ	87 meq per 100g	99.99 meq per 100g
% below 0.2 μ	88 meq per 100g	99.8 meq per 100g
% below 2 μ	84 meq per 100g	80± 3 mwq per 100g

2.7 Solvents

All solvents were obtained from commercial sources. Methanol was distilled by standard techniques as given in Vogel.[39]

2.8 Elemental Analysis

Micro-analysis for carbon, hydrogen, nitrogen, and halogen was carried out by the micro analytical laboratories of the chemistry department of Aston University.

2.9 Copper Analysis

The determination of copper was carried by titration with standard EDTA.

Reagents : EDTA solution 0.1M ; 37.225g of disodium dihydrogen ethylenediaminetetra-acetate dihydrate was dissolved in water and diluted to 1 litre in a volumetric flask.

2.9.1 Indicator Solution

This was a 0.5% alizarin complexone solution in dilute ammonium acetate buffered to a pH of 4.3 with a solution containg 105g sodium acetate and 100ml of acetic acid made up to 1 litre.

Procedure : A solution containg copper (25ml) was diluted with water (25ml) and then 5-8 drops of alizarin complexone indicator was added to obtain a red to magenta colour depending on the content, upon addition of 3-4ml of buffer solution. This was titrated with standard EDTA solution until the colour changed from red to green.

1ml 0.1M EDTA 6.354 mg.Cu

2.9.2 Indicator Solution

Aqueous solution of Fast Sulphon Black F 0.5% was prepared. Procedure : Solid product (0.1 g) was dissolved in concentrated ammonia solution (5ml), then was diluted with water (25ml), and 5 drops of the indicator solution was added. This was titrated with standard EDTA solution until the colour changed from blue to dark green.

2.10 Chromium Analysis

The determination of chromium was carried out by flame atomic absorption techniques. The instrument used was a Perkin Elmer Model 460 Absorption Spectrophotometer. Absorbance of the solutions was automatically recorded and was converted to parts per million of metal ion in solution.

CHAPTER THREE

CLAY-SUPPORTED CATALYSTS TO PROMOTE REACTION OF PHENOLS IN WASTE

CLAY-SUPPORTED CATALYSTS TO PROMOTE REACTIONS OF PHENOLS IN WASTE

3.1 Introduction

The use of the Mitco site for the disposal of waste products has been outlined in the general introduction. A bore-hole sunk near this site indicated that there was a little movement of liquid into the surronding rocks. In this site there is no problem with pollution hazards to groundwater because of the very low permeability of the quarried materials. However, other sites in more permeable materials would probably leak, hence wastes must be rendered harmless or be attenuated sufficiently, so that their escape from the site would not constitute a danger to the environment. This represented no problem for acids such as sulphuric acid, which were easily neutralized, but a problem arose with phenol. It was feared that phenol contamination of groundwater was possible and the present work is concerned with removal of this hazard. The work began with an investigation of methods of determination of phenol in solution and is extended to investigate ways of rendering phenol harmless under the sort of chemical conditions experienced at the Mitco site. The possibility of finding a clay to strongly adsorb phenol on site was investigated using some common naturally occurring clays. In addition the possibility of finding a catalyst which may promote chemical reactions of phenol to afford less problematical compounds is investigated. Attention was devoted to catalysts which may be supported on clays, such as montmorillonite, hence some compounds of copper(II), active under homogenous condition, are evaluated.

The use of phase transfer catalysis is outlined in the general introduction and the possibility of using this type of system to convert phenols to ethers is investigated in the present work, again with emphasis on the development of clay supported catalysts. This aspect of the work had wider implications and was extended beyond the waste disposal context.

3.2 Experimental

3.2.1 Determination of Phenol in Solution by Bromate

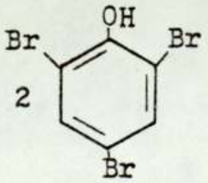
The phenol solution was brominated with a standard solution of potassium bromate and bromide and the excess bromine was determined by titration.

Free bromine from the solution of potassium bromate (1 mol) sulphuric acid (6 mol) and potassium bromide (5 mol) was treated with phenol solution. Iodide was then added to the remaining bromine and the tribromophenol formed from the above treatment.

The free iodine was titrated by sodium thiosulphate to determine the amount of phenol. This method was not satisfactory due to poor reproducibility.

$$BrO_3^- + 6H^+ + 5Br^- \longrightarrow 3Br_2$$

$$3Br_2 + 2C_6H_5OH \longrightarrow 2$$



$$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$$

I_2 was titrated by $Na_2S_2O_3$

3.2.2 Colorimetric Determination of Phenol in the Visible Region

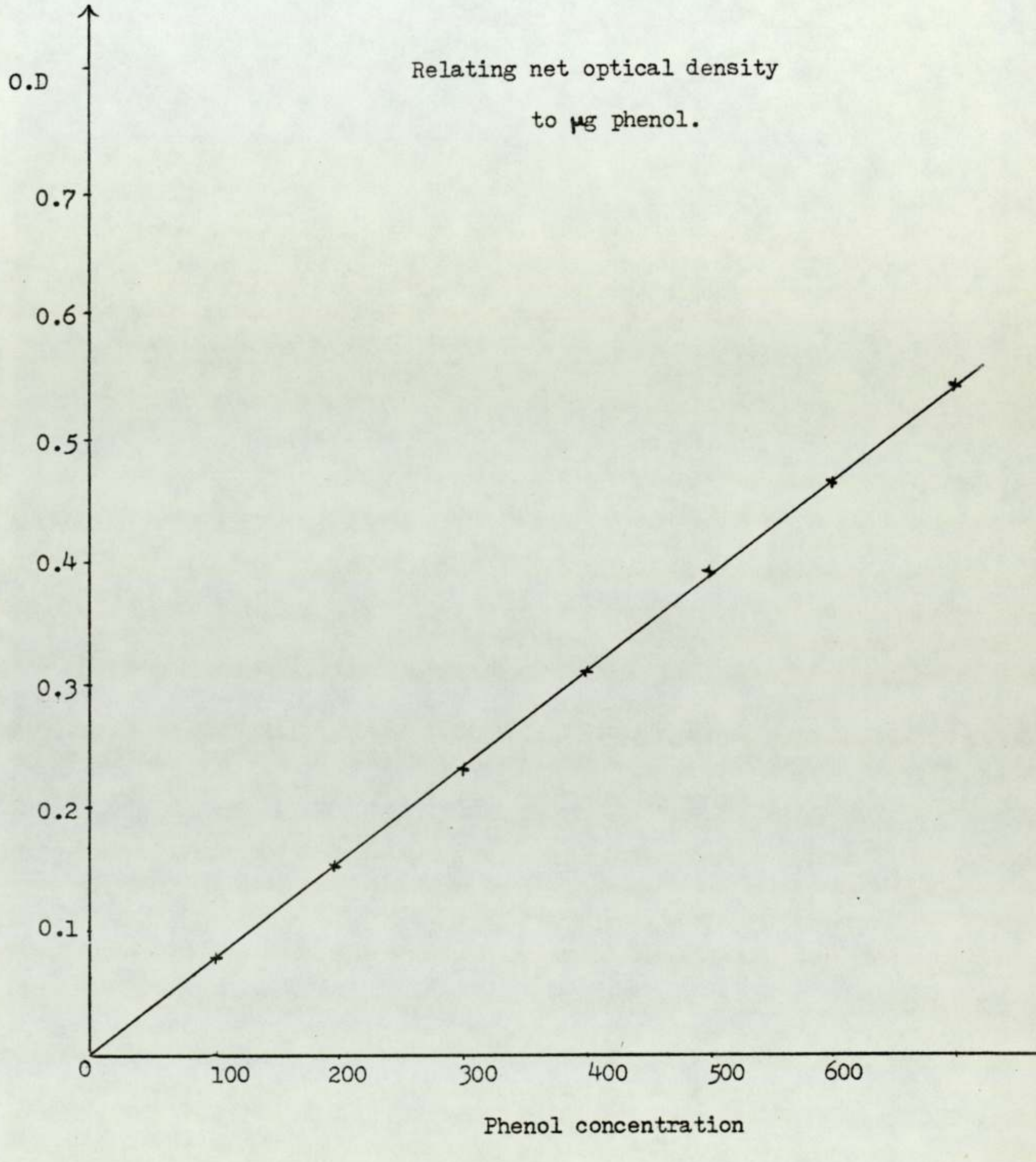
Phenol reacts with p-amino-NN-dimethylaniline sulphate in the presence of a mild oxidizing agent to give a blue colour which is measured either photoelectrically or compared with a standard. A series of solutions covering the range 100 to 1000 $\mu g\,ml^{-1}$ were prepared from appropriate volumes of phenol standard solutions ($1 g l^{-1}$) including a blank determination on the reagents. Phenol (SLR) detached crystals were used.

A standard solution of phenol ($1 g l^{-1}$) was prepared as required and then aliquots of 5,10,15,20,25,30,35,40,45 ml were diluted to 50 ml with distilled water to give standard dilute solutions of phenol (100 to 1000 $\mu g ml^{-1}$)

The optical density of the blank was deducted from those of the standard solutions and a graph relating net optical density to $\mu g ml^{-1}$ of phenol was obtained (Fig 6).

To a solution of phenol (100 ml) was added sodium bicarbonate (2ml) and p-amino-NN-dimethylaniline sulphate reagent (2ml). Sodium hypochlorite was gradually introduced from a burette and the solution was stirred until the pink colour changed to blue owing to the formation of indophenol.

Phenol was determined photoelectrically. This method of phenol determination was found to be accurate enough, but because of the long


O.D
Relating net optical density
to µg phenol.
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
200
300
400
500
600
Phenol concentration

(Fig 6)

period required to complete the determination it is not recomended as a convenient method for routine analysis of many samples.

3.2.3 Colorimetric Determination of Phenol in the Ultra Violet Region

The phenol analyses were carried out using a Pye Unicam, SP800 Ultra Violet Spectrophotometer.

The phenol was detected by measuring absorption at a wavelength of 269 nm. The concentration was 10^{-3} molar.

Although this method was rapid and convenient but it was not very accurate, since several phenolic compounds co-exist in wastes and it was found that differences in U.V profiles were too slight to allow discrimination between them. Because of this no more than an order of magnitude estimate of concentration can be made by this method under field conditions.

3.2.4 Determination of Phenol by Gas Liquid Chromatography

Gas liquid chromatography is the best method for the determination and identification of phenol.(see chapter 2 for equipment) Consequently, products of the reaction between phenol and clay minerals were checked for purity by gas liquid chromatography means and also were identified by this means using the authentic samples.

This method was judged to combine rapidity and accuracy and was used to determine the phenol in the samples.

3.3 Interaction of Phenol with Clay Minerals (montmorillonite and kaolinite)

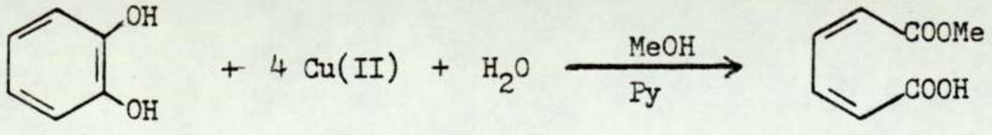
Montmorillonite or kaolinite (10 g) was covered with standard solutions of phenol (100ml of 0.1, 0.01, and 0.001 molar) and these separate solutions were stirred for 24h. The solutions were filtered and the concentration of phenol was measured by U.V, G.L.C and colorimetric methods. (This was used for evaluation of the different analytical methods).

The infrared spectrum of the clay absorbed phenol showed, in the case of kaolinite, no uptake of phenol. However the presence of hydroxyl groups at 3,200 cm^{-1} indicated that phenol was absorbed onto montmorillonite. This hydroxyl band was easily distinguished from the OH group of natural montmorillonite which occurs at 3,600 cm^{-1}.

The analysis of the filtrate by spectroscopic means and gas liquid chromatography showed only a very small loss of phenol.

3.4 The possible Use of Complexes to Decompose Phenol

It was been demonstrated that catechol reacts with copper(II) methoxy chloride in pyridine containing methanol and water under anaerobic conditions to give the cis,cis-muconic acid monomethyl ester, as in the following equation (Cu(II) = CuClOMe).



Copper(II) methoxy chloride is a stable light yellow-green solid which readily reacts with atmospheric moisture. Hay ,Endres and their co-workers[40] reported that copper(II) methoxy chloride reacts with pyridine to give a deep green complex, (PyCuClOMe), which according to them exists as a dimer. The pyridine copper(II) methoxy chloride complex (PyCuClOMe) appears more stable and consequently it is more convenient to use than the copper(II) methoxy chloride itself.

3.5 Preparation of Complexes

3.5.1 Dichlorobispyridinecopper(II)

$[Cu(Py)_2Cl_2]$

Anhydrous copper(II) chloride (1.345 g) was dissolved in methanol (25ml) and then pyridine (2ml) was added and then the mixture was stirred under reflux for 2 h. A blue precipitate was formed. This complex was prepared for comparison with the pyridine-chloromethoxy copper(II) complex.

Analytical data for this compound are presented in table (1).

Far infrared data indicate that the observed frequencies at 293 cm^{-1} and 236-219 cm^{-1} for the complex under study can be assigned to the (Cu-Cl) stretching modes. The presence of two chlorine-copper stretching bands for the $[Cu(Py)_2Cl_2]$ complex indicate that the stereochemical configuration of complex under study is distorted polymeric octahedral.[41] (Fig 7)

The band at 293 cm^{-1} is assigned to the stretching of the shorter chlorine-copper bonds and that at 236 cm^{-1} is assigned to the bridging chlorine-copper bonds. An absorption at 268 cm^{-1} could be assigned to a metal-nitrogen " stretching " vibration.

The electron spin resonance spectrum showed two g-factors,[42,43] $g_{\parallel} = 2.204 \pm 0.020$ and $g_{\perp} = 2.052 \pm 0.020$ (Fig 8).

Compound	Found %		Requried % For $C_{10}H_{10}Cl_2CuN_2$
$Cu(Py)_2Cl_2$	C	41.4	41.3
	H	3.69	3.41
	Cu	21.6	21.7
	N	9.25	9.57

Table (1)

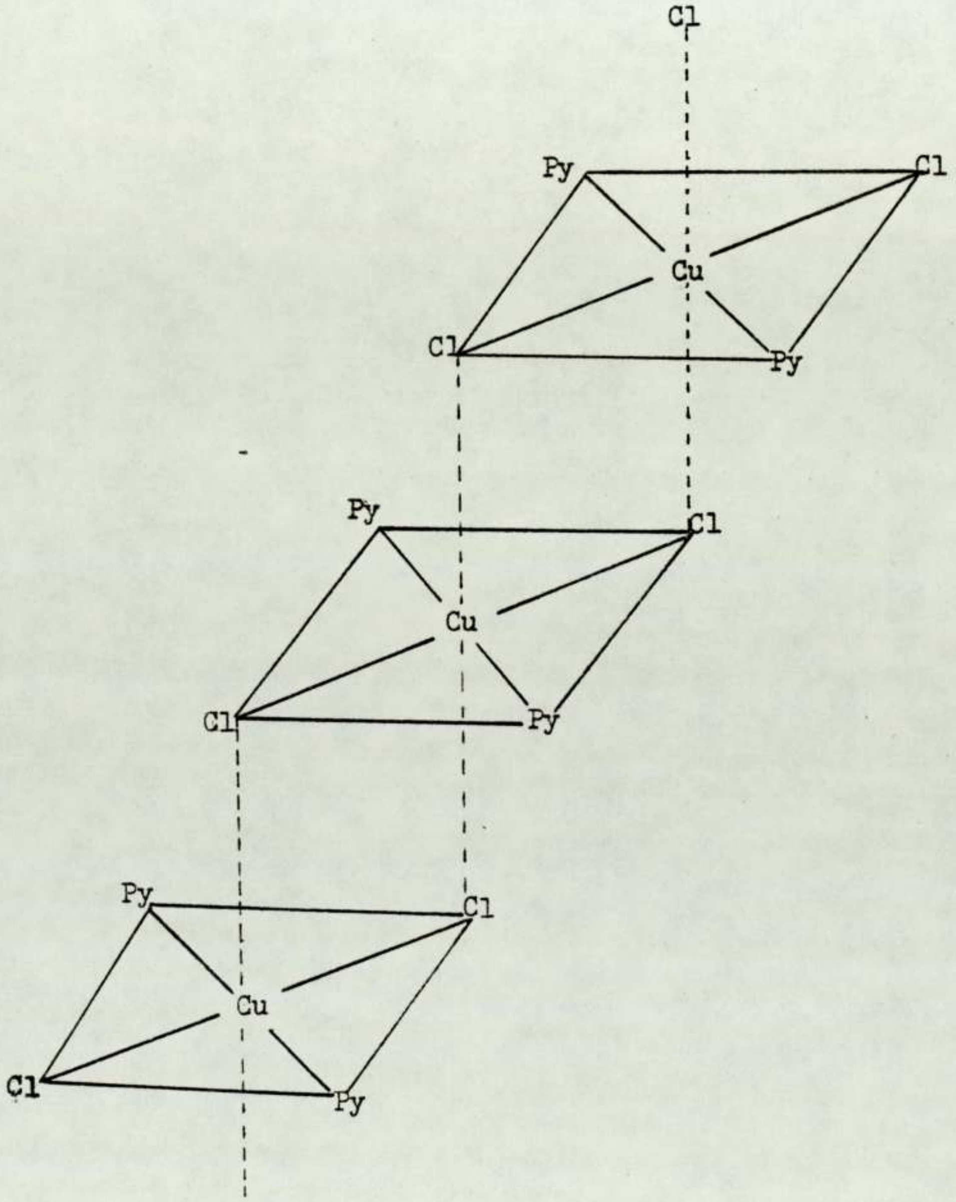


Fig 7

Stereochemical - configuration of the

$[Cu(Py)_2Cl_2]$

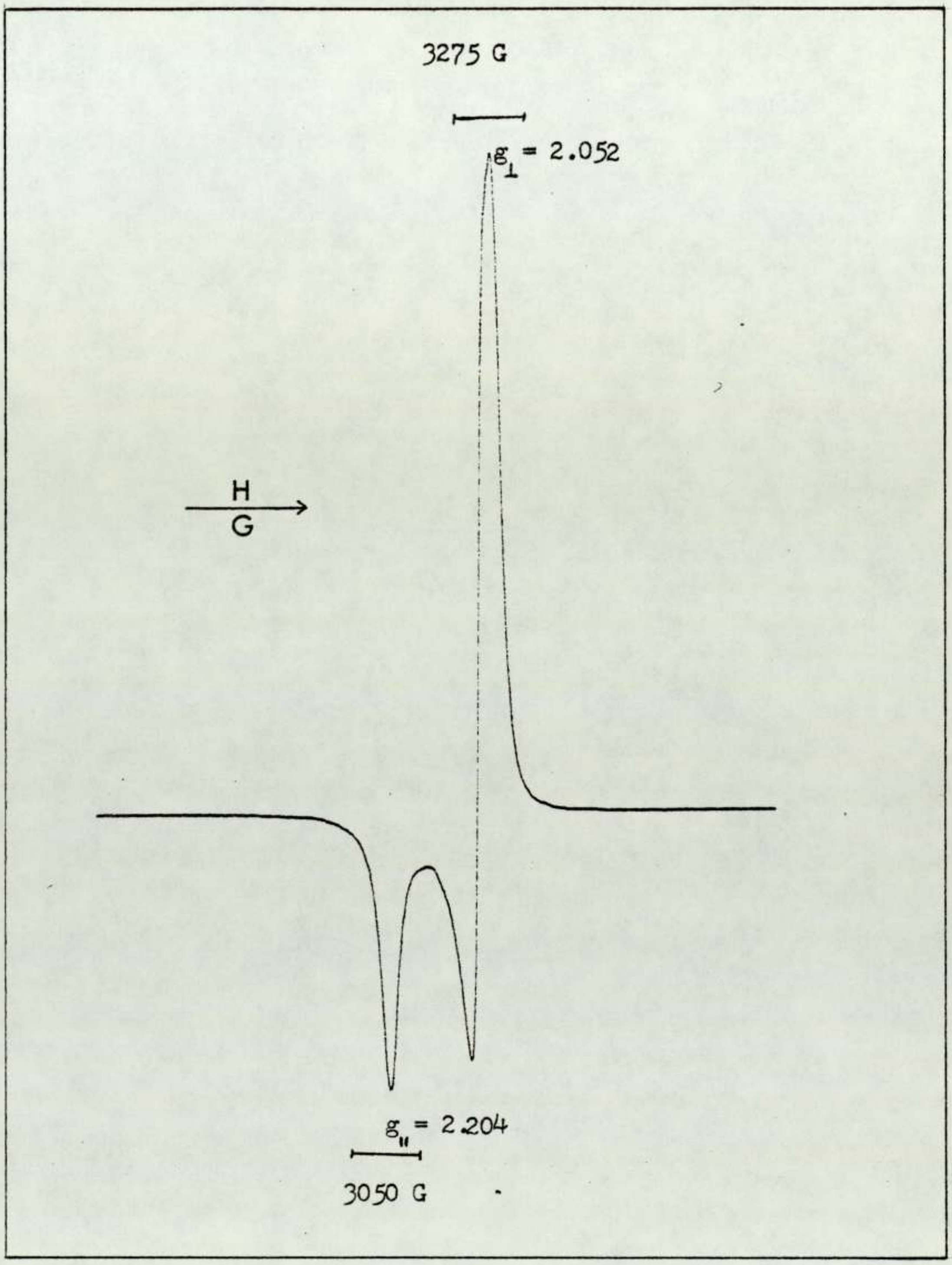


Fig 8

ESR spectrum of $Cu(Py)_2Cl_2$

3.5.2 Di-μ-methoxobis(chloropyridinecopper(II))

$(PyCl)Cu(OMe)_2Cu(PyCl)$

Anhydrous copper(II) chloride (1.345 g) was dissolved in anhydrous methanol (50 ml) and added to a solution of sodium methoxide (0.54 g) in anhydrous methanol (15 ml). Pyridine (2 ml) was added and the reaction mixture was then stirred and heated for 2h at the temperature of refluxing methanol using a magnetic hot plate stirrer setting of 30% . A deep green solid was formed. The compound was characterised by means of analysis and infrared and electron spin resonance spectroscopy together with a magnetic susceptibility determination.

This reaction was also performed at room temperature, and gave a product with e.s.r g-factors essentially equal to those of $[Cu(Py)_2Cl_2]$, with which it was probably contaminated. The agreement between the expected and found elemental analysis was also poor. However, the compound produced under reflux gave a good elemental analysis and a two g-factor e.s.r. spectrum.

Physical data for these compounds are given in table (2).

3.5.3 Dibromobispyridinecopper(II) $[Cu(Py)_2Br_2]$ and

Di-μ-methoxobis(bromopyridinecopper(II)

$(PyBr)Cu(OMe)_2Cu(PyBr)$

Copper(II) bromide (1.345 g) was dissolved in anhydrous methanol (50 ml) and was then added to a solution of sodium methoxide

Complexes	Cu(OMe)(Py)Cl/under reflux			Cu(OMe)(Py)Cl/room temperature	
		Found%	Required% For $C_{12}H_{16}Cl_2Cu_2N_2O_2$	Found%	Required% For $C_{10}H_{10}Cl_2CuN_2$
Analytical data	C	32.8	34.4	41.5	41.3
	H	3.00	3.82	3.69	3.41
	Cu	29.3	30.3	21.59	21.70
	N	6.86	6.69	9.25	9.57
E.S.R data	$g_{\parallel}$	2.223 ± 0.012		2.225 ± 0.012	
	$g_{\perp}$	2.061 ± 0.012		2.062 ± 0.012	
Magnetic moment		1.30 B.M		—	
I.R data	$\mathrm{Cu}\overset{\mathrm{O}}{\wedge}\mathrm{Cu}$	575 cm^{-1}		—	
	Cu — Cl	—		293 cm^{-1}	

Table 2

(0.54 g) in anhydrous methanol (15 ml) and finally pyridine (1 ml) was added. The reaction mixture was stirred and heated for 2h at the temperature of refluxing methanol using a magnetic hot plate stirrer setting of 30% .

Green and brown solids were formed. The first product which precipitated was brown and after filtering, the green material was deposited from the green filtrate on cooling to room temperature. Analytical data showed that the green product was Dibromobispyridine-copper(II) and the brown one was Di-μ-methoxobis(bromopyridinecopper(II).

Physical data are given in table (3).

3.6 Experiments to form the above Described Complex on Montmorillonite

This was attempted in three ways :

a) contact of clay with solution of the dry complex in an organic solvent.

b) synthesis of the complex in the presence of clay.

c) synthesise complex,add clay without separation of complex.

a) $[Cu(OMe)(Py)Cl]_2$ complex (1 g) was dissolved in acetonitrile (100 ml) and then montmorillonite (5 g) was added and stirred and heated for 2h at the temperature of refluxing methanol using a magnetic hot plate stirrer setting of 30% .

b) anhydrous copper(II) chloride (1.35 g) was dissolved in anhydrous methanol (50 ml) and then it was mixed with a solution of sodium methoxide (0.54 g) in anhydrous methanol (15 ml) and pyridine (1 ml). This mixture was added to a natural montmorillonite (5 g) and it was stirred and heated for 2h at the temperature of refluxing methanol

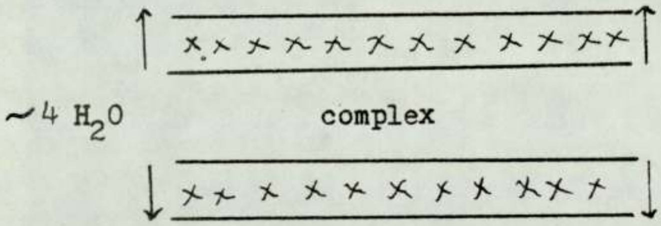
Complexes	$Cu(OMe)(Py)Br$			$Cu(Py)_2Br_2$	
		Found%	Required% For $C_{12}H_{16}Br_2Cu_2N_2O_2$	Found%	Required% For $C_{10}H_{10}Br_2CuN_2$
Analytical data	C	22.6	28.4	32.7	31.4
	H	2.12	3.15	3.09	2.69
	Cu	25.4	25.0	16.50	16.61
	N	5.15	5.52	7.23	7.33
I.R data	Cu–O–Cu		570 cm^{-1}		———
	Cu — Br		———		257 cm^{-1}
Magnetic moment		1.40 B.M		———	
E.S.R data		too broad to get g-value		$g = 2.116 \pm 0.050$	

Table (3)

using a magnetic hot plate stirrer setting of 30% .

c) $[Cu(OMe)(Py)Cl]_2$ complex was made as was described in the preparation section, and then montmorillonite (5 g) was added and the mixture was stirred for 24 h.

In practice (c) was the most effective method for preparation of $[Cu(OMe)(Py)Cl]_2$ on clay. It was necessary to develop a method to check that the complex had been taken up by the clay. Infrared spectroscopy was chosen. If the complex is truly taken up, the molecules should be located in the inter layer region of the clay sturcture. (Fig 9)



separation of layers is believed to be sufficient to accommodate 4 water molecules.

(Fig 9)

Since this environment must differ from that in the crystal, some small change in infrared spectrum should occur. In particular the following may be observed.

i) small frequency shifts.

ii) some change of band multiplicity.

In practice a small but significant frequency shift was observed which is considered not to be consistent with a mixture of crystals of " Cu(OMe)(Py)Cl " and clay, but is consistent with absorption of the above type (Fig 9).

This technique has been much used by soil scientists.[12] The infrared spectra of the products from the three methods and the complex itself are illustrated in figures 10 and 11 respectively.

The e.s.r spectra of the products from the three methods and of the complex itself are shown in figures 12,13,14,15 respectively. An e.s.r spectrum with two g-values was obtained for preparation (c), $g_{\parallel} = 2.223 \pm 0.024$ and $g_{\perp} = 2.068 \pm 0.019$, and an isotropic e.s.r spectrum for preparation (b) , with a g-value of 2.116 ± 0.007 and also a signal with a shoulder for preparation (a) with g-values of $g_{\parallel} = 2.192 \pm 0.002$ and $g_{\perp} = 2.109 \pm 0.002$. Therefore (c) was judged to be the best method, but no further information was obtained from e.s.r data.

Elemental analyses for percent of copper in the complex which was formed on the clay was performed by mixing clay plus copper complex (0.5 g) in boiling concentrated nitric acid. The solid was filtered and was dried in an oven at 40°C. The difference between the weight of clay plus complex before treatment with acid, and after was due to the amount of complex on the clay. The acid solution was diluted with distilled water to 250 ml then (5ml) of this solution was diluted with distilled water to 100 ml and was titrated with EDTA (chapter II section 2.9.1). Elemental analyses for percent of C H N also were performed by the microanalytical laboratories of the chemistry department. Magnetic susceptibility of the anchored copper complex with clay was also measured. Data are presented in table (4).

A sedimentation technique for X-Ray analysis was used to determine the (001) basal spacing of the silicate layer after uptake of the copper (II) complex. Natural montmorillonite and the clay supported copper complex (1 g) were suspended separately in 50 ml of 0.1 %

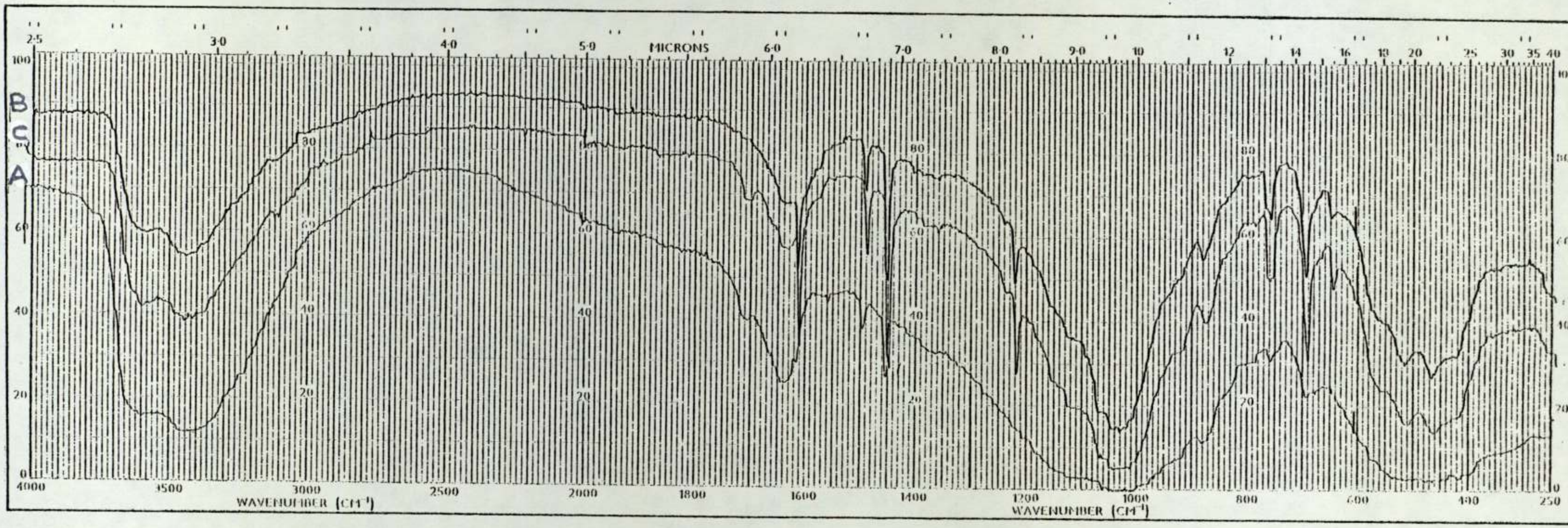
sodium hexametaphosphate and shaken up for 10 min, then set aside for 5 min. After this time some material from the centre of the suspension was taken by pipette and placed on a glass slide and allowed to dry in air and then analysed by x-ray diffraction. Data are given in table (5).

Compounds		method (a)	method (b)	method (c)	Cu(OMe)(Py)Cl
			Found %		Required %
Analytical data	C	16.06	28.80	35.31	34.40
	H	2.70	2.70	3.92	3.82
	Cu	15.65	33.60	29.66	30.30
	N	3.60	6.60	6.86	6.69
Magnetic moment		0.576 B.M	0.689 B.M	1.06 B.M	1.30 B.M

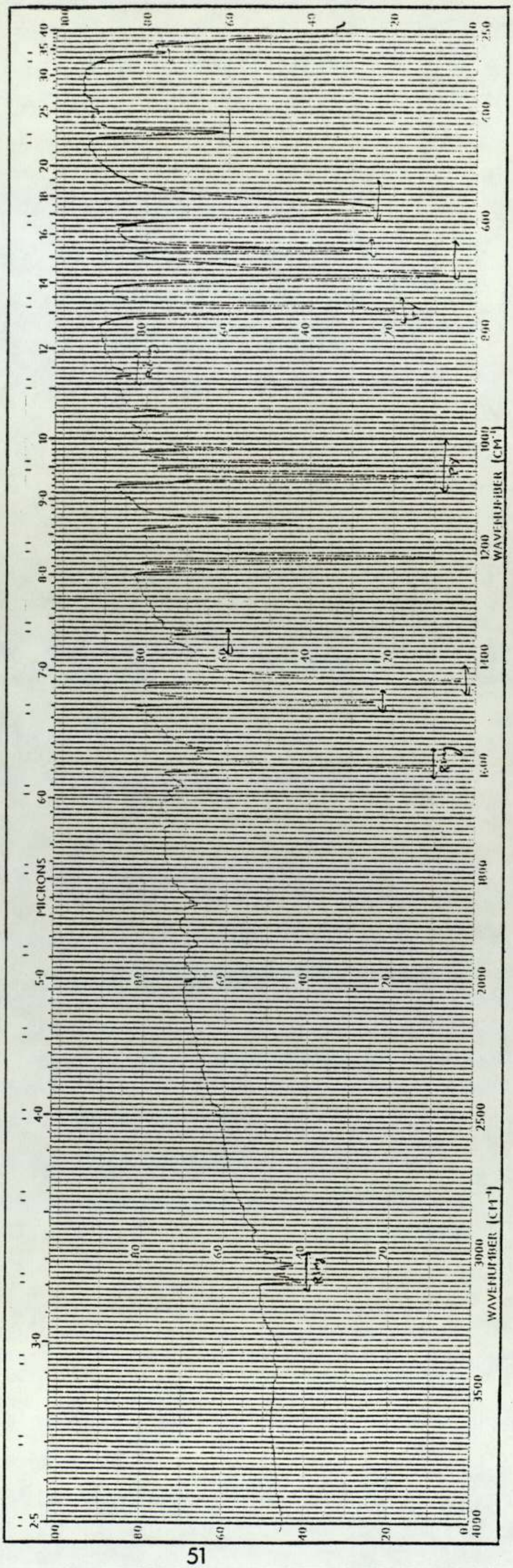
Table (4)

Compound	montmorillonite	method (a)	method (b)	method (c)
(001) spacing Å	13.6	13.5	21.8	2o.7

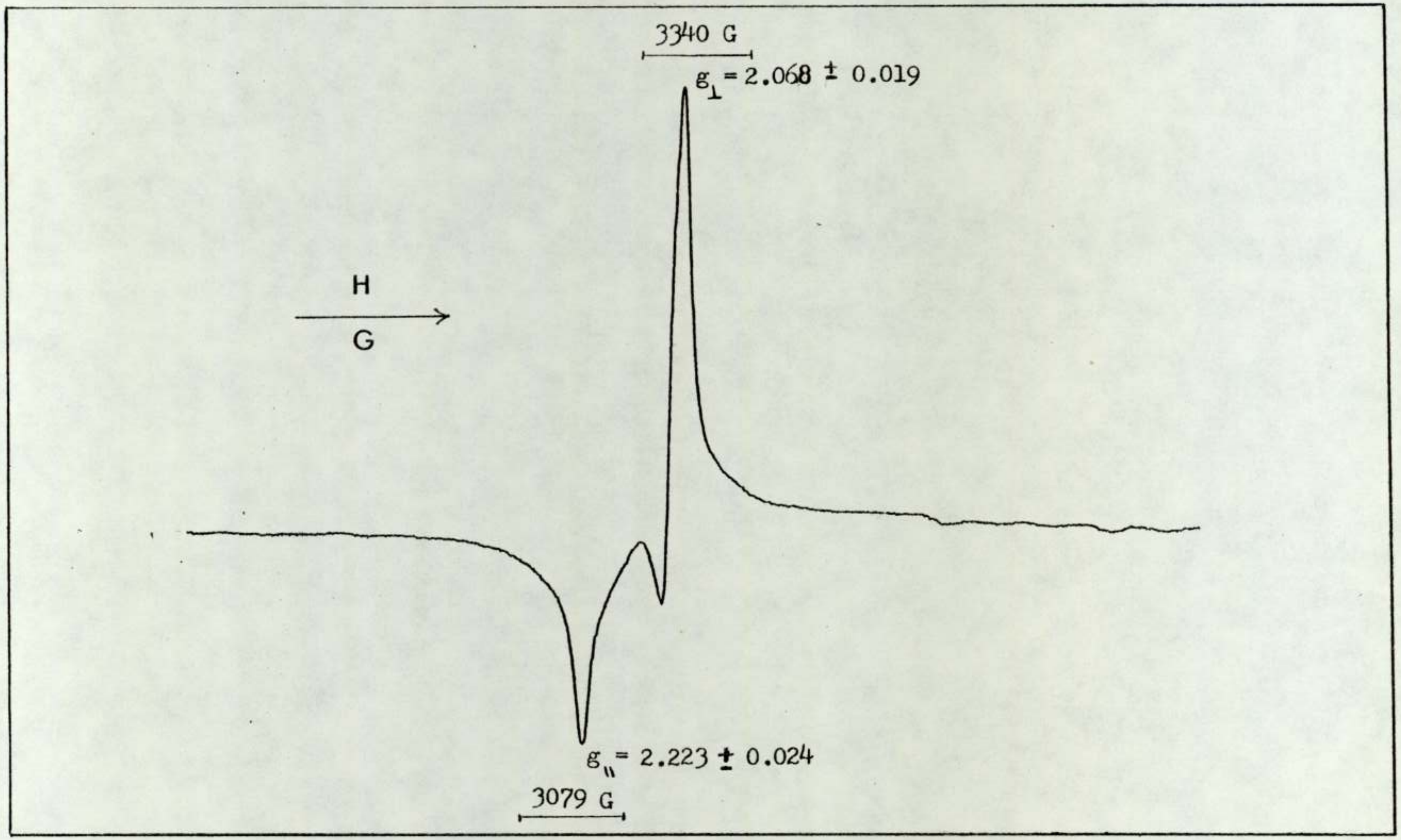
Table (5)


MICRONS
2·5
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
18
20
25
30
35
40
B
C
A
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)

(Fig 10)

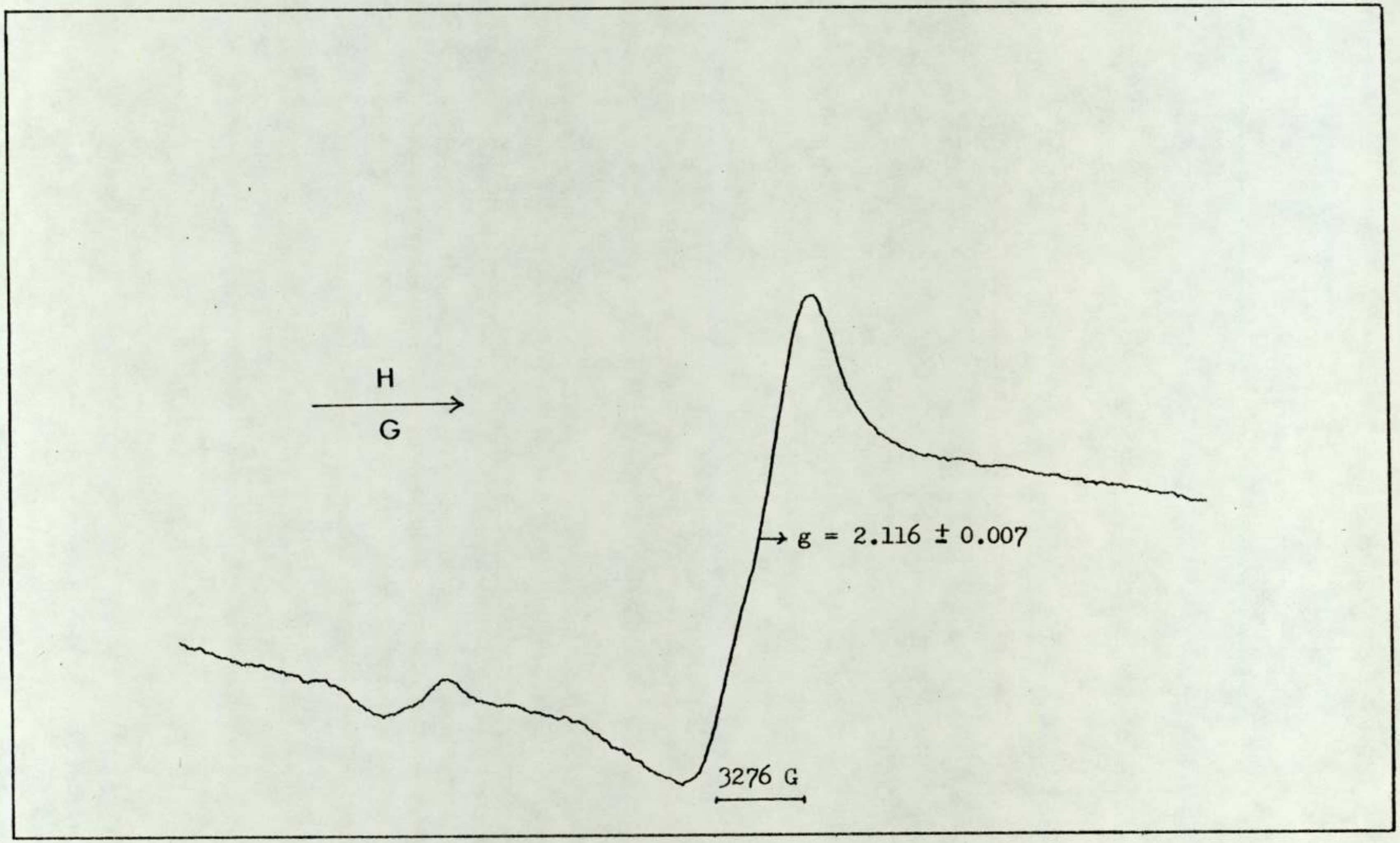

MICRONS
2·5
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
18
20
25
30
35 40
WAVENUMBER (CM^{-1})
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
0
20
40
60
80
100
Py

(Fig 11)

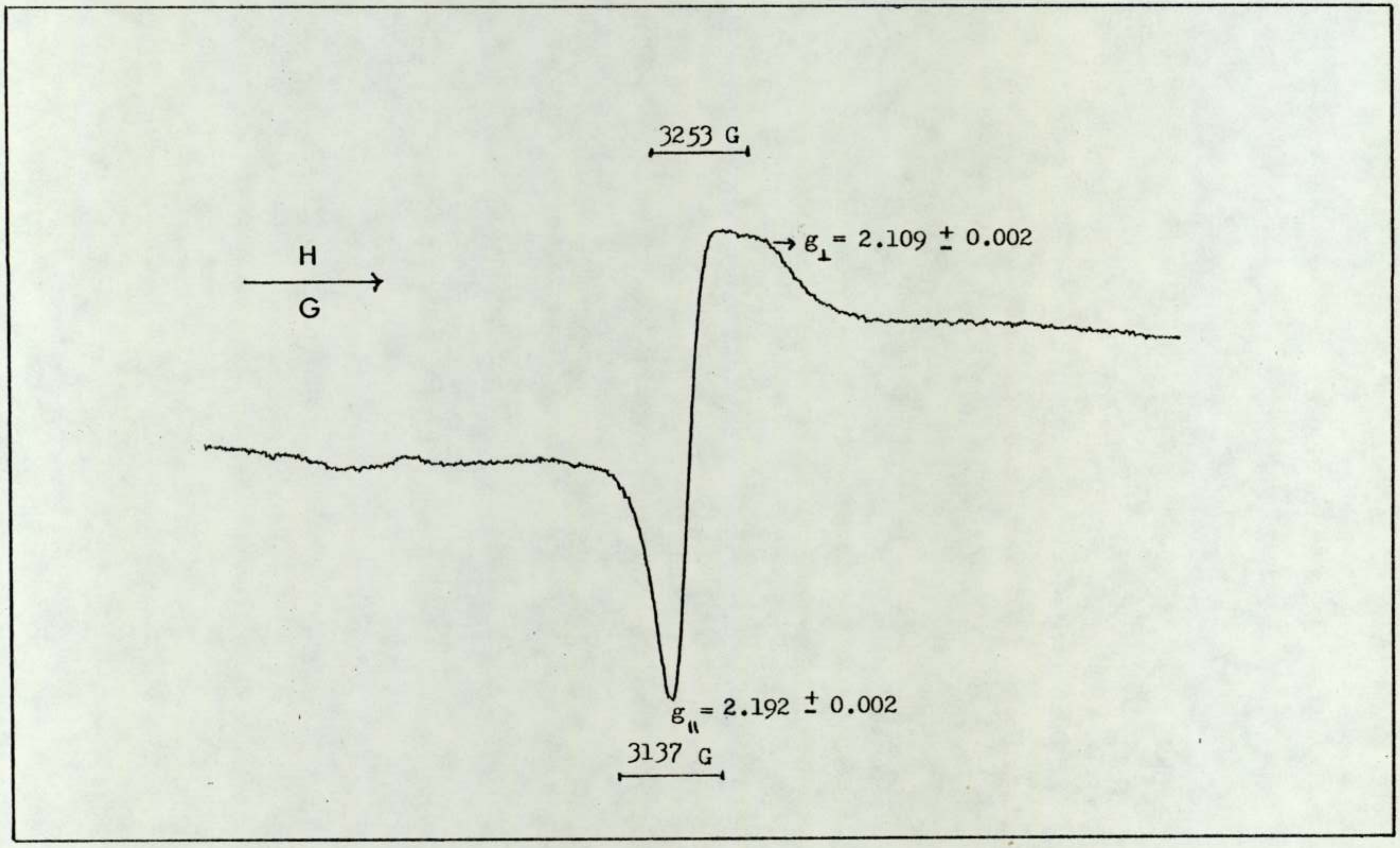


(Fig 12)

ESR spectrum of method (c)

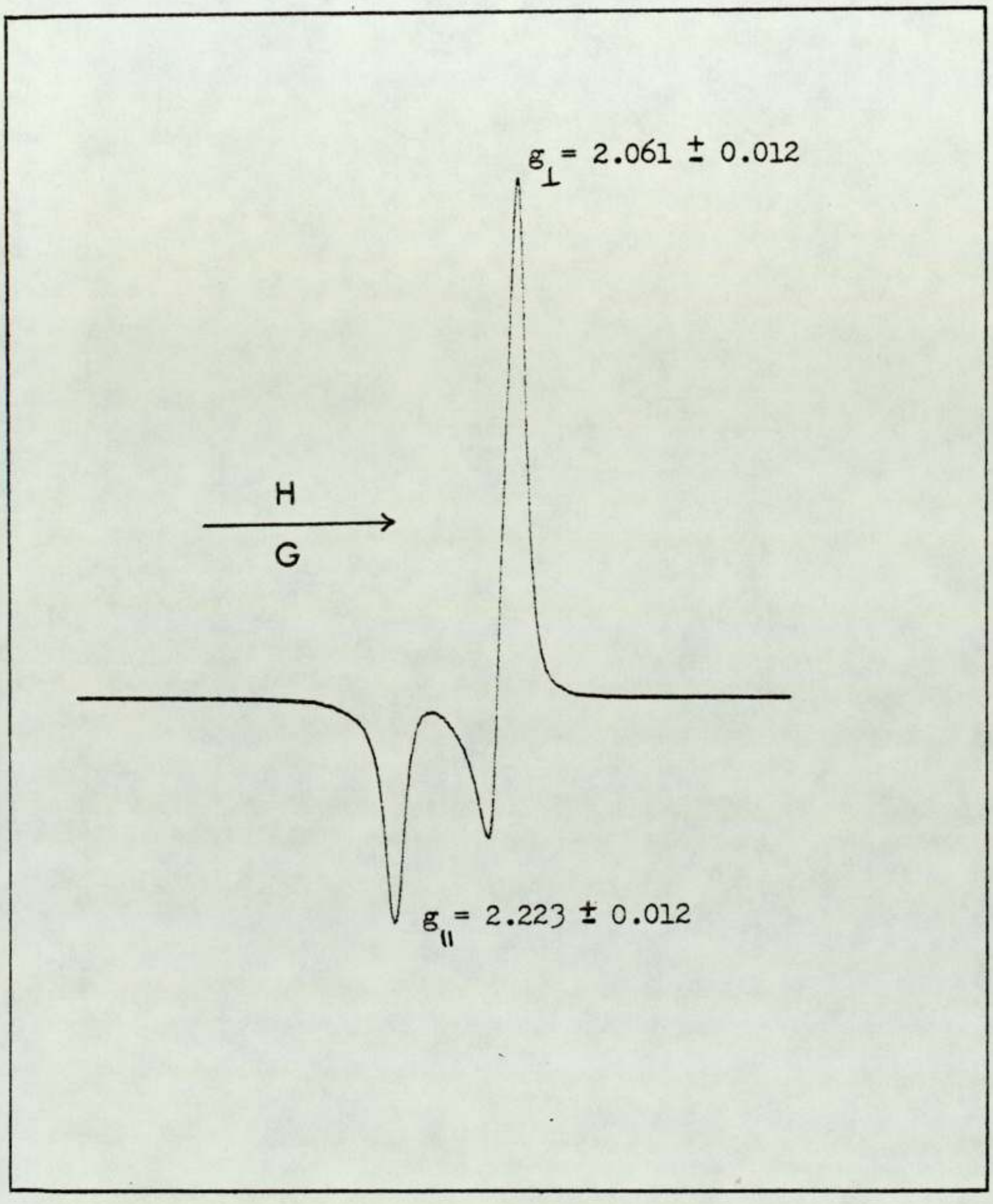


(Fig 13)
ESR spectrum of method (b)



(Fig 14)

ESR spectrum of method (a)



(Fig 15)
ESR spectrum
of
$(Cu(OMe)(Py)Cl)_2$

3.7 The Carbon-Carbon Bond Cleavage of Phenol in the Presence of Complex

3.7.1 : Phenol (0.5 g) was dissolved in chloroform (25 ml) and then was mixed with $[Cu(OMe)(Py)Cl]_2$ complex (0.1 g), then warmed and stirred for 2 h. The reaction mixture was cooled and the solid product isolated on a No4 sintered glass crucible, and dried at room temperature under vacuum.

3.7.2 : Phenol (0.5 g) was dissolved in pyridine (10 ml) and methanol (1 ml), then this solution was mixed with $[Cu(OMe)(Py)Cl]_2$ complex (0.2 g) and stirred and heated for 2 h.

3.7.3 : $[Cu(OMe)(Py)Cl]_2$ complex (0.1 g) was mixed with an aqueous solution of phenol (25 ml/0.1M) and stirred for 24 h.

3.7.4 : Montmorillonite supported $[Cu(OMe)(Py)Cl]_2$ complex (1 g) was mixed with an aqueous solution of phenol (25 ml/0.1M) and stirred for 24 h.

3.7.5 : Montmorillonite supported $[Cu(OMe)(Py)Br]_2$ complex (0.1 g) was mixed with an aqueous solution of phenol (25 ml/0.1M) and warmed and stirred for 2 h.

In all cases infrared spectra were obtained and compared with the copper complex and clay supported complex spectra. No change was observed.

3.8 Preparation of other Copper Complexes

3.8.1 : Di-μ-ethoxo-bis-[di-(2-aminopyridine)copper(II)] dinitrate and Di-μ-methoxo-bis-[di-(2-aminopyridine)copper(II)] dinitrate.

$[(2\text{-ampy})_2Cu(OR)_2Cu(2\text{-ampy})_2](NO_3)_2$

(R = Et or Me)

Copper(II)nitrate trihydrate (0.48 g) and 2-aminopyridine (2.0 g) were dissolved in ethanol (or methanol) (20 ml) and stirred for 6 h. An olive-green product separated slowly from the ethanolic, and a dark green product from the methanolic solution. Complexes were filtered on a No4 glass sintered crucible and dried at room temparature under vacuum.

Physical data[44] for these compounds are presented in table (6).

3.8.2 : Di-μ-hydroxo-bis-[2,2'-bipyridylcopper(II)]diperchlorate

$[(bipy)Cu(OH)_2Cu(bipy)(ClO_4)_2]$

Copper(II)perchlorate (0.34 g) in water (10 ml) buffered at pH = 9 was mixed with 2,2'-bipyridyl (0.16 g) and a mauve-grey solid was formed after 2 h stirring under reflux. This was filtered off on a No4 glass sintered crucible and washed with water and dried at room temperature under vacuum. The blue solution which was isolated after cooling gave blue crystals.

Physical data of these compounds are shown in table (7).

3.8.3 : [2,2'-bipyridylcopper(II)] chloride

$[Cu(bipy)Cl_2]$

Anhydrous copper(II)chloride (1.34 g) was dissolved in methanol (25 ml) and then 2,2'-bipyridyl (1 g) was added and the mixture was stirred and warmed. A light green precipitate was isolated and dried. Physical data are given in table (8).

3.8.4 : [2,2'-bipyridylcopper(II)]nitrate

$Cu(bipy)(NO_3)_2$

2,2'-bipyridyl (0.4 g) was dissolved in ethanol (25 ml) and then was added to a solution of copper nitrate (0.96 g) in ethanol (25 ml). This mixture was stirred for 24 h and a navy-blue product was separated by filtration.

Analytical data are presented in table (9).

3.8.5 : Di-μ-butanoxo-di[bis-(2-aminopyridine)copper(II)] dinitrate.

$(2\text{-ampy})_2Cu(OC_4H_9)_2Cu(2\text{-ampy})_2(NO_3)_2$

Copper nitrate (0.96 g) was dissolved in butan-1-ol (50 ml) whilst 2-aminopyridine (4 g) was dissolved also in butan-1-ol (50 ml) and these solutions were mixed and stirred for 2 h. A dark green product was formed and its physical data are shown in table (10).

3.8.6 : Di-μ-methoxo-bis-(2-aminopyridine)chlorocopper(II)

$(2\text{-ampy } Cl)Cu(OMe)_2Cu(2\text{-ampy } Cl)$

2-aminopyridine (0.94 g) was dissolved in anhydrous methanol (50 ml) and was added to solution of anhydrous copper chloride (1.34 g) in anhydrous methanol (50 ml) and then sodium methoxide (0.54 g) in anhydrous methanol (10 ml) was added and stirred for 18 h. The green product was isolated on a No4 glass sintered crucible and dried at room temperature under vacuum. Pysical data are presented in table (11).

Complexes		$[(2\text{-ampy})_2(OC_2H_5)CuNO_3]_2$		$[(2\text{-ampy})_2(OCH_3)CuNO_3]_2$	
		Found%	Required% For $(C_{12}H_{17}CuN_5O_4)_2$	Found%	Required% For $(C_{11}H_{15}CuN_5O_4)_2$
Analytical data	C	38.10	40.15	36.95	38.30
	H	4.80	4.78	4.7	4.5
	Cu	17.78	17.70	20.6	20.3
	N	19.8	19.5	17.14	18.40
Magnetic moment		0.673 B.M		0.796 B.M	
E.S.R data		g = 2.058 ± 0.020		g = 2.063 ± 0.010	
I.R data cm^{-1}	NH_2(stretch)	3420,3220		3400,3350	
	NH_2(deform)	1632		1648,1630	
	Anion bands	1380s,1320s 1050m,828m		1380s,1322s 1o55m,832m	
	700-800 cm^{-1}	780s ,772 741		776,772 742	

Table (6)

Compounds		$[(bipy)(OH)(Cu)ClO_4]_2$ mauve-grey		$Cu(bipy)_3(ClO_4)_2$ blue	
		Found%	Required% For $(C_{10}H_9ClCuN_2O_4)_2$	Found%	Required% For $C_{30}H_{24}Cl_2CuN_6O_8$
Analytical data	C	37.6	37.7	48.35	49.28
	H	2.99	2.67	3.15	3.28
	Cl	10.60	10.56	10.90	9.71
	Cu	18.41	18.89	8.89	8.69
	N	8.52	8.33	11.15	11.49
I.R data cm^{-1}	OH	3620		——	
	700-800 cm^{-1}	775,733		760,735,750	
	Anion band ClO_4^-	1087s,b,933w		1087s,b,930w	
E.S.R data		g = 2.072 ± 0.019		——	

Table (7)

Complex	Analytical Data			E.S.R Data	Magnetic moment
		Found%	Required% $C_{10}H_8Cl_2CuN_2$		
Cu(bipy)Cl_2	C	41.6	41.3	$g_{\parallel} = 2.253 \pm 0.010$ $g_{\perp} = 2.050 \pm 0.010$	1.39 B.M
	H	3.03	2.75		
	Cl	25.70	24.44		
	Cu	22.0	21.9		
	N	9.38	9.64		

Table (8)

Complex	Analytical Data			E.S.R Data	I.R Data
		Found%	Required% $C_{10}H_8CuN_4O_6$		
Cu(bipy)$(NO_3)_2$	C	33.7	34.9	$g_{\parallel} = 2.260 \pm 0.010$ $g_{\perp} = 2.060 \pm 0.011$	$\nu(NO_3)^-$ 1375 cm^{-1}
	H	2.65	2.32		
	Cu	18.41	18.48		
	N	16.40	16.30		

Table (9)

Complex	$(2\text{-ampy})_2(OC_4H_9)CuNO_3)_2$		
Analytical data		Found%	Reqired% $(C_{14}H_{21}CuN_5O_4)_2$
	C	43.55	43.46
	H	5.65	5.43
	Cu	16.51	16.42
	N	18.55	18.11
I.R data cm^{-1}	NH_2(stretch)		3420 , 3220
	NH_2(deform)		1635
	700-800 cm^{-1}		770 , 739
	Anion bands		1360 s , 1385 s , 1050-830
Magnetic moment	0.774 B.M		
E.S.R data	$g = 2.063 \pm 0.006$		

Table (10)

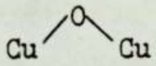
Compex	$(Cu(OMe)(2\text{-}ampy)Cl)_2$		
Analytical data		Found%	Reqired% $(C_6H_9ClCuN_2O)_2$
	C	29.00	32.14
	H	3.80	4.01
	Cu	28.57	28.34
	N	11.9	12.5
I.R data cm^{-1}	NH_2(stretch)		3440 , 3330
	NH_2(deform)		1630
	 $Cu\overset{O}{\wedge}Cu$		580
	Cu——Cl		345
Magnetic moment	1.32 B.M		
E.S.R data	g = 2.080 ± 0.005		

Table (11)

3.8.7 : $Cu_4(Py)_4Cl_8.BuOH$

Anhydrous copper chloride (1.34 g) was dissolved in butan-1-ol (50 ml) and then pyridine (1.5 ml) was added and stirred for 24 h. The light green product was filtered on a No4 glass sintered crucible and dried at room temperature under vacuum. Analytical and e.s.r data are shown in table (12).

Complex	$Cu_4(Py)_4Cl_8.BuOH$		
		Found%	Required% $C_{24}H_{30}Cl_8Cu_4N_4O$
Analytical data	C	30.90	31.03
	H	3.00	3.23
	Cl	30.6	30.6
	Cu	27.30	27.37
	N	6.60	6.03
E.S.R data	$g_{\parallel} = 2.222 \pm 0.002$ $g_{\perp} = 2.066 \pm 0.002$		

Table (12)

3.9 Synthesis of Clay Supported Complexes

3.9.1 : Di-μ-ehtoxo-di-[bis-2-aminopyridinecopper(II)] dinitrate and Di-μ-methoxo-di-[bis-2-aminopyridinecopper(II)] dinitrate :

a) montmorillonite (10 g) was covered with copper nitrate solution (100 ml/0.1M) and stirred for 24 h. The mixture was filtered and the solid dried in air at room temperature. This solid (5 g) was mixed with ethanol (or methanol) (25 ml) and added to a solution of 2-aminopyridine (2 g i.e. excess) in ethanol (or methanol) (25 ml) and stirred for 48 h. The product was isolated on a filter paper and dried at room temperature under vacuum.

b) the above 2-aminopyridine complexes were prepared as discribed in the preparative section then montmorillonite (5 g) was added to these and stirred for 2 h.

c) the above 2-aminopyridine complexes (0.5 g) were dissolved in acetone (100 ml) montmorillonite (5 g) then added and the mixture stirred for 24 h.

From the infrared spectra which were obtained for each case, it was deduced that preparations (a) and (b) were the most effective methods for introducing the complexes to the clay. Some small frequency shifts were observed which was not thought to be consistent with a mixture of crystals of complex and clay, but is consistent with absorption of the complex by clay.

Physical data for these complexes supported on the clay are presented in tables (13) and (14).

Compounds	$(2\text{-ampy})_2(OC_2H_5)CuNO_3)_2$	method (a)	method (b)	method (c)	montmorillonite
I.R data cm^{-1}	NH_2(stretch) 3420,3220	3400,3220	3420,3220	—	—
	NH_2(deform) 1632	1630	1632	1632	
	Anion bands 1380,1320 1050,828	1380,1325 —,825	1380,1320 —,825	1380,1320 — ,—	
	700-800 cm^{-1} 780, 772	—, 776	778, 771	—	
X-Ray data (001)d spacing Å	—	15.5	15.7	13.6	13.6
E.S.R data	g = 2.058 ± 0.020	g = 2.064 ± 0.014	g = 2.069 ± 0.009	g = 2.035 ± 0.014	—
Magnetic moment	0.673 B.M	1.12 B.M	1.31 B.M	0.801 B.M	—

Table (13)

Compounds	$(2\text{-ampy})_2(OCH_3)CuNO_3)_2$	method (a)	method (b)	method (c)	montmorillonite
I.R data cm^{-1}	NH_2(stretch) 3400,3350	3398,3345	3400,3350	——	——
	NH_2(deform) 1648,1630	1668,1630	1668,1630	1648,1630	
	Anion bands 1380,1322	1380,1321	1382,1322	1380, ——	
	1055, 832	— , 832	— , 832	——	
	700-800 cm^{-1} 776, 772 742	778, 770	777, 772 742	——	
X-Ray data (001)d spacing Å	——	16.7	16.0	13.5	13.6
E.S.R data	g = 2.063 ± 0.010	g = 2.067 ± 0.010	g = 2.066 ± 0.002	g = 2.005 ± 0.024	——
Magnetic moment	0.796 B.M	1.22 B.M	1.13 B.M	0.902B.M	——

Table (14)

3.9.2 : Di-μ-hydroxo-bis-[2,2'-bipyridylcopper(II)] diperchlorate

a) montmorillonite (10 g) was covered with a copper perchlorate solution (100 ml/0.1M) and stirred for 24 h. The mixture was filtered and dried in air at room temperature. This solid (5 g) was mixed with water (50 ml), buffered at pH = 9, and then added to a solution of 2,2'-bipyridyl (0.16 g) in water (50 ml) also buffered at pH = 9 and the mixture was stirred and refluxed for 8 h. The reaction mixture was then filtered and dried at room temperature under vacuum.

b) the above 2,2'-bipyridyl complex was prepared as discribed in the preparation section and montmorillonite (5 g) was added and the mixture stirred for 24 h.

c) the above 2,2'-bipyridyl complex (0.5 g) was dissolved in methanol then montmorillonite (5 g) was added and the mixture stirred for 24 h.

The infrared spectrum showed that preparation (a) was the best method in this case. Some evidence of absorption of complex by clay was observed.

Physical data for this complex supported on the clay are given in table (15).

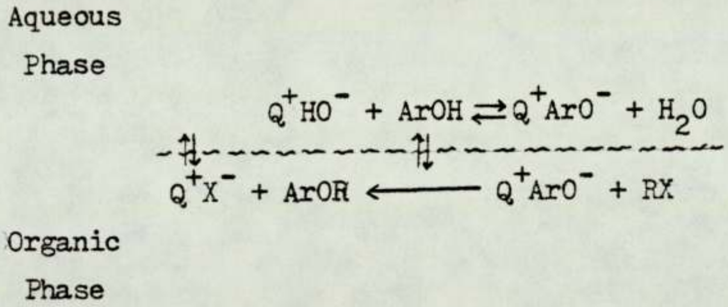
The complexes supported on the clay as well as the pure complexes themselves were reacted with phenol as described in a previous section (page 56, section 3.7). The infrared spectrum of the complex after reaction with phenol was compared with the infrared spectrum of the pure complex and no changes were observed. Similarly no changes were observed when the infrared spectrum of the clay plus complex after reaction with phenol was compared with the infrared spectrum of the clay plus complex.

Compounds	(bipy)(OH)CuClO$_4$)$_2$	method (a)	method (b)	method (c)	montmorillonite
I.R data cm^{-1}	OH 3620 700-800 cm^{-1} 775,733 Anion band ClO_4^- 1087,933	3620 765,739 obscured by vibration of silicate structure	3600 —— ——	3600 —— ——	3600 ——
E.S.R data	g = 2.072 ± 0.019	g = 2.097 ± 0.001	g = 2.111 ± 0.001	g = 2.077 ± 0.001	——
X-Ray data (001)d spacing Å	——	19.2	13.1	13.6	13.6
Magnetic moment	1.51 B.M	1.18 B.M	0.650 B.M	0.845 B.M	——

Table (15)

3.10 The Use of Phase-Transfer Catalysis (PTC) for the Synthesis of Phenol Ethers.

Phase-transfer catalysis is a technique which has been the subject of much interest in recent years. As applied to the alkylation of phenols, the process can be represented schematically as shown in (Fig 16). ($Q^+ = R_4N$)



(Fig 16)

In practice, the phenol is added to a two-phase system consisting of an aqueous solution of the quaternary ammonium hydroxide and a dichloromethane solution of the alkylating agent. The phenol, which in most cases is partitioned naturally between the two phases, is converted into the corresponding quaternary ammonium phenoxide in the aqueous phase. This latter salt has a discrete solubility in the organic phase; consequently, transport of the phenoxide ion into the dichloromethane solution is followed by rapid irreversible alkylation and formation of the phenol ether.

In this work the use of clay supported PTC was investigated since it is thought that the water associated with the exchangable cations may be able to function as the aqueous phase when the clay is present in an organic medium.

Quaternary Ammonium Salts : Benzyl bromide (12 ml) was added to tri-n-butylamine (24 ml), and stirred for 2 h. A white solid which was benzyltri-n-butylammonium bromide was formed. The quaternary ammonium hydroxide was prepared first by the passage of an aqueous solution of benzyltri-n-butylammonium bromide through a basic ion exchange resin as described in the literature.[37] However this method did not appear to be successful in making quaternary ammonium hydroxide. A second method involved the mixing of sodium hydroxide (4M) with an anion resin (C$\bar{l}$) and the mixture was stirred for 24 h. The mixture was filtered and dried in air. This solid (2 g) was mixed with quaternary ammonium salt (2 g) in water (100 ml) and stirred for 24 h. This method proved to be successful in the preparation of quaternary ammonium hydroxide.

Phenol ether was prepared as is described in the literature.[37] Mass spectroscopy and g.l.c showed that the desired compound was made.

e.g. P^+ m/e = 150 (calculate = 150.10417) $C_{10}H_{14}O_1$(given=150.104459)

3.11 Synthesis of Phenol Ethers in the Presence of Clay

3.11.1 : Quaternary ammonium salt (5 g) and anion resin (O$\bar{H}$) (2 g) were mixed in water (100 ml) and stirred for 24 h , then montmorillonite (10 g) was added to above solution after separation of the resin and the mixture was stirred for 24 h, filtered and dried in air.

This solid (6.5 g) was mixed in water (150 ml) and was added to a solution of phenol (1.92 g) in dichloromethane (150 ml) and 1-bromobutane (10 ml) was added and stirred at room temperature for 7 days. A solid was isolated by filtration and washed with dichloromethane. The organic layer was then separated and the aqueous layer extracted twice with (20 ml) portions of dichloromethane. The combined organic extracts were evaporated, the residue mixed with water, and the mixture extracted with ether. The organic extract was washed twice with sodium hydroxide solution (2M) to remove unreacted phenol, and finally with saturated sodium chloride solution. After drying with sodium sulphate, the solvent was evaporated.

3.11.2 : (clay + Q^+ + OH^-) (6 g) was mixed with dichloromethane (150 ml) and then phenol (1.92 g) and 1-bromobutane (10 ml) was added and the mixture stirred for 5 days. The mixture was filtered and washed and the organic layer was separated as described above.

3.11.3 : Quaternary ammonium salt (5 g) was dissolved in water (100 ml) and montmorillonite (10 g) was added and stirred for 24 h. Then the solid was isolated on filter paper and dried in air. This material (5 g) was mixed with dichloromethane (150 ml) and phenol (1.92 g), 1-bromobutane (10 ml) and sodium hydroxide (22.5 ml/4M) were added and the mixture was stirred for 24 h. A solid was separated and the organic layer was extracted as described previously.

In all cases the product obtained showed a mass spectrum of (PhOBu) and infrared spectrum and g.l.c compared with commercial (PhOBu) was the same.

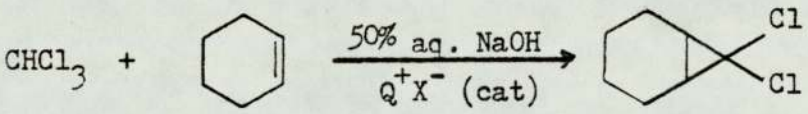
3.11.4 : A mixture of dichloromethane (100 ml), water (100 ml), phenol (1.88 g), sodium hydroxide (1.2 g), quaternary ammonium salt

(0.712 g) and ethylmonobromoacetate (8 ml) was mixed and stirred at room temperature for 24 h. Some of the organic layer was separated and g.l.c showed there was some unreacted phenol, but after 48 h all of phenol was reacted and converted to the ether.

3.11.5 : (clay + Q^+ + OH^-) (2.5 g) was mixed with water (100 ml) and then phenol (1.88 g) in dichloromethane (100 ml) and ethylmonobromoacetate (8 ml) were added and the mixture stirred for 24 h. Every 24 h g.l.c showed that the ether had formed, but there was also some unreacted phenol.

3.12 The Reaction of Dichlorocarbene with Alkenes

The observation that dichlorocarbene could be generated in a two phase aqueous -organic system containing sodium hydroxide was the first to capture the attention of the organic chemical community to phase transfer techniques. Both Starkes[45] and Makosza[46] reported the dichlorocyclopropanation of cyclohexene in the late 1960's. The reaction was conducted as shown in the following equation.



Dichlorocyclopropane was prepared as described in literature.[45]

3.12.1 : Montmorillonite (10 g) was covered with a solution of quaternary ammonium bromide (5 g) in water (100 ml) and stirred for 24 h. The solid was then isolated on a filter paper and dried in air. This solid (2 g) was mixed with cyclohexene (17 ml) and sodium hydroxide

(21.5 ml, 50%) and stirred at 45°-50°C and then chloroform (8 ml) was added dropwise over a period of 30 minutes and when it finished the reaction mixture was stirred at room temperature for 1 h. The mixture was filtered and the organic layer separated and washed with water (200 ml) twice. The last wash gave an emulsion which was broken by the addition of saturated sodium chloride solution (10 ml), and also with chloroform. Analysis of the organic layer by g.l.c showed that the expected compound was obtained.

3.12.2 : 1-phenyl-2,2-dichlorocyclopropane was made as described in literature.[46]

3.12.3 : (clay + Q^+) (1 g), styrene (11.44 ml) and chloroform (16.02 ml) and aqueous solution of sodium hydroxide (20 ml, 50%) were stirred at 40°C for 4 h. Then the organic layer was separated.

3.13 The Use of Phase-Transfer Catalysis in Organometallic Chemistry

Bis-p-ethoxy-phenylditelluride was prepared as described in literature.[47]

3.13.1 : Ditelluride (1 g) was dissolved in benzene (50 ml) and stirred; dibromobutane (3.5 ml) in benzene (25 ml) was then added dropwise. A mixture of sodium hydroxide (0.6 g) in water (25 ml) and sodium-borohydride (1 g) in water (25 ml) was added dropwise over a period of 30 minutes. Finally (clay + Q^+) (2 g) was mixed with water (25 ml) and added to the above mixture and the container was covered with aluminium foil and stirred for 42 h. The mixture was filtered off. The off-white solid was then extracted in a soxhlet extractor with acetonitrile for 2 h.

3.13.2 : Ditelluride (2 g) was dissolved in benzene (50 ml) with stirring, then sodium-borohydride (1 g) in water (25 ml) was added drop by drop. Then (clay + Q^+ + $O\bar{H}$) (2 g) mixed with water (25 ml), was added. Finally dibromobutane (3.5 ml) in benzene (25 ml) was added and the container was covered and stirred for 48 h. The product was filtered and the solid dried in air. A white solid was obtained by extraction in a soxhlet extractor with acetonitrile for 2 h. The yield of product was more than that of former experiment.

3.13.3 : Ditelluride (1 g) was dissolved in benzene (25 ml) and a mixture of sodium-borohydride (1 g) in a solution of sodium hydroxide (3 ml/4M) was added dropwise. Following this a mixture of (clay + Q^+) (2 g) and dibromobutane (3.5 ml) in benzene (25 ml) was added and the container was covered and stirred for 24 h. A white compound was obtained as previously described. In this reaction the product was formed in a short time compared with the two former methods, but the product yield was less.

All of these reactions were repeated with dichlorobutane and similar results were obtained. Elemental analyses for these compounds are given in table (16).

3.13.4 : Reaction between chloro-tris(triphenylphosphine)-rhodium(I) and sodium acetate under phase-transfer conditions.

Chloro-tris(triphenylphosphine)rhodium(I) was prepared as was reported in the literature.[48]

Chloro-tris(triphenylphosphine)rhodium(I) (0.1 g) was dissolved in benzene (50 ml) and a mixture of sodium acetate (1 g) and quaternary ammonium salt (0.5 g) and sodium hydroxide (0.6 g) was dissolved in water (50 ml) and then this solution was added to the above solution and stirred for 24 h. A yellow product was formed between two layers. This product was separated by evaporating the organic phase. Physical data are presented in table (17).

3.13.5 : Chloro-tris(triphenylphosphine)rhodium(I) (0.1 g) was dissolved in benzene (50 ml) then a mixture of sodium acetate (1 g) and (clay + Q^++OH^-) (1 g) was mixed with water (50 ml) and was added to the above solution and stirred for 24 h. A yellow product was formed at the interface of clay and organic layer. This product was separated by evaporating the organic layer.

3.13.6 : Trichloro(tripyridine)chromium(III). This compound was prepared by the method in the literature.[49] A green product was obtained which was shown to be a dimer instead of the expected monomer. This compound was insoluble in organic solvents, therefore no reaction was made in phase-transfer between acetate and the above compound.

Physical data for the new material are given in table (18).

Compounds	Analytical data		
		Found%	Required% $C_{12}H_{17}BrOTe$
$pEtOC_6H_4Te(CH_2)_4Br$	C	36.7	37.5
	H	4.40	4.42
	Br	23.00	20.83
		Found%	Required% $C_{12}H_{17}ClOTe$
$pEtOC_6H_4Te(CH_2)_4Cl$	C	41.30	42.41
	H	5.1	5.0
	Cl	10.95	10.45

Table (16)

Compound	$Rh(P(C_6H_5)_3)_3CO_2CH_3$		
Analytical data		Found%	Required% $C_{56}H_{48}O_2P_3Rh$
	C	70.60	70.88
	H	5.50	5.06
	P	9.22	9.81
Mass spectrum data	m/e 262 $C_{18}H_{15}P$ calculated = 262.09124 i.e Ph_3P^+ given = 262.09113		
I.R data cm^{-1}	$[\nu_{as}(OCO)]$	1650	

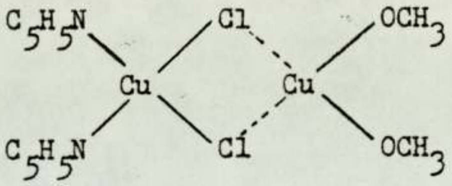
Table (17)

Compound	$[Cr_2(Py)_2Cl_2(OH).H_2O]_2$		
Analytical data		Found%	Required% $(C_{10}H_{13}Cl_2Cr_2N_2O_2)_2$
	C	39.50	37.97
	H	4.10	4.11
	N	8.53	8.86
Magnetic moment	2.02 B.M		
E.S.R data	$g = 1.988 \pm 0.011$		

Table (18)

3.14 Discussion

It is known that certain complexes of copper(II) can catalyse ring opening reactions of phenols (see introduction) one such complex is "Cu(OMe)(Py)Cl" formulated by Finkbeiner et.al [50] as :



The reaction of copper(II)chloride and bromide, with pyridine in methanol as a solvent, gives "Cu(OMe)(Py)X" and "$Cu(Py)_2X_2$" where X = Cl, Br. These compounds were identified by means of elemental analysis, infrared and e.s.r spectroscopy.

Dichlorobispyridinecopper(II) is a well known compound and was prepared for comparison with the material "Cu(OMe)(Py)Cl". "Cu(OMe)(Py)Cl" was prepared at room temperature and at the temperature of refluxing methanol (i.e.64°C). The room temperature preparation gave a product where the agreement between the expected analysis and that determined was poor; however the preparation at 64°C gave an elemental analysis which was in good agreement with the empirical formula. Evidence for the dimeric nature of this complex comes from three sources:

a) magnetochemistry : When the individual copper(II) ions in a complex are physically well separated from each other ($>$ 5 Å), then the effective magnetic moment[51] may be given by the spin-only value, (μs.o.), of 1.73 B.M. In practice, the experimental values at room temperature lie in the range 1.8-2.0 B.M., but when the individual copper(II) ions in a complex are not well separated from each other, then interactions can occur . In copper(II) complexes, these are antiferromagnetic in form and result in a reduction of the observed magnetic moment below the spin-only value. Thus, the observed magnetic moment of 1.30 B.M. for "Cu(OMe)(Py)Cl" is related to the close proximity of the two copper (II) ions. Such interaction is consistent with antiferromagnetically coupled copper(II) ions in a dimer. Antiferromagnetism has also been reported[52] for dichlorobispyridinecopper(II), which has been indicated to have a distorted polymeric octahedral structure.

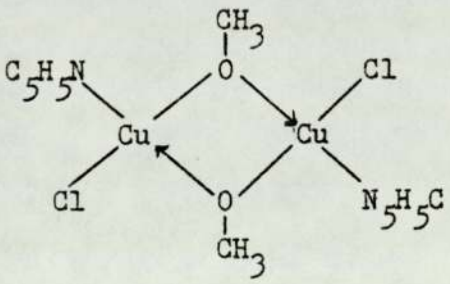
b) infrared spectroscopy : The infrared spectrum contains bands characteristic of $\nu(\mathrm{Cu}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{Cu})$ at 575 $\mathrm{cm^{-1}}$, in common with other well documented examples[53] e.g. $[(\text{2-ampy})_2\mathrm{Cu(OR)_2}](\mathrm{NO_3})$, where R = Me, Et and $[(\mathrm{bipy})\mathrm{Cu(OH)_2Cu}(\mathrm{bipy})](\mathrm{ClO_4})_2$. Paraffins, nitrate ion and perchlorate, chloride ions do not absorb strongly between 500 and 600 $\mathrm{cm^{-1}}$ and metal-nitrogen frequencies are belived to lie below 400 $\mathrm{cm^{-1}}$. [54]

c) e.s.r spectroscopy : "Cu(OMe)(Py)Cl" has an e.s.r spectrum with $g_{\perp} = 2.061 \pm 0.012$, $g_{\parallel} = 2.223 \pm 0.012$ and G = 3.65 measured as a powder.

Copper(II) has a free-ion ground state ^2D which is split by an octahedral crystal field to give doubly degenerate E_g ground state and a triply degenerate T_{2g} excited state. Axial distortions, as well as the Jahn-Teller effect in many cases, remove the degeneracy of the E_g orbital doublet and partially remove the degeneracy of the T_{2g} triplet. Generally the ground state is $dx^2 - y^2$ with an effective spin of 1/2 where

$g_{\parallel}=2.3$ and $g_{\perp}=2.07$. The g-values are related by the expression $G = g_{\parallel} - 2 / g_{\perp} - 2 = 4.0$. If $G > 4.0$ then local tetragonal axes are aligned parallel or only slightly misaligned, if $G < 4.0$ significant exchange coupling is present and the misalignment is appreciable.[55] From the result which was obtained for "Cu(OMe)(Py)Cl" it was found, for the two g-value spectrum, that the lowest g-value was greater than 2.0 thus indicating a $dx^2 - y^2$ ground state rather than a dz^2 ground state. Therefore it is consistent with an elongated tetragonal stereochemistry for individual copper(II) ions. The observation of a G-value lower than 4.0 (i.e. 3.65) indicates the presence of exchange coupling in tetragonal systems, which would be expected for a dimer complex. In this case dichlorobispyridinecopper(II) complex also gave good evidence, because it has a similar e.s.r spectrum to the complex under study. ($g_{\parallel} = 2.204 \pm 0.020$ and $g_{\perp} = 2.052 \pm 0.020$ and $G = 3.92$).

The balance of evidence suggests that the correct formulation of "Cu(OMe)(Py)Cl" is :



The preparation involving copper(II)bromide also gave two compounds : green "$\mathrm{Cu(Py)_2Br_2}$" and brown "Cu(OMe)(Py)Br" .

A copper-bromine stretching vibration is seen in the far infrared at 257 $\mathrm{cm^{-1}}$ (comparison with $\mathrm{Cu(Py)_2Cl_2}$). This compares with bands at 293 and 236 $\mathrm{cm^{-1}}$ for the chloro-analogue . A simple prediction, based on mass difference of the halogens would have predicted ν(Cu—Br) around 223 $\mathrm{cm^{-1}}$, thus it would be unwise to assume that "$\mathrm{Cu(Py)_2Cl_2}$" and green "$\mathrm{Cu(Py)_2Br_2}$" necessarily have the same structure. However, Morosin[56], has suggested that the structures are in fact similar.

An isotropic e.s.r spectrum was observed for dibromobispyridinecopper(II) which implies extensive exchange coupling between grossly misaligned local copper(II) ions, as in $\mathrm{Cu(NH_3)_2Br_2}$[57].

In the case of the methoxo-complex the infrared spectrum showed a band characteristic of $\nu(\mathrm{Cu}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{Cu})$ at 570 $\mathrm{cm^{-1}}$, thus suggesting a dimeric structure similar to the chloro-methoxo complex. The e.s.r spectrum was too broad to obtain any g-values, which probably results from spin-spin or spin-lattice relaxation effects.

It was noticed that stirring the room temperature preparation of the copper chloride system for a long period of time (e.g. 6 days) produced the same dimeric product.

Montmorillonite was treated with the chloro-methoxo complex "Cu(OMe)(Py)Cl" by three different methods:

a) contact of clay with solution of the dry complex in an organic solvent (see page 45).

b) synthesis of the complex in the presence of clay (see page 45).

c) synthesis of the complex, then addition of clay without separation of complex (see page 45).

All of the different techniques used to identify the presence of the complex on the clay showed that method (c) was the most effective.

Elemental analysis of the anchored complex gave good agreement between expected and determined elemental analysis for the complex. The magnetic susceptibility measurement gave a small positive moment of 1.06 B.M., which may also be considered good evidence for the presence of the copper complex on the clay. The infrared spectrum showed some small frequency shifts compared with the free complex. The I.R spectrum of the complex supported on the clay is somewhat obscured by silicate vibrations. Four normal modes are, however observed in the region 1700-600 cm^{-1} for coordinated pyridine in the free complex; comparison with the spectrum of the clay supported complex then showed the following : C-C stretching vibrations ν_{19a} and ν_{19b}, at 1482 and 1445 cm^{-1} for free complex , 1488-1448 cm^{-1} for clay plus complex. The C-H out-of-plane deformation ν_{11} at 758 cm^{-1} for free complex and 760 cm^{-1} for clay plus complex, and out-of-plane skeletal vibration ν_4 at 698 cm^{-1} for free complex and 690 cm^{-1} for clay plus complex. All of the observed vibrational frequencies undergo small and undramatic shifts relative to those for the free complex. The other modes due to metal-nitrogen vibrations and metal-oxygen vibrations are either too weak to observe or are obscured by vibrations of the silicate structure. Therefore it was deduced that introducing the complex to the clay is not consistent with a mixture of crystals of complex and clay, but is consistent with intercalation of the complex by the clay. In conclusion the small and undramatic shifts of vibrational frequencies showed that the environment of the complex absorbed by clay is similar but not identical to that in the crystals of the free complex; also it was clear that no chemical decomposition had occurred.

Further information was obtained from e.s.r spectroscopy and x-ray diffraction.

The e.s.r spectrum showed anisotropy with $g_{\parallel} = 2.223 \pm 0.024$ and $g_{\perp} = 2.068 \pm 0.019$ and $G = 3.27$ (defined on page 82), which is indicative of having a dimer copper complex. Moreover, the magnitude of $g_{\parallel}$ is greater than $g_{\perp}$. This result is consistent with Cu(II) ion being in an axially elongated tetragonal crystal field and the unpaired electron occupying a $dx^2 - y^2$ orbital. Axial elongation is also indicated by the magnitudes of the interlamellar thickness. The copper(II)chloro-methoxo complex "Cu(OMe)(Py)Cl" formed on the clay exhibits a basal spacing of 20.7 Å, since the silicate lattice c dimension is 13.6 Å. The height of the interlayers was determined by subtracting the c dimension of the silicate sheet (13.6 Å) from the observed basal spacing for clay plus copper complex (20.7 Å). Therefore, the thickness of the interlamellar region (7.1 Å) indicates the presence of complex between the silicate layers. In conclusion, from the x-ray results, together with those from e.s.r and I.R, it was deduced that absorption of the copper(II)chloro-methoxo complex "Cu(OMe)(Py)Cl" on the montmorillonite results in the formation of a complex having a planar or axially elongated tetragonal structure on the interlamellar surfaces of montmorillonite.

As well as the complex under study, other dimeric copper(II) complexes such as Di-μ-hydroxo-bis-[2,2'-bipyridylcopper(II)]diperchlorate and Di-μ-ethoxo(or methoxo)-bis[di-(2-aminopyridine)copper(II)] dinitrate, which are well known compounds[44] were reacted with montmorillonite using the three different methods (see page 65).

When montmorillonite was mixed with copper perchlorate solution a dark green solid was obtained, which after reaction with 2,2'-bipyridyl in a buffered solution ($pH \simeq 9$) gave a pale green solid. Elemental analysis of the anchored complex with clay gave reasonable agreement between expected and determined elemental analysis for the complex. The infrared spectrum of the clay supported complex showed unshifted bands of the C-C stretching vibrations at 1475 and 1445 cm^{-1} compared with the free complex. The C-H out-of-plane deformation at 773 cm^{-1} for the free complex and at 762 cm^{-1} for clay plus complex, and the out-of-plane skeletal vibration at 625 cm^{-1} for free complex and at 615 cm^{-1} for clay plus complex was observed, which showed a reasonable shift of frequency for these regions. The remaining bands in the spectrum are obscured by vibration of the silicate structure. The presence of hydroxyl vibrations at 3620 cm^{-1} compared with the free complex value at 3620 cm^{-1} was observed, but we could not distinguish with certainly silicate lattice OH groups near 3600 cm^{-1}, and complex OH groups.

The x-ray diffraction pattern showed a basal spacing of 19.2 Å. The difference between basal spacing of montmorillonite before and after treatment with copper complex (5.6 Å) was obtained. This fact indicates that the copper complex was surely formed between the silicate layers.

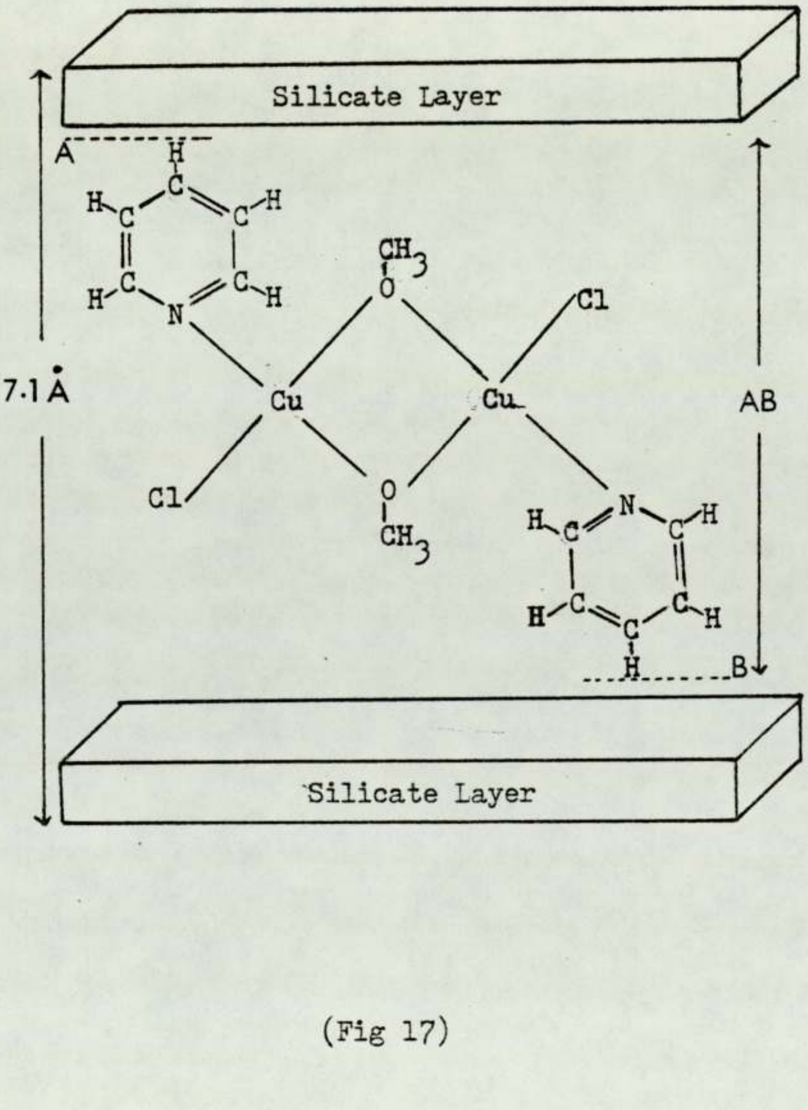
In the case of 2-aminopyridine as a ligand x-ray data (tables 13 and 14) showed the difference between basal spacing of clay before and after treatment with copper complex around 2.0 Å, which it was deduced to have copper complex between the silicate layers. Elemental analysis and e.s.r, I.R showed also the presence of copper complex on the clay.

A closer inspection of the x-ray data showed that the basal spacing fall into two distinct classes. For $[Cu(OMe)(Py)Cl]_2$ and $[Cu(bipy)(OH)]_2(ClO_4)_2$ the spacing is approximately 20 Å whereas for

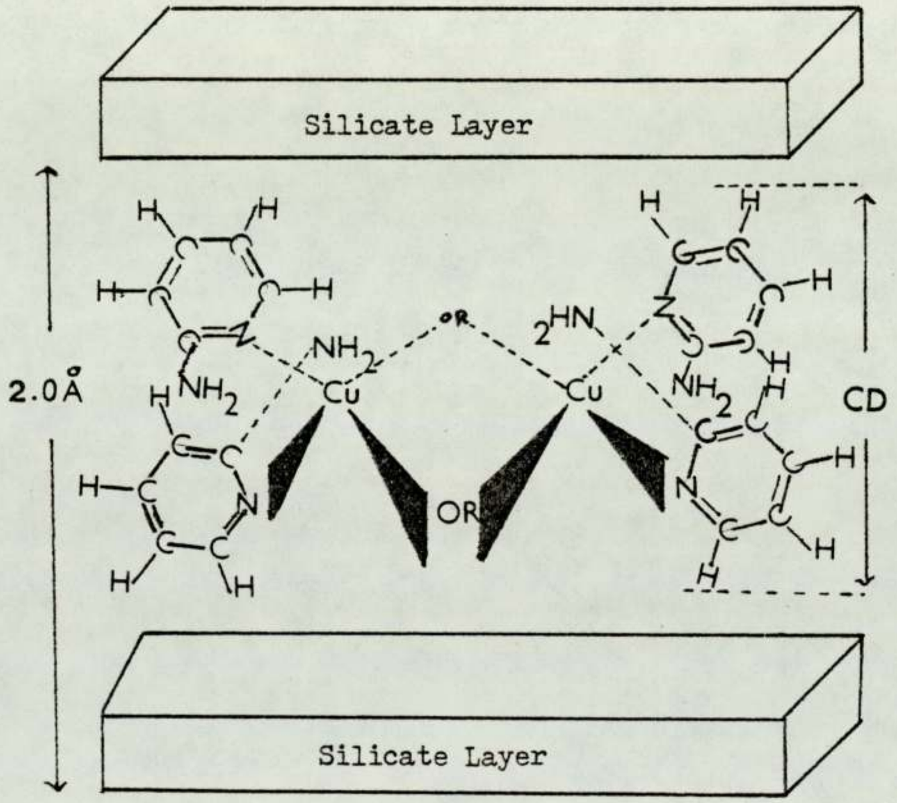
$[Cu(2\text{-ampy})_2(OR)]_2(NO_3)_2$, (R = Me, Et) it is about 16 Å. The difference of ~4 Å is surely significant. Theng[12] has shown that aromatic molecules such as pyridine or pyridinium cation may orientate themselves either perpendicular or parallel to the clay c axis. Thus an attractive explanation is that in the above cases also this difference is observed (Fig 17). The distance AB in figure (17) could then represent the effective dimension of the complex. The 2,2'-bipyridyl complex would seem to be similarly orientated, in this instance the corresponding distance AB is likely to be less, and indeed the observed basal spacing is less.

If the above argument is accepted, then the 2-aminopyridine complexes must be considered to be aligned perpendicular to the c axis. It is of interest to speculate why this should be. A possible explanation is that the amino-group enjoys weak interaction with copper(II) (Fig 18). i.e. if this is so, the plane of the pyridine ring is in fact still parallel to c axis as for the other complexes. However we argue that the preferred orientation of pyridine ring is parallel to the c axis, in other words CD (Fig 18) $<$ AB (Fig 17).

In this work we have measured the basal spacing for montmorillonite itself at 13.6 Å. This figure appears to depend on the degree of hydration, thus heating the clay at 350°C reduces the figure to 11.0 Å and we further observed that when the complexes are taken up from organic solution by the dried clay, an increase in basal spacing is seen but the measured figure is less than the measured spacing for the hydrated clay used in an aqueous environment, however the increase in basal spacing is virtually the same for both natural and pre-heated clay.


Silicate Layer
A
7.1 Å
Cu
Cu
Cl
Cl
CH_3
O
O
CH_3
N
N
AB
B
Silicate Layer

(Fig 17)


Silicate Layer
Silicate Layer
2.0Å
CD
Cu
Cu
NH2
2HN
NH2
NH2
OR
OR
N
H
C

(Fig 18)

The interest in this study was to decompose phenol, which was absorbed on the clay, using the above copper complexes. The experiments clearly demonstrated that the oxidative carbon-carbon bond cleavage in phenol was not effected by the particular copper(II) systems used. Hence, this part of work was not taken further. However, $[Cu(OMe)(Py)Cl]_2$ has been completely characterised and furthermore method (c) (page 46) has been shown to be effective in transferring such material onto montmorillonite.

The next step was the use of phase-transfer catalysis. In these experiments phenol was converted into phenol ethers between the two phases under phase-transfer catalysis conditions. One particularly attractive feature of phase-transfer catalysis is that the method is theoretically catalytic with respect to the quaternary ammonium salt, provided that sufficient base is present in the aqueous layer to regenerate the quaternary ammonium hydroxide from the halide which is formed in the irreversible alkylation step. All reactions were carried out at room temperature, and as expected there was no reaction in the absence of a quaternary salt. The identification of products was confirmed by comparison of infrared spectra and analytical gas-liquid chromatograms with those of commercial samples. As well as g.l.c and infrared, mass spectroscopy was a valuable technique.
Benzyltri-n-butylammonium salts were used throughout, due to the high crystallinity and ease of manipulation of the chloride, bromide and iodide derivatives. Quaternary ammonium bromide was prepared by the reaction of benzyl bromide with tri-n-butylamine. An aqueous solution of benzyl tri-n-butylammonium bromide was passed through a basic ion exchange resin,[37] in order to produce quaternary ammonium hydroxide,

however no exchange was thought to occur as the eluate when added to the phase-transfer system did not initate any reaction. Consequently a second method was tried in which anion resin was stirred overnight with sodium hydroxide (4M) in order to produce the basic resin. An aqueous solution of benzyltri-n-butylammonium bromide was stirred overnight with the treated resin and the benzyltri-n-butylammonium hydroxide was separated in solution from the resin by filtration. This product when added to the phase-transfer system initiated the alkylation of phenol.

Phenol was reacted under phase-transfer conditions with 1-boromobutane to produce phenyl ether which was separated from the reaction system. Mass spectroscopy showed that this product had a molecular weight of 150. An accurate mass determination gave a empirical formula of $C_{10}H_{14}O$, in agreement with the formation of butylphenylether ($C_6H_5O(CH_2)_3CH_3$). The reaction was also followed using g.l.c. The starting materials were characterised independently and the butylphenylether was identified by comparison with a commercial sample. Measurement of the relative areas of the g.l.c peaks indicated that 100% of the original phenol had reacted to form butylphenylether. The conversion of phenol into ether was then carried out in the presence of montmorillonite. Quaternary ammonium hydroxide was supported on the clay and then it was reacted with phenol and 1-boromobutane between two phases, one organic and one aqueous. Butylphenylether was formed between two layers. This product was identified by infrared and mass spectroscopy and g.l.c. In this reaction data indicated that 100% of ether was formed. Then in the next experiment the quaternary ammonium hydroxide supported on the clay was used instead of the aqueous phase, and was reacted with phenol and 1-boromobutane in the organic phase. The yield of the product was 41% . Finally clay was used to support the quaternary ammonium bromide, then this was reacted with phenol and 1-boromobutane in an organic solvent in the presence of a concentrated aqueous solution of sodium hydroxide which had been used to make the clay a thick paste, so that in this case clay acted as an aqueous phase. The yield of the product was 100% .

Ethylphenoxyacetate was prepared under PTC conditions and was stirred at room temperature for 24 h and some of the organic layer was isolated and g.l.c showed that there was some unreacted phenol (69%). But after 48 h stirring all of the phenol had reacted and was converted to ether (100%). In this case the yield of product in the presence of clay was less than that in the absence of clay. The conversion of phenol into the ether could not be completed in 2-12 h as reported in the literature.[37] (see page72).

It is apparent that the water molecules associated with the exchangable cations were able to function as the aqueous phase when montmorillonite was present in an organic medium. The advantage of this comes in the separation step when simple filtration is all that is necessary to afford the organic layer in which the product is dissolved. The same advantage can be obtained if the clay is converted to a paste with sodium hydroxide solution, this has the added value of enabling the quaternary salt to be employed as bromide.

These results were supported by the reaction of dichlorocarbene generated from chloroform with alkenes at 45-50°C in the presence of montmorillonite under PTC conditions. When styrene was reacted with chloroform in the absence of clay but in the presence of a concentrated aqueous solution of sodium hydroxide, under PTC conditions.

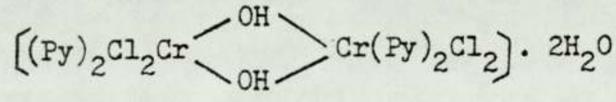
Mass spectroscopy showed that the product had a molecular weight of 187. An accurate mass determination gave a empirical formula of $C_9H_8Cl_2$ in agreement with the formation of 1-phenyl-2,2-dichlorocyclopropane. The product was also identified using g.l.c and the starting materials were characterised independently as before. The yield of this product was about 42% . Positive results were also obtained in the presence of montmorillonite supported catalyst for this reaction but the yield of product measured by g.l.c was only around 26% .

At this point it was felt that this method may be more generally applicable, and in particular it was decided to evaluate it in the synthesis of organometallic and coordination compounds. Due to the strong interest in tellurium chemistry in our laboratory it was decided to study the application of PTC in the presence of montmorillonite to the reaction between ditelluride and diboromobutane in alkaline sodiumborohydride. After apporpriate work up the product was shown to be identical with that obtained by another worker[58] in the laboratory using conventional PTC methods, in fact the yield using the clay supported catalyst was greater.

Subsequently the clay anchored quaternary ammonium bromide was added to a mixture of ditelluride and dibromobutane together with sodiumborohydride in the presence of a concentrated aqueous solution of sodium hydroxide (i.e. clay paste) under PTC conditions and the yield of product was found to be less than that of the two former experiments, but compound formation occurred after a shorter time.

Further attempts were then made to apply PTC to different inorganic reactions. It was decided to investigate the possible use of PTC to prepare acetato-complexes, thus avoiding the commonly used and expensive silver carboxylate route. We chose to investigate the reaction of chloro-tris(triphenylphosphine)rhodium(I) with sodium acetate using PTC. A yellow product was formed where the agreement between the expected and determined elemental analysis was good (i.e. $Rh\left[(C_6H_5)_3P\right]_3\ CH_3COO$). The infrared spectrum of this product contains bands characteristic of acetate at 1650 $cm^{-1}\left[\nu_{as}(OCO)\right]$. This reaction was also carried out in the presence of montmorillonite supported with quaternary ammonium hydroxide under PTC conditions. A similar product was formed at the interface of the clay and organic layer.

The idea to react sodium acetate with trichloro(tripyridine)-chromium(III) under PTC conditions was the last experiment in this part of the work. The preparation of $\left[Cr(Py)_3Cl_3\right]$[49] using the technique described in the literature gave trouble and a new compound, insoluble in organic media was obtained. Elemental analysis for carbon, hydrogen and nitrogen gave reasonable agreement with formulation of $Cr(Py)_2Cl_2(OH).H_2O$. The magnetic moment of the complex was 2.02 B.M lower than the spin-only prediction of 3.88 B.M. for three unpaired electrons. This is consistent with antiferromagnetically coupled chromium(III) ions in a dimer. i.e. probably :



$$\left[(Py)_2Cl_2Cr\overset{OH}{\underset{OH}{\rightleftarrows}}Cr(Py)_2Cl_2\right].\ 2H_2O$$

The infrared spectrum gave clear indication of $\nu(OH)$ and of strong hydrogen bonding. Differentiation between $\nu(Cr—Cl)$ and $\nu(Cr—N)$ was not possible, however bands were noted between 300 and 400 cm^{-1} which may have these origins. The insolubility made the compound unsuitable for experiments with acetate under PTC conditions. Some hydrolysis had obviously occurred during its preparation.

In conclusion PTC on montmorillonite has been shown to be effective in a number of circumstances. In the waste disposal context, it is likely that organic waste containing phenol residue could be pre-treated prior to disposal. Of more general chemical interest is the possibility of eliminating the aqueous phase in some circumstances, with the attractive feature of increasing the ease of work up of the reaction mixture.

3.15 Miscellaneous

Attempts to make different dimeric copper(II) complexes to support the proposed formulation of $\left[\mathrm{Cu(OMe)(Py)Cl}\right]_2$. The reaction between copper(II)chloride and 2-aminopyridine in anhydrous methanol gave a new product, which was identified by means of physical methods. Elemental analysis of this product gave a good agreement with the empirical formula $\left[\mathrm{(2\text{-}ampy)(OMe)CuCl}\right]_2$. The infrared spectum showed a band characteristic of $\nu(\mathrm{Cu}\diagup^{\mathrm{O}}\diagdown\mathrm{Cu})$ at 580 cm^{-1}. The magnetic moment measurement gave a value of 1.32 B.M which is lower than the spin-only predication of 1.73 B.M for one unparied electron. This is consistent with antiferromagnetically coupled copper(II) ion in a dimer. This compound has not been reported previously.

CHAPTER FOUR

THE SORPTION OF COPPER SPECIES BY MONTMORILLONITE

THE SORPTION OF COPPER SPECIES BY MONTMORILLONITE

4.1 Introduction

It has been shown in a number of studies[59,60,16] that the uptake of heavy metal ions by clay minerals can be a function of several factors, including solution pH, the concentration of the metal and the nature of any ligands present. Minimal uptake of metal ions occurs when they are present as anionic complexes.[18]

Montmorillonite is a naturally occurring layer aluminosilicate whose structure is similar to that of pyrophyllite except that there is isomorphous replacement of aluminium(III) by magnesium(II) in the octahedral sheet. The resulting negative charge is balanced by exchangeable cations positioned between the aluminosilicate layers, and the large internal surface area (ca. 800 m^2/g) thus becomes available for the adsorption of a variety of molecules. The adsorption mechanisms, which have been recently reviewed,[61] differ considerably, depending on the nature of the interlamellar cation and the adsorbate molecule. Aromatic molecules have been previously known to bond to silica[62,63], layer silicates,[64,65] and three-dimensional zeolites[66,67] via physical adsorption processes. It has been suggested in the case of silica[62] and the zeolites that important adsorption forces result from an interaction of the π electrons of the adsorbate aromatic molecules and the hydroxyl groups or oxygen atoms of the adsorbent.[66,68] A similar interaction may occur between the adsorbate aromatic molecules containing π electrons and transition metal ion exchange on the clay minerals, therefore mechanisms involving the formation of discrete donor-acceptor complexes are common.[22,23] The coordination chemistry of the metal ion is often related to that of the ion in homogenous solution, but it can sometimes be greatly influenced by the unique environment at the silicate surface. A case in point will be illustrated in this thesis involving the formation of two types of copper(II) complexes on the clay.

4.2 Experimental

4.2.1 : Montmorillonite was dried overnight at 350°C. Portions (10 g) of dry montmorillonite were placed in polythene bottles and covered with standard solutions of copper chloride and copper sulphate (100 ml/0.1M) separately and were then shaken for 24 h. The mixture was filtered and the solid component was dried at room temperature in air. The amount of copper remaining in the solution was determined volumetrically using EDTA (chapter II section 2.9.1). The amount of copper taken up by clay is given in table (19).

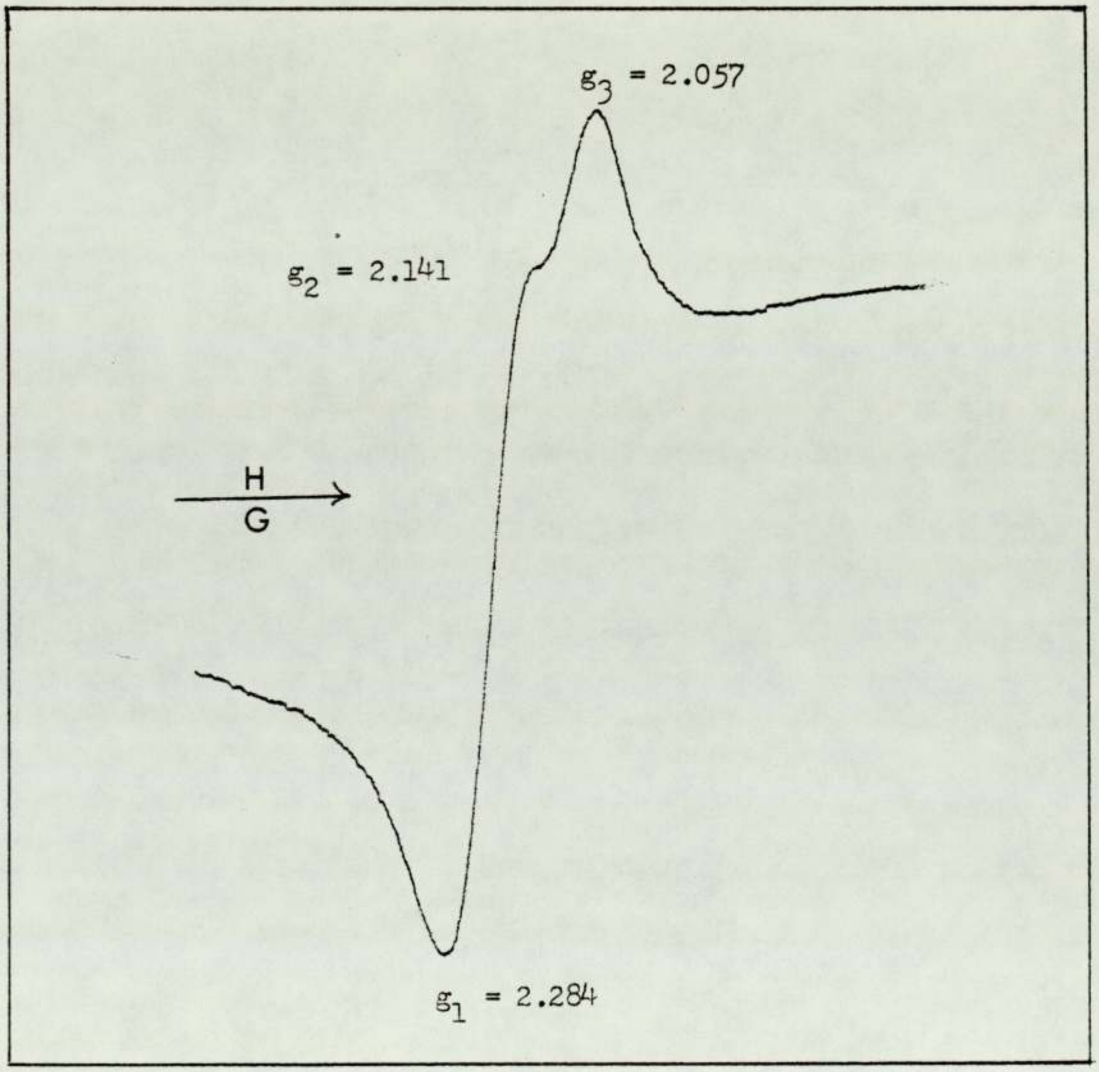
Infrared investigation of the solid showed no observable change in the clay spectrum. The e.s.r spectrum of solid is shown in (Fig 19).

4.2.1 : Portions (10 g) of natural montmorillonite were placed in polythene bottles and covered separately with standard solutions of copper sulphate, copper chloride, copper nitrate and copper perchlorate (100 ml/0.1M) at $pH \simeq 2$ and were then shaken for 24 h. The mixture was filtered and the amount of copper remaining in the solution component was determined by atomic absorption spectroscopy. Data are given in table (20).

In the case of clay treated with copper nitrate, infrared showed a peak at 1400 cm^{-1} due to the NO_3^-(ν_{as} NO) vibration in the solid.

Copper Solution 0.1M	Copper Taken up mg g^{-1}
Montmorillonite + $CuCl_2$	3.2
Montmorillonite + $CuSO_4$	11.4

Table (19)



(Fig 19)

Copper Solution 0.1M pH ≈ 2	Amount of Copper in Solution $\mu g\ ml^{-1}$		Copper Taken up $mg\ g^{-1}$
	standard solution (initial)	after treatment with clay	
Montmorillonite + $CuSO_4$	6300	4260	20.56
Montmorillonite + $CuCl_2$	6180	3540	27.12
Montmorillonite + $Cu(NO_3)_2$	5800	3380	26.49
Montmorillonite + $Cu(ClO_4)_2$	5000	4000	12.7

Table (.20)

4.2.3 : Portions (10 g) of natural montmorillonite were placed in four polythene bottles and covered separately with different concentrations of copper nitrate (100 ml/1M, 0.1M, 0.01M, 0.001M) at pH 2 . The bottles were then shaken for 48 h. The solid component was separated and the amount of copper in the solution was determined by atomic absorption spectroscopy. Data are given in table (21).

The intensity of the observed e.s.r signal as well as the intensity of the infrared absorption band at 1400 cm^{-1} both decreased in going from the 1M solution to the 0.001M solution.

4.2.4 : Portions (10 g) of natural montmorillonite were placed in two sets of seven polythene bottles and covered with standard solutions of copper chloride (100 ml/0.1M) at pH 2 and in neutral solution(i.e.pH$\approx$7) separately and were then shaken from periods of 1 day to 7 days. The mixture was filtered and the amount of copper remaining in the solution component was determined volumetrically using EDTA(chapter II section 2.9.1). Data are presented in table (22), and curves A and B in (Fig 20).

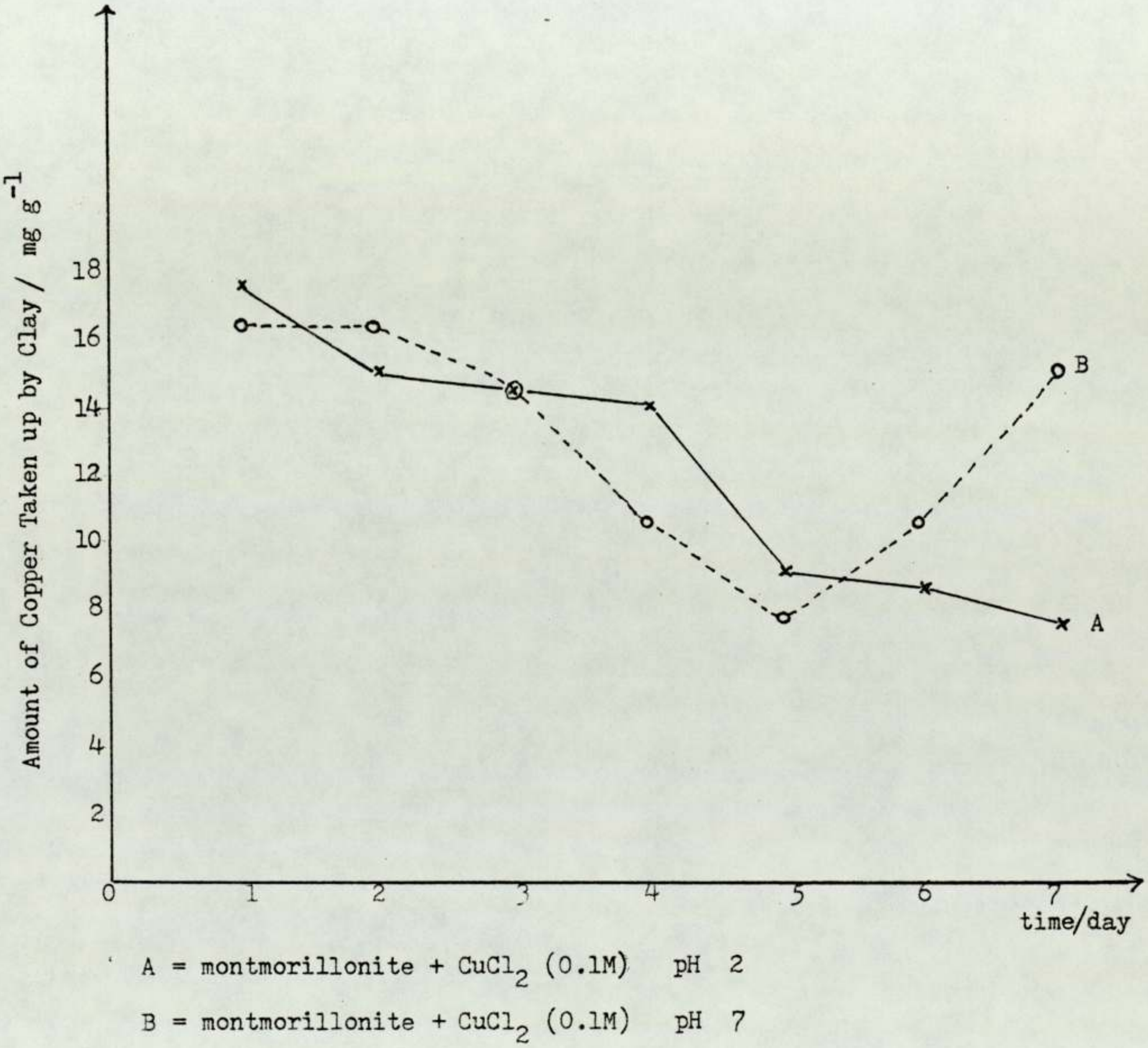
4.2.5 : Portions (10 g) of natural montmorillonite were placed in three sets of seven polythene bottles and separately covered with standard solutions of copper sulphate, copper chloride and copper perchlorate (100 ml/0.1M) and then shaken for periods of 1 to 7 days. The solid was filtered and the amount of copper in the solution component was determined by using EDTA. Data are given in table (23) and curves A, B and C in (Fig 21).

Copper Solution pH $\approx$ 2	Amount of Copper in Solution $\mu g\ ml^{-1}$		Copper Taken up $mg\ g^{-1}$
	standard solution (initial)	after treatment with clay	
Montmorillonite+$Cu(NO_3)_2$ 1M	68000	63600	41.08
Montmorillonite+$Cu(NO_3)_2$ 0.1M	6000	5440	5.92
Montmorillonite+$Cu(NO_3)_2$ 0.01M	600	144	4.826
Montmorillonite+$Cu(NO_3)_2$ 0.001M	52	5.2	0.571

Table (21)

Time/day	Amount of Copper taken up by Clay mg g^{-1}	
	montmorillonite + $CuCl_2$ 0.1M pH ≈ 2	montmorillonite + $CuCl_2$ 0.1M pH ≈ 7
1	15.87	14.60
2	13.33	14.60
3	12.70	12.70
4	12.38	10.79
5	9.52	7.93
6	8.89	10.79
7	7.62	13.33

Table (22)



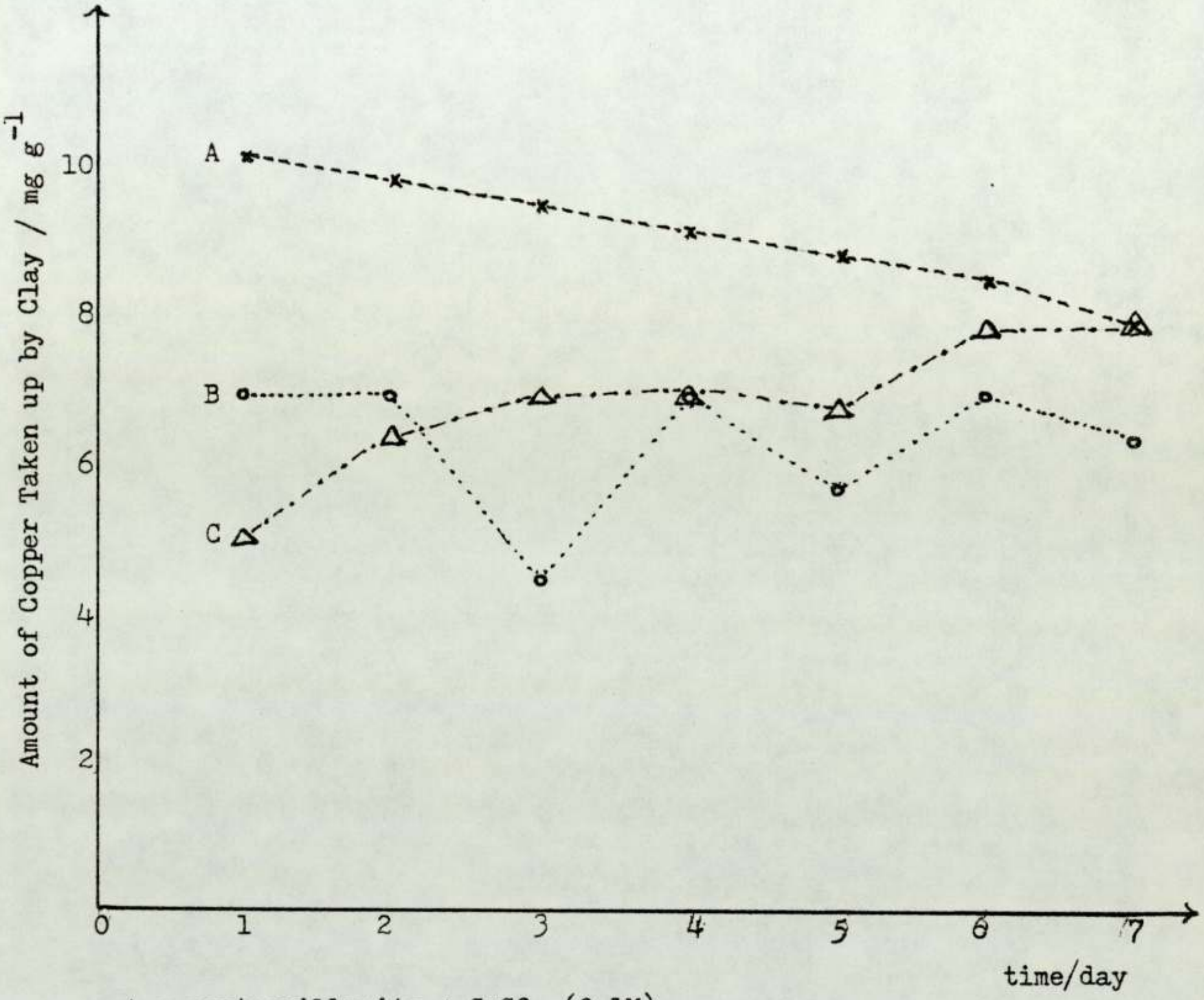
A = montmorillonite + $CuCl_2$ (0.1M) pH 2

B = montmorillonite + $CuCl_2$ (0.1M) pH 7

(Fig 20)

Time/day	Amount of Copper Taken up by Clay mg g^{-1}		
	montmorillonite + $CuSO_4$ 0.1M	montmorillonite + $CuCl_2$ 0.1M	montmorillonite + $Cu(ClO_4)_2$ 0.1M
1	10.16	6.98	5.08
2	9.84	6.98	6.35
3	9.52	4.44	6.98
4	9.20	6.98	6.98
5	8.89	5.71	7.62
6	8.57	6.98	8.89
7	7.93	6.35	6.98

Table (23)



A = montmorillonite + $CuSO_4$ (0.1M)

B = montmorillonite + $CuCl_2$ (0.1M)

C = montmorillonite + $Cu(ClO_4)_2$ (0.1M)

(Fig 21)

4.2.6 : Portions (10 g) of natural montmorillonite were placed in four polythene bottles and separately covered with standard solutions of copper chloride, copper nitrate and copper sulphate, copper perchlorate (100 ml/0.1M) and were left for 1 to 7 days. Every day the pH of solutions was checked. Data are given in table (24). Then after 7 days the solid was filtered and the amount of copper in the solution component was determined volumetrically using EDTA. Data are presented in table (25).

4.2.7 : Portions (10 g) of natural montmorillonite were placed in eleven polythene bottles, a series of 0.1M copper chloride solutions which were 0.1M-5.0M in sodium chloride (NaCl) were added (100 ml) separately to these and shaken for 24 h. The solid was then isolated and the amount of copper remaining in the solution was determined volumetrically using EDTA. The amount of copper taken up by clay was obtained. Then the solid was dried at room temperature in air. This solid was covered with distilled water (100 ml) and was shaken for 24 h. The mixture was filtered and the amount of copper which was released from the clay into solution was determined volumetrically using EDTA. Data are given in table (26).

4.2.8 : Portions (10 g) of natural montmorillonite were placed in four sets of seven polythene bottles and separately covered with standard solutions of copper chloride, copper sulphate and copper nitrate, copper perchlorate (100 ml/0.1M) then shaken from periods of 1 day to 7 days. The solids were isolated and dried at room temperature in air. The amount of copper in the solutions was determined volumetrically using

EDTA. Then the above solids were covered with distilled water (100 ml) and shaken for 24 h. The solids were removed and the amount of copper which came out from clay into the solution was determined by using EDTA. Data for strongly and weakly absorbed copper for different compounds of copper are given in tables (27,28,29,30). Relevant e.s.r spectra are shown in figures (22,23).

4.2.9 : Portions (10 g) of natural montmorillonite were placed in four polythene bottles and separately covered with standard solutions of copper chloride, copper sulphate and copper nitrate, copper perchlorate (100 ml/0.1M) and shaken for 24 h. The solids were separated and dried at room temperature in air. These solids were covered with distilled water (100 ml) and the amount of copper which came out from clay into the solution was determined after 10 minutes, 30 minutes and 1 hour, 2 hours and finally 24 hours. Data are given in table (31).

Copper Solution 0.1 M	pH(initial)	pH(1-7 days)						
		1	2	3	4	5	6	7
Clay + $CuCl_2$	4.2	4.1	3.6	3.7	3.8	4.0	3.8	3.8
Clay + $CuSO_4$	5.0	4.5	4.2	4.3	4.5	4.5	4.5	4.5
Clay + $Cu(NO_3)_2$	4.4	4.6	3.9	4.0	4.0	4.0	4.0	4.0
Clay + $Cu(ClO_4)_2$	2.5	3.1	2.9	3.0	3.1	3.1	3.1	3.1

Clay = montmorillonite

Table (24)

Copper Solution 0.1M	Amount of Copper taken up by Clay mg g^{-1}
Montmorillonite + $CuCl_2$	8.25
Montmorillonite + $CuSO_4$	7.62
Montmorillonite + $Cu(NO_3)_2$	6.35
Montmorillonite + $Cu(ClO_4)_2$	5.71

Table (25)

Compounds	Amount of Copper taken up $mg\ g^{-1}$	Amount of Copper Released from Clay $mg\ g^{-1}$	Difference $mg\ g^{-1}$
Clay + $CuCl_2$	7.62	1.27	6.35
Clay + $CuCl_2$ + NaCl 0.1M	8.25	1.27	6.98
Clay + $CuCl_2$ + NaCl 0.2M	7.30	1.27	6.03
Clay + $CuCl_2$ + NaCl 0.4M	4.79	1.11	3.65
Clay + $CuCl_2$ + NaCl 0.6M	4.44	1.11	3.33
Clay + $CuCl_2$ + NaCl 0.8M	3.49	1.11	2.38
Clay + $CuCl_2$ + NaCl 1M	2.22	1.11	1.11
Clay + $CuCl_2$ + NaCl 2M	1.90	0.95	0.95
Clay + $CuCl_2$ + NaCl 3M	1.58	1.11	0.47
Clay + $CuCl_2$ + NaCl 4M	1.27	1.27	0
Clay + $CuCl_2$ + NaCl 5M	0.06	0.06	0

Clay = Montmorillonite

Table (26)

Montmorillonite covered by $CuSO_4$ (0.1M)

Time/day	Amount of Copper exchanged+adsorbed by clay mg g^{-1}	Amount of Copper exchanged by clay mg g^{-1}	Amount of Copper adsorbed by clay mg g^{-1}
1	8.89	5.08	3.81
2	7.62	3.81	3.81
3	7.62	3.81	3.81
4	8.89	4.77	4.12
5	6.98	1.90	5.08
6	9.52	5.08	4.44
7	8.25	3.17	5.08

Table (27)

Montmorillonite covered by $Cu(NO_3)_2$ (0.1M)

Time/day	Amount of Copper exchanged+adsorbed by clay mg g^{-1}	Amount of Copper exchanged by clay mg g^{-1}	Amount of Copper adsorbed by clay mg g^{-1}
1	8.25	6.86	1.39
2	8.89	7.62	1.27
3	6.35	4.96	1.39
4	8.25	6.98	1.27
5	8.25	6.35	1.90
6	6.35	4.45	1.90
7	5.71	4.19	1.90

Table (28)

Montmorillonite covered by $CuCl_2$ (0.1M)

Time/day	Amount of Copper exchanged+adsorbed by clay mg g^{-1}	Amount of Copper exchanged by clay mg g^{-1}	Amount of Copper adsorbed by clay mg g^{-1}
1	8.25	6.35	1.90
2	6.98	4.95	2.03
3	6.98	5.46	1.52
4	7.62	6.23	1.39
5	6.98	5.46	1.52
6	6.35	4.83	1.52
7	5.71	3.17	2.54

Table (29)

Montmorillonite covered by $Cu(ClO_4)_2$ (0.1M)

Time/day	Amount of Copper exchanged+adsorbed by clay mg g^{-1}	Amount of Copper exchanged by clay mg g^{-1}	Amount of Copper adsorbed by clay mg g^{-1}
1	5.08	3.69	1.39
2	6.35	4.96	1.39
3	6.98	5.71	1.27
4	6.98	5.71	1.27
5	7.62	6.23	1.39
6	8.89	7.50	1.39
7	6.98	5.59	1.39

Table (30)

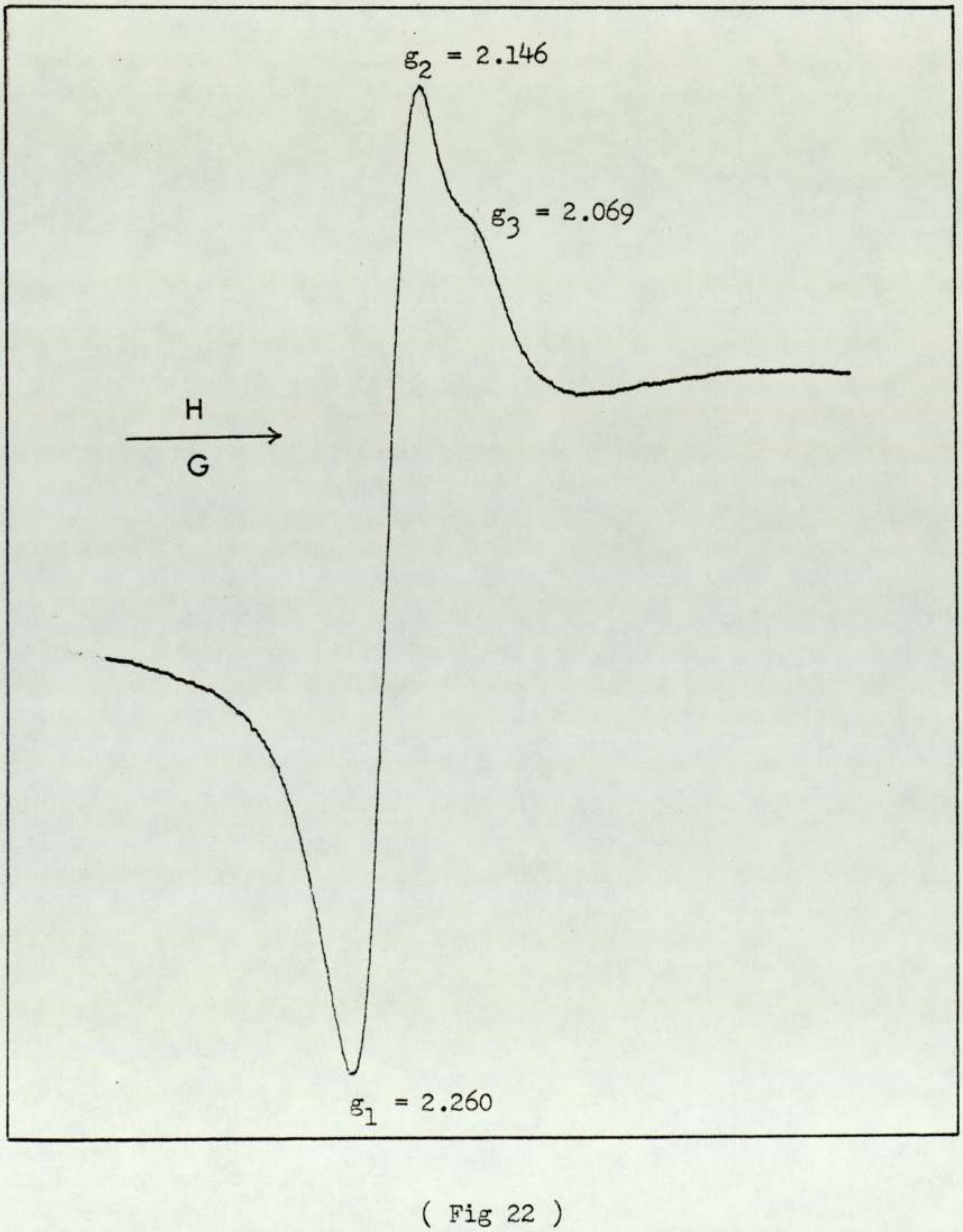
Clay+Copper Solution 0.1M	Amount of Copper which was Adsorbed on the Clay mg g^{-1}				
	10 min	30 min	1 h	2 h	24 h
Clay+$CuSO_4$+H_2O	4.44	4.76	4.76	4.76	5.08
Clay+$CuCl_2$+H_2O	1.58	1.90	1.90	2.22	2.22
Clay+$Cu(NO_3)_2$+H_2O	1.58	1.58	1.90	1.90	1.90
Clay+$Cu(ClO_4)_2$+H_2O	1.58	1.58	1.90	1.90	1.90

Clay = Montmorillonite

Table (31)

E.S.R Spectrum of Montmorillonite+$Cu(NO_3)_2$

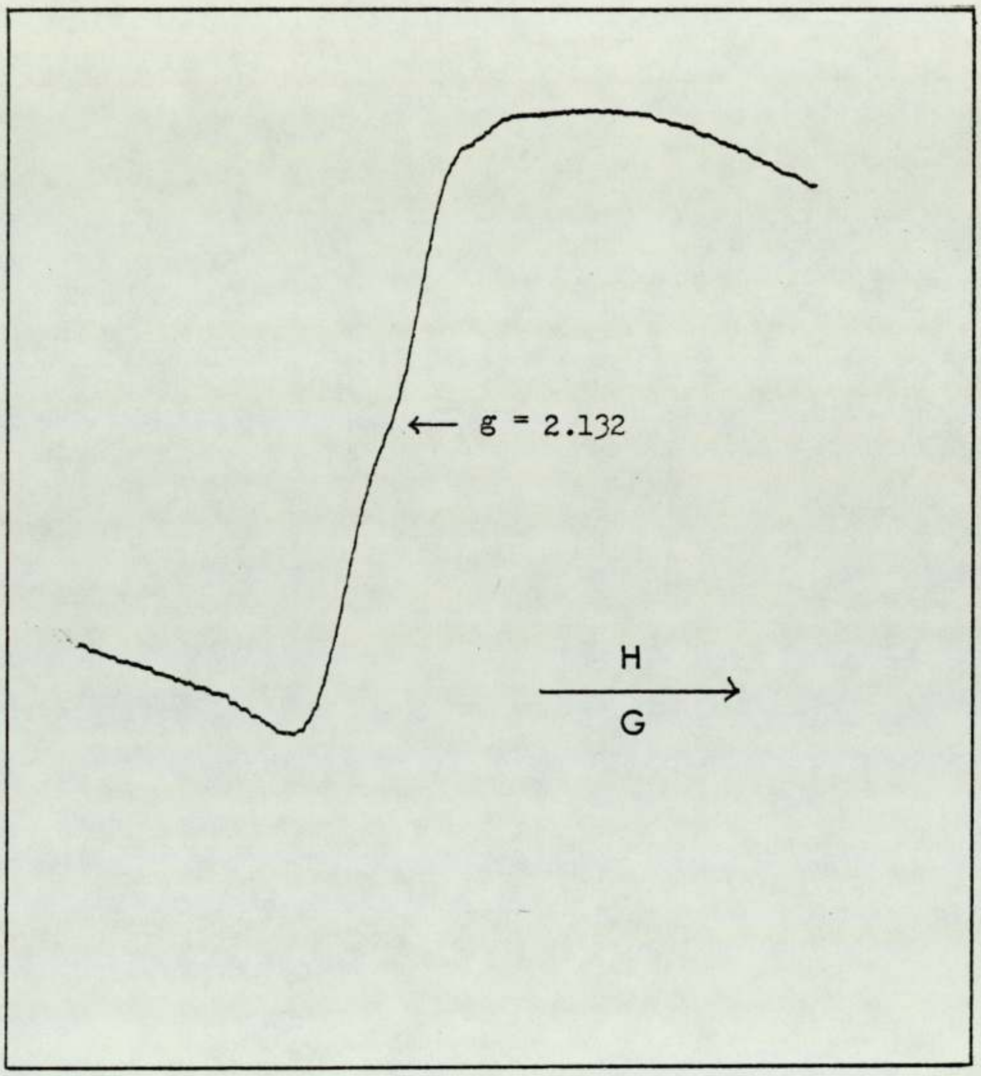
Exchanged+Adsorbed



(Fig 22)

E.S.R. Spectrum of Montmorillonite+$Cu(NO_3)_2$

Exchanged



(Fig 23)

4.3 Discussion

Interest in the ability of clays to adsorb or release heavy metal ions has increased greatly in recent years, and while many aspects have been clarified, much remains to be learnt about relative ion-affinities and the adsorption process. Ion-exchange is the property of clays to sorb cations and anions and retain these in an exchangeable state, that is they may be exchanged for other ions in aqueous solution. The literature survey has indicated that the mechanism of ion exchange on the clay minerals arises from a range of different phenomena.[14] Exchanged ions are not necessarily permanently held and may be released later by being replaced by other ions.

In the previous work[24] it was determined whether any significant removal of metal ions could be expected when effluent reacts with rocks at disposal sites. Carter[24] studied the ion-exchange phenomena on the pure clay minerals using solutions of different heavy metal ions both individually and in combination. She found a reduction in the absorption of a particular ion from mixed element solutions compared with the absorption of the single element by clays.

The present work was done to investigate the exchange-absorption phenomena of copper(II) ions by montmorillonite. Montmorillonite was chosen, because it sorbed approximately five times more heavy metal from solution than kaolinite. The work concentrated on the copper(II) compounds, because we were able to study the ion-exchange process by e.s.r spectroscopy and also by selecting different copper(II) salts to study the effect of different anions on the metal uptake.

Montmorillonite was covered with the different solutions of copper(II) compounds separately and stirred for between one and seven days (see page 107). After filtration the excess copper in the solution was measured either volumetrically using EDTA or by atomic absorption and the quantity of copper on the clay was calculated. But when this material was covered with distilled water and stirred, some of the copper was readily released from the solid to the solution. Therefore, it was deduced that some of the copper was absorbed weakly, the remainder being held more strongly on the clay. The data (expt. see tables 27, 28, 29, 30) are conveniently tabulated in table 32 when we compare the average amount of a given copper(II) salt adsorbed and exchanged over the period day two-day six. The data points were somewhat scattered, but it does appear that a steady state exists during the period day two to day six. The day seven data points often differ, but the experiments would need to have been run much longer to assess if this is real, however Carter's work[24] with copper(II)perchlorate suggests that we are justified in our assumption that a steady state has been attained.

Table 32

Copper(II) salt	days 2-6	
	AV. Exch.	AV. Ads
$CuCl_2$	5.39	1.59
$CuSO_4$	3.87	4.25
$Cu(NO_3)_2$	6.07	1.54
$Cu(ClO_4)_2$	6.02	1.34

The decision was taken to base discussion of the day two-day six data. Carter[24] has implied that the metal content of liquids disposed of at a site will be reduced by absorption of metal ions from the solution by the clay minerals present. But from our results, there is the possibility that part of the metal taken up may be very labile and could well be remobilised by aqueous media strata.

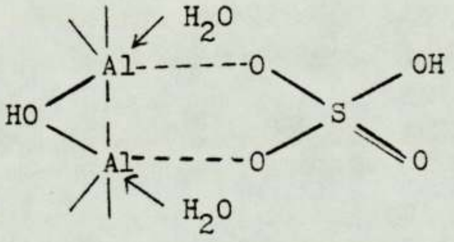
A significant effect was observed on the exchange-absorption of the copper(II) ions by clay for different anions. Data from tables (27, 28, 29, 30) suggested that anion effects on the absorption depends on properties such as the size and charge of the anion. If we take the average for the amount of absorption between day two and day six, at this period of equilibration, it can be deduced that the percentage of the total copper(II) taken up which is exchanged is least for copper(II) sulphate, and greater for copper(II) nitrate and perchlorate. Thus it follows that the order of preference for adsorption into the clay was, as a function of anion :

$$ClO_4^- < NO_3^- < Cl^- < SO_4^{--}$$

When the average of the exchanged form of the copper(II) ion between day two and day six was calculated the order of preference as a function of anion was :

$$SO_4^{--} < Cl^- < ClO_4^- \simeq NO_3^-$$

The nitrate and perchlorate ions are not readily polarised and are relatively poor ligands. Hence the tendency both to absorb to the positive edges of clay crystals and to complex copper(II) ions in solution should be a minimum, thus adsorption should be minimised and exchange maximised. The adsorption that does occur may be due mainly to the interaction of the cations with the negative surface of the silicate layer. The sulphate and chloride ions are better ligands and may form stronger complexes with copper(II) in solution than with the released calcium(II), hence the effective exchange capacity of the clay can appear less. Furthermore, sulphate with two negative charges may have a good affinity for the positive edge of the clay crystal and this could enhance adsorption. Stereochemically such interaction is also favourable (fig 24).



(Fig 24)

Illustration of how SO_4^{2-} (or HSO_4^-)
may bond to positive edge of clay crystal.

Chloride, due to its smaller size, may be better absorbed to the positive edge of clay crystal than either nitrate or perchlorate . It is thus intuitively reasonable that, in terms of the amount exchanged and absorbed, it should appear between sulphate and nitrate.

Our data clearly indicate that for a particular metal ion and a particular clay, the total amount of metal removed from the solution depends on the counter ion present. Our model implies that the affinity of the anion for the positive edge of the crystal is the major factor explaining the influence on the absorbed component, whereas the ability to form complexes in solution is the major factor influencing exchange. It so happens that the same factors which maximise absorption also minimise exchange as shown, by the ratios in table 32.

There are several pieces of evidence to establish the coordination chemistry of the clay supported copper(II) ions. A measurement of basal spacing (001) for the copper(II) ion doped into the montmorillonite gave a value of 13.6 Å which was equal to the value for montmorillonite alone (13.6 Å). This observation can be explained by the replacement of calcium(II) by copper(II). It has been reported[69] that for swollen montmorillonite, the first layer hydrate would thus have a spacing of about 12.0 - 13.0 Å , and a hydrate with two water layers about 15.0 -16.0 Å . It has also been indicated that the exchangeable cations are located between the silicate layers of which the mineral is formed. In the magnesium and alkaline earth salts, the first step of water sorption is the hydration of the cation with six molecules of water which is followed by competion of a water layer having a hexagonal type structure. A second water layer of similar structure is taken up at high relative humidities. An analysis by atomic absorption of the copper solution, after treatment with the clay for the amounts of calcium(II) and magnesium(II), sodium and potassium which were released in the solution, gave more release of calcium(II) than release of magnesium(II), which follows the order of :

$$Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$$

Moreover, when the excess copper(II) in the solution was determined volumetrically using EDTA (chapter II section 2.9.2) the amount of EDTA was greater than that for the solution of copper before treatment with clay. This observation can be explained by the interference of calcium(II)[70]. Another worker[71] has indicated that on montmorillonite, displacement occurred in order of :

$$Ca^{2+} > Pb^{2+} > Cu^{2+} > Mg^{2+} > Cd^{2+} > Zn^{2+}$$

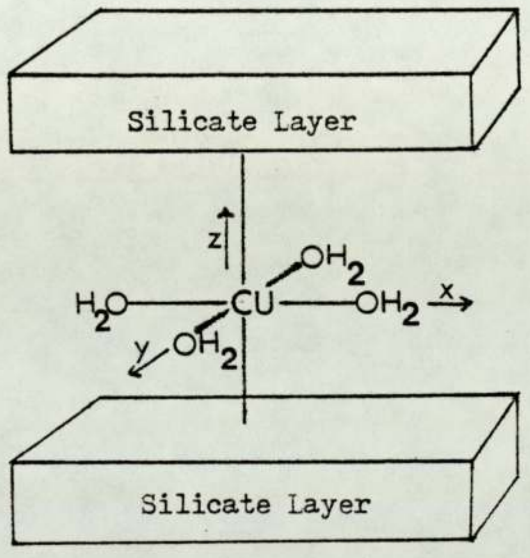
which means replacement of calcium(II) by copper(II) is easier than, replacement of magnesium(II) by copper(II). Hence, it is possible to replace calcium(II) by copper(II) both being in their hydrated form i.e. $[M(H_2O)_6]^{2+}$.

The stereochemistry of exchangeable hydrated copper(II) ions in the interlamellar silicate layers was also investigated by means of e.s.r spectroscopy. E.S.R spectra of the copper(II) ions absorbed and exchanged are illustrated on pages (117, 118) respectively. For the copper(II) ions absorbed, the spectrum consists of clearly defined $g_{\perp} = 2.069$ and $g_{\parallel} = 2.260$ components as expected for axial symmetry, but the exchanged copper(II) ions gave an isotropic spectrum with $g_{av} = 2.132$.

The isotropic or broadened spectrum with $g_{av} = 2.132$ indicates that the ion is in a solution-like environment in which it can rapidly tumble and average the anisotropic components of g, just as is the case for the $[Cu(H_2O)_6]^{2+}$ ion in solution. However in the absence of rapid tumbling $g_{\parallel}$ and $g_{\perp}$ should be resolved as is the case in fig 22. The large line width observed for the exchanged copper(II) ion is probably due to magnetic interactions between copper(II) and iron(III) which is present in the silicate structure. The observation of unchanged basal spacing (001) after treatment with copper(II), together with the observed release of calcium(II) as indicated by atomic absorption, it can be concluded that hydrated copper(II) has replaced calcium(II) an ion with similar hydrated radius.

When natural montmorillonite was heated at 350°C the basal spacing (001) decreased to a value of 11.0 Å, the thickness of the interlamellar region (2.6 Å) indicates that a monolayer of water is removed[72] and that two layers of water were initially present.

On the other hand an isotropic spectrum could be due to the random orientation of the clay particles. The e.s.r spectrum of an oriented sample in the resonance cavity with the silicate layers perpendicular or parallel to H, gave only an isotropic spectrum. Thus when several layers of water are present the copper(II) ion tumbles rapidly, averaging the $g_{\parallel}$ and $g_{\perp}$ components.[73] When copper(II) ions are hydrated by a monolayer of water molecules, the planar $[Cu(H_2O)_4]^{2+}$ is confined to lying flat between the silicate sheets[72] as illustrated in (Fig 25 A). We turn now to the deduction of the stereochemistry of hydrated copper(II) ions when two layers of water molecules occupy the interlamellar region. Earlier X-ray diffraction studies of layer



A

Fig 25

Schematic representation of the stereochemistry of hydrated Cu(II) where one layer of water occupy the interlamellar regions silicates[74] indicate that when two layers of water are present, divalent metal ions should be octahedrally coordinated to six water molecules. However, in the case of copper(II) the octahedron should be distorted , as required by the Jahn-Teller theorem. Therefore it is possible that the environment of $[Cu(H_2O)_6]^{2+}$ is as illustrated in (Fig 25 B).

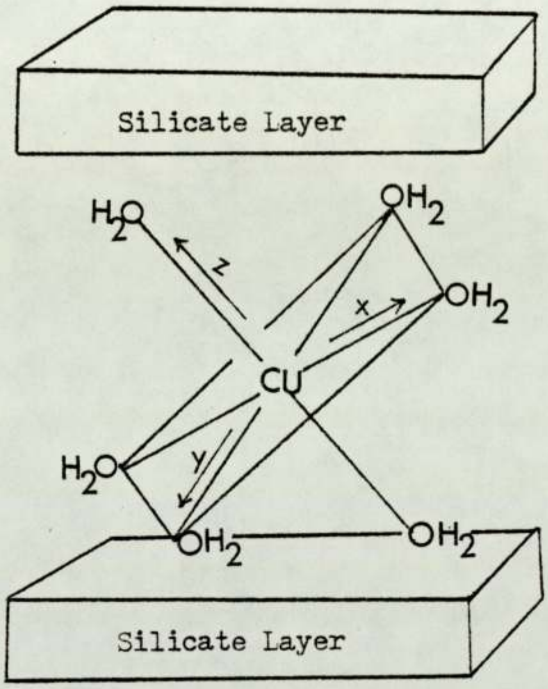
4.3.1 Influence of High Concentration of Anion

When the concentration of anion, for example chloride was increased, the amount of copper(II) ions absorbed by montmorillonite was decreased. Complex formation, between the anion and metal, can result in a lower percentage absorption of the metal from solution as fewer metal ions will be available, and will therefore compete less favourably in the equilibrium process of absorption. From the data present in table (26) it may be concluded that in the absence of chloride ions or from dilute copper(II) chloride solution the $[Cu(H_2O)_6]^{2+}$ ion is sorbed on the clay, while in the presence of chloride ions some chloro-cuprate(II) species may be sorbed. By introducing the chloride ion into the copper(II) chloride solution the displacement of molecules of water by chloride ion can be occur as in the following equations :

$$Cu(H_2O)_6^{2+} + Cl^- \rightleftharpoons Cu(H_2O)_5Cl^+$$

$$Cu(H_2O)_5Cl^+ + Cl^- \rightleftharpoons Cu(H_2O)_4Cl_2$$

$$Cu(H_2O)_4Cl_2 + Cl^- \rightleftharpoons Cu(H_2O)_3Cl_3^-$$



B

Fig 25

Schematic representation of the stereochemistry of hydrated Cu(II) where two layers of water occupy the interlamellar regions and finally :

$$CuCl_3^- + Cl^- \rightleftharpoons CuCl_4^{2-}$$

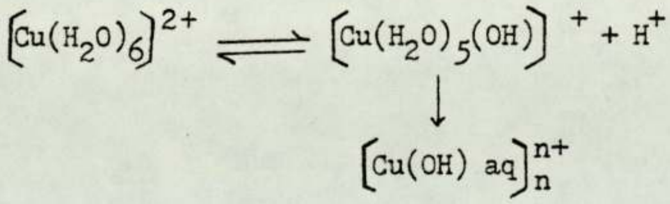
E.S.R spectroscopy together with the analysis for excess of the copper in the solution indicate that, with increasing molarity of chloride ion from zero up to two molar the amount of exchanged copper(II) ions has decreased, while e.s.r gave an isotropic spectrum. But from three molar to five molar there was no exchange of copper(II) ions, because after contact of material with distilled water all of the copper(II) ion absorbed on the clay was released into the solution. The e.s.r spectrum is resolved into $g_{\parallel}$ and $g_{\perp}$, the $g_{\parallel}$ shows further hyperfine splitting into four lines ($A_{\parallel} = 80$ G). The observed e.s.r spectrum has $g_{\parallel} = 1.966$ and $g_{\perp} = 2.197$. Furthermore, $g_{\parallel} \simeq 2.0$ (1.966) is consistent with a dz^2 ground state. The ability to distinguish a dz^2 ground state is consequently of particular importance in recognising the most common of the stereochemistries associated with this ground state, namely trigonal bipyramidal. It may therefore be suggested that the species containing chloride sorbed on the clay is $CuCl_5^{3-}$, e.g. :

$$CuCl_4^{2-} + Cl^- \rightleftharpoons CuCl_5^{3-}$$

Studies of copper ions in HCl (0.5-12M) solutions[75] made with anion exchange resins have shown the possible sorption of the complex ions $CuCl_3^-$ and $CuCl_4^{2-}$ no previous claims for $CuCl_5^{3-}$ have been noted.

Experiments in neutral and acidic (pH <6) solutions of copper(II) showed, as was expected[76] the amount of copper(II) absorbed by clay increased with increasing pH, and it has been proposed[77] that this effect is due to decreased competition from protons for adsorption sites with metal ions.

When the pH of the solution after treatment with clay was compared with the initial pH of the solution there was no change. Therefore, it can be deduced that there was no significant hydrolysis of copper(II) ions to produce species such as $[Cu(OH)]_n^{n+}$ e.g. :



$$\begin{tikzcd}\left[Cu(H_2O)_6\right]^{2+} \arrow[r, shift left] & \left[Cu(H_2O)_5(OH)\right]^{+} + H^{+} \arrow[l, shift left] \arrow[d] \\ & \left[Cu(OH)\ aq\right]_n^{n+}\end{tikzcd}$$

Infrared spectroscopy was found not to be a very useful technique to identify the presence of anions on the clay. It was impossible to observe any band due to sulphate and perchlorate anions, because they were obscured by the vibrations of the silicate structure. However, a band at 1385 cm^{-1} which was due to a nitrate vibration $[\nu_{as}(NO)]$ was observed. The presence of this single band indicates that the nitrate anion has not been coordinated, but it may be just absorbed by electrostatic attraction between positive and negative charges. The e.s.r spectra showed no difference between the absorption of different copper compounds. The anion effects are due to different strength of physical absorption onto the surface was also confirmed by the experiment (section 4.2.9). Data presented in the table (31) showed that the sulphate anion with two negative charge is more absorbed than the others with less than two negative charges.

It is probably appropriate to conclude with a few brief comments on the points of interest to waste disposal. Absorption of metallic ions by clay minerals is believed to play an important role in waste disposal. The absorption of heavy metal ions by clay minerals can lead to both weakly and strongly held components on the clay. The presence of anions or any other potential ligands in solution may alter the ratio of labile to non-labile metal. The formation of metal complexes can reduce exchange capacity even to zero. Moreover anions such as SO_4^{2-}, Cl^-, NO_3^- which may be present in waste disposal situations can influence the ratio of labile to non-labile.

CHAPTER FIVE

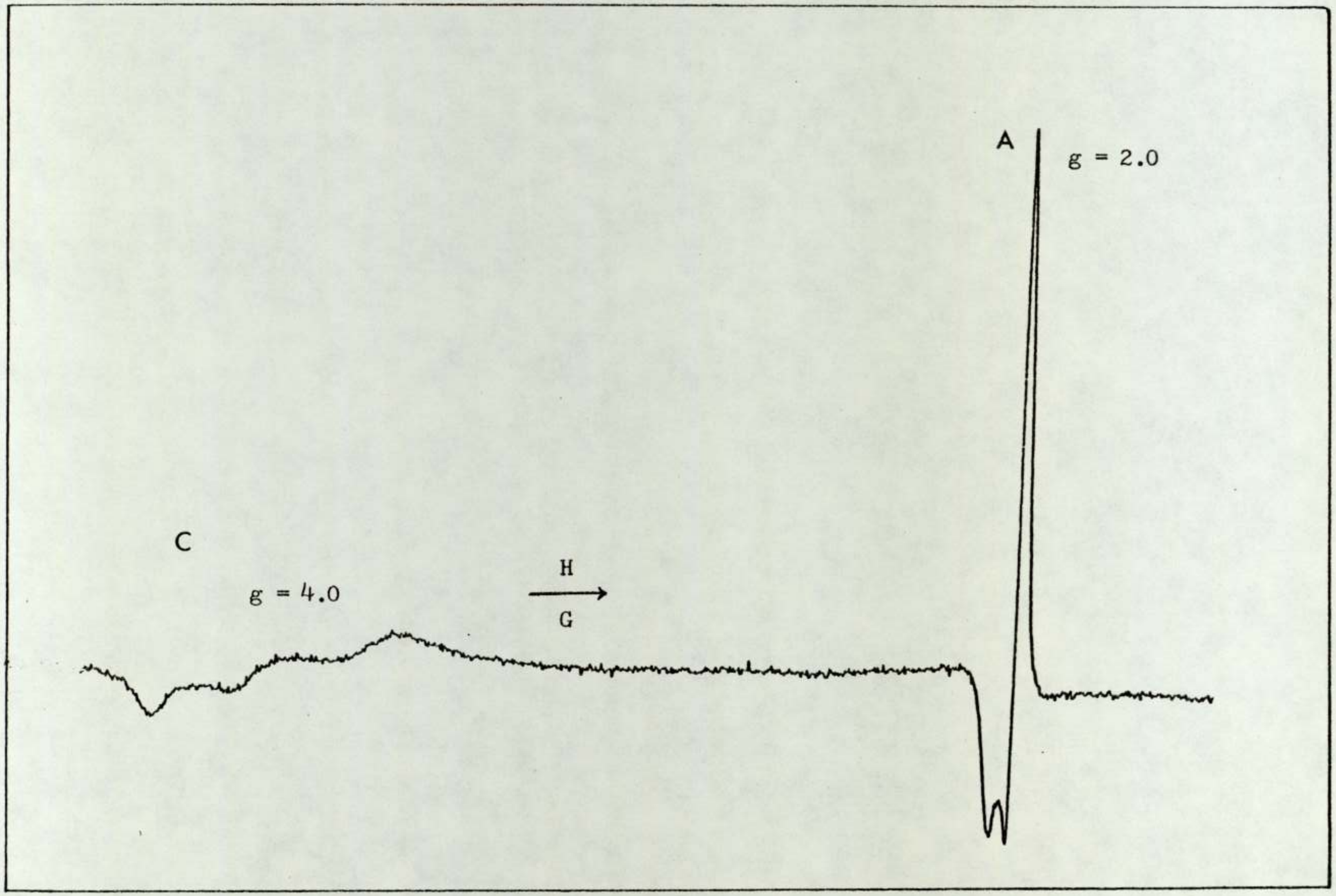
KAOLINITE

KAOLINITE

5.1 Introduction

Kaolinite is the most common of the Kandite minerals. The theoretical composition of pure kaolinite ($Al_4(Si_4O_{10})(OH)_8$) is 46.54% SiO_2, 39.5% Al_2O_3 and 13.96% H_2O, this composition being seldom found in nature. The common chemical impurities are Fe_2O_3, TiO_2,MgO, CaO, K_2O, Na_2O and generally SiO_2 or Al_2O_3 is in excess. Certain physical and chemical properties such as viscosity and cation exchange capacity, occur because the surface of kaolinite is coated with amorphous aluminium and silicon hydroxides.[78] The cation exchange capacity is the ability to hold and exchange cations such as sodium, potassium, calcium and hydrogen and in kaolinite is normally attributed to broken bonds at the edges of the flakes.[14,15]

As well as being substituted in the kaolinite lattice, iron impurities in the kaolin minerals occur in a number of forms, including various oxides, pyrites, micas and montmorillonites. Hence it is difficult to determine the exact location of the total iron impurity in kaolin minerals as combustion or fusion of samples for chemical analysis results in the total iron content being determined as Fe_2O_3 and is usually in the range 0.1 to 2 % . The extent of iron impurity in the kaolinite lattice has been demonstrated by Mossbauer[79] and E.S.R spectroscopy techniques.[25] Both techniques show that iron is a common substitutional impurity in kaolinite. A typical E.S.R spectrum of a relatively pure bulk sample of natural kaolinite is shown in (Fig 26). The E.S.R spectra usually contained two main groups of resonance lines centred at about



(Fig 26)

g = 2.0 and g = 4.0 respectively. A series of experiments were carried out to establish that the E.S.R signals associated with kaolinite could be attributed to impurities substituted whithin the crystal structure and not to mineralogical impurities or surface contaminants.[25] For the signal at g = 2.0 it was clear that there was no measurable contribution from the organic fraction.[26] This being so, it seemed feasible to seek the source of the resonances from comparisons of the chemical analysis of natural samples with the known structure of kaolinite; results indicated that iron was most probably responsible. Malden and Meads[79] removed most of the mineral impurities and free iron oxides from kaolinite by acid washing and magnetic separation, and concluded from Mossbauer spectroscopy, that the iron remaining (0.3%) was substituted in the kaolinite lattice. By comparing the Mossbauer spectra of gibbsite ($Al(OH)_3$) and kaolinite they were able to infer that the iron in kaolinite is in the octahedral layer. Most kaolinites contain appreciable amounts of MgO (0.01% to 1.0% but usually 0.2% to 3%). Bundy et.al[80] found that variations in MgO content, as well as total iron and soluble iron content, were directly related to cation exchange capacity. They suggest therefore, that the magnesium and iron were present not as substituted impurities in kaolinite, but as impurities within a montmorillonite fraction. They also pointed out that the montmorillonite content in kaolinite is usually less than 5%, and is not readily observable by X-ray diffraction. It is possible, although to date there is no direct experimental proof, that the cation exchange capacity is contributed to by the magnesium and iron substituted in the kaolinite lattice, which in turn causes charge imbalance. Follet[81] has shown by electron microscopy that adsorption of sols on the kaolinite particles occurs preferentially at the edges and on one of the two faces.

These results support the view that the cation exchange capacity is due to broken bonds at the edges of the flakes, and due to impurities substituted within the lattice, probably in the silicate layer (Al^{3+} substituted for Si^{4+}).

The use of clays as catalysts in organic chemistry is very extensive. Certain clays with a high alumina content, such as kaolinite and aluminium rich montmorillonites, are used in the petrochemical industry as catalysts. The occurence of iron, whether free or coordinated with oxygen or hydroxyls, and the pattern of distribution are essential factors in the action of clay catalysts. Although the main use of kaolinite is in the production of ceramics, which does not put any serious constraints on the purity of the clay. High purity clays from deposits such as those in Cornwall U.K. and Georgia U.S.A. are used in the paper industry. For these purposes relatively small levels of impurity cause two major problems in the industrial application. First the impurities can alter the viscosity of the clay, and secondly they can cause the discolouration of an otherwise white clay. Some authors have shown substituted iron to be extremely effective in discolouring the kaolinite.[82] Szpila[82] pointed out that manganese, lead and copper cause a greater discolouration of kaolinite than titanium or iron at the same level of concentration. From the previous description of the wide range of impurities which can exist in the kaolinite minerals and in particular the conflicting opinions with respect to the effect of substituted iron impurities, it follows that great caution must be exercised when interpreting experimental results. The identification of the discolouration due to any one defect is difficult if not impossible.

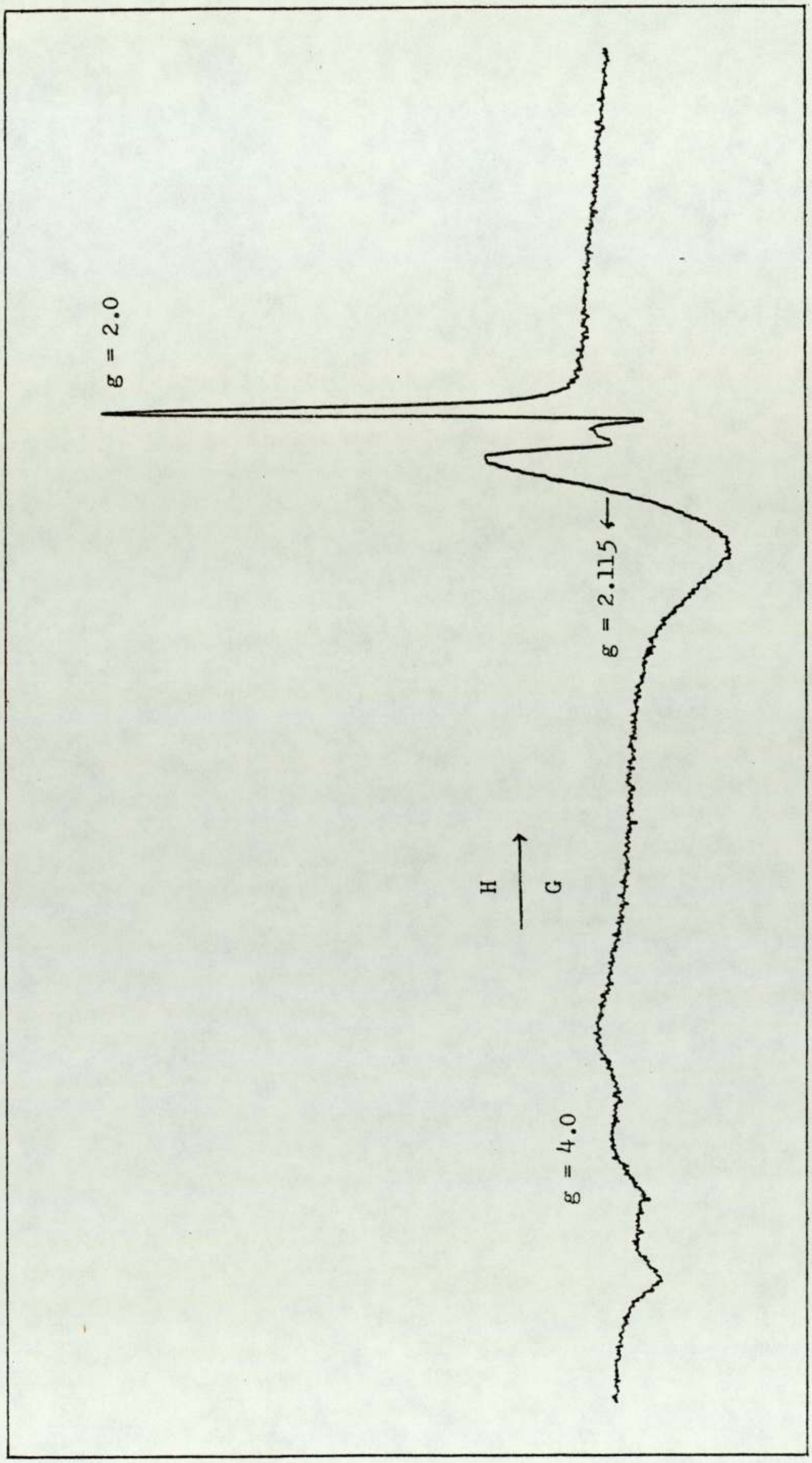
The most outstanding property of kaolinite is its relative chemical inertness. It is practically insoluble in strong alkalis and acids. It is possible to dehydroxylate kaolinite by heating it above 500°C, when it transforms into an X-ray amorphous phase known as metakaolinite[14], thus illustrating that the mineral is also of considerable thermal stability.

5.2 Experimental

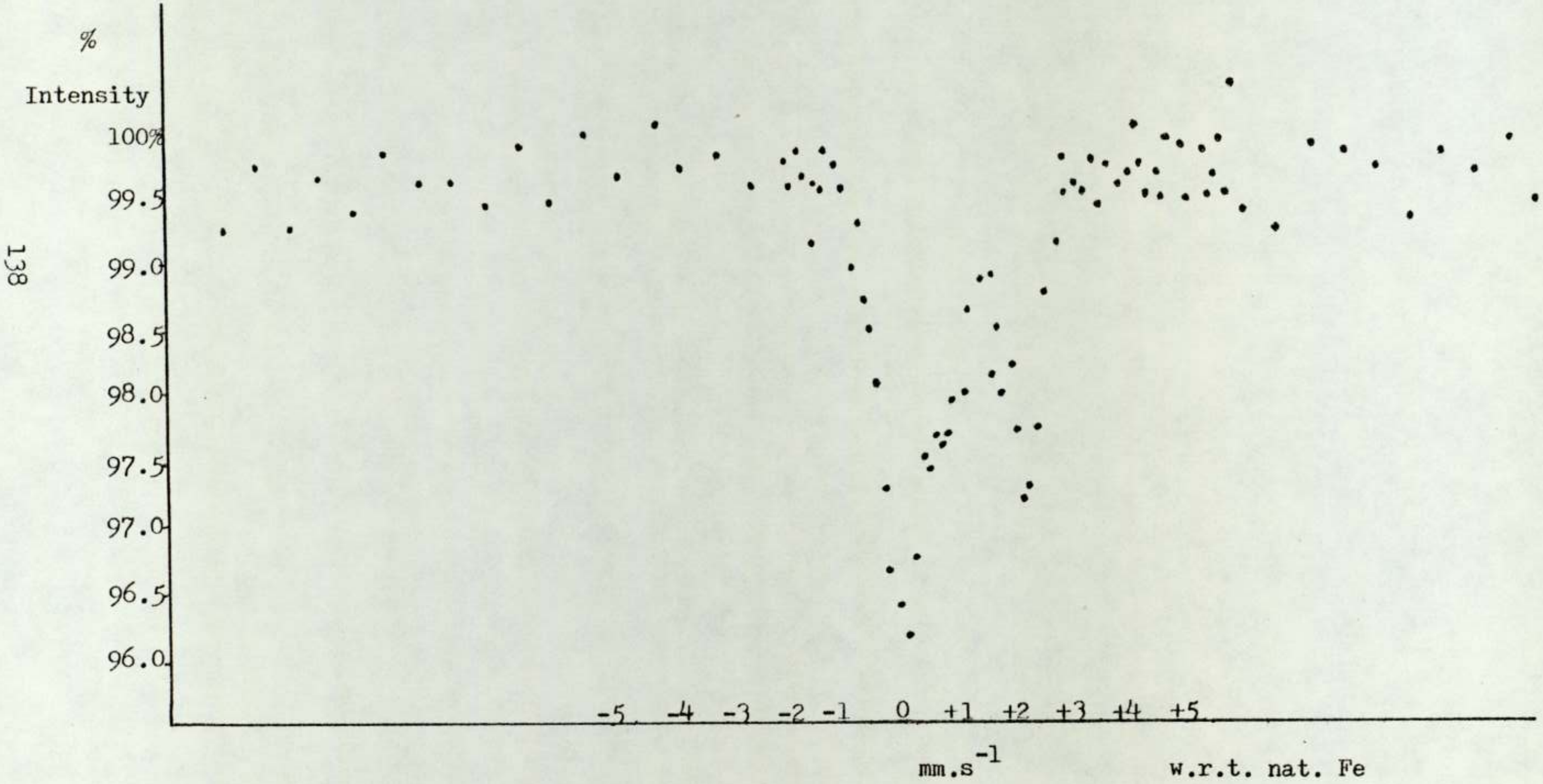
5.2.1: Kaolinite (10 g) was covered with nitric acid (100ml/4M), stirred for 2 h and the solid was then isolated and dried at room temperature in air. This solid (2 g) was covered with solution of 2,2'-bipyridyl (1 g) in the mixture of ethanol and water (50ml+50ml) and stirred for 24 h. A pink solid was obtained and was separated from solution. For this solid, e.s.r and Mossbauer spectra were measured and are shown in figures (27, 28) respectively.

5.2.2: 2,2'-bipyridyl (2 g) was dissolved in hot water (300 ml) and was treated with a mixture of kaolinite (10 g) in solution of sodium perchlorate (excess). The mixture was heated on the water-bath for 5 h. A pink solid was obtained which was isolated from solution. E.S.R spectrum showed no change in the kaolinite signal.

5.2.3: Kaolinite (0.5 g) was covered with a solution of galvinoxyl (0.5M) in benzene and stirred under nitrogen for one week. The e.s.r spectrum of solid was measured and no change was observed in the spectrum compared with spectrum of natural kaolinite.



(Fig 27)


%
Intensity
100%
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
-5
-4
-3
-2
-1
0
+1
+2
+3
+4
+5
mm.s^{-1}
w.r.t. nat. Fe

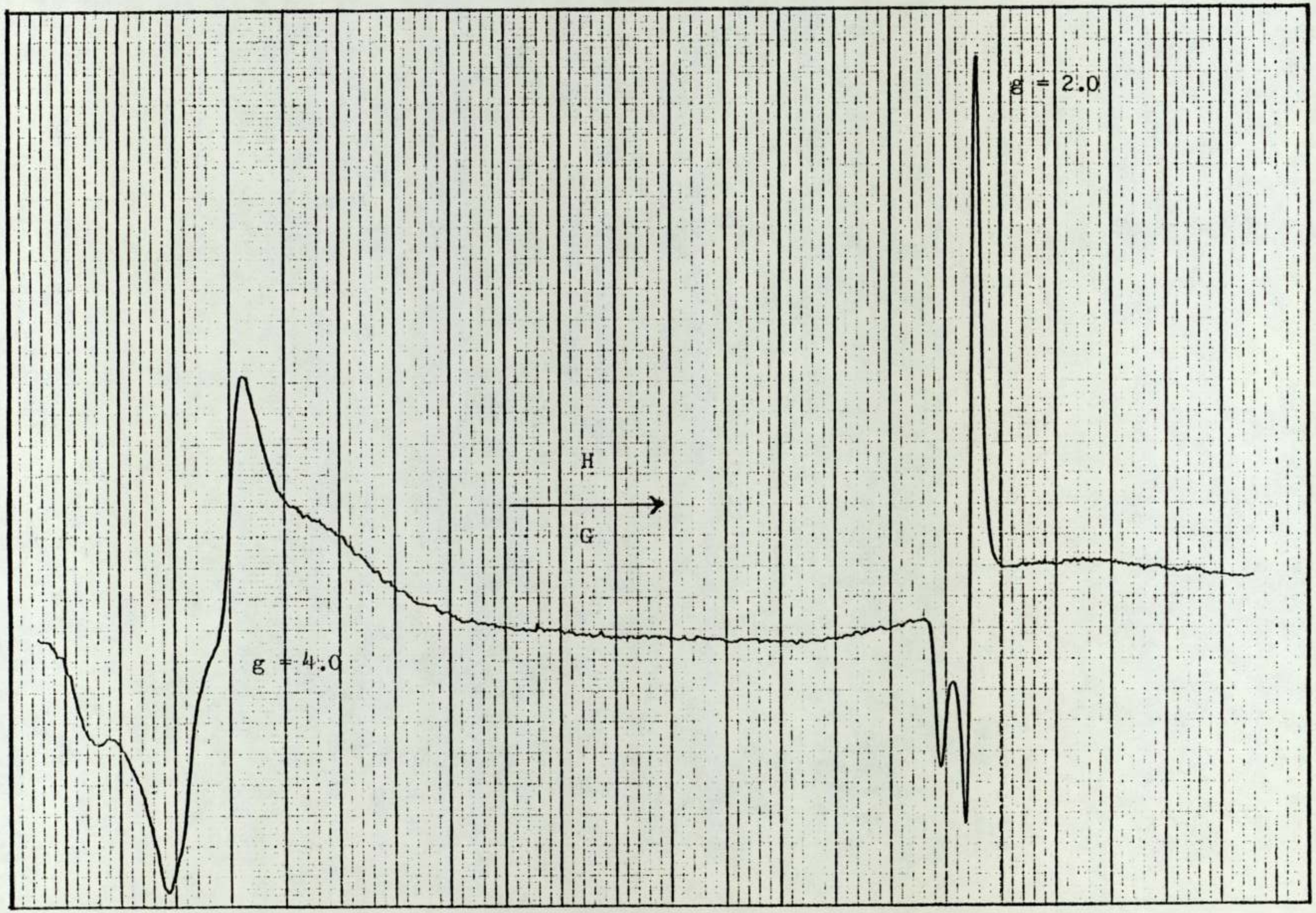
(fig 28)

5.2.4: Kaolinite (5 g) was covered with hydrazine (50 ml) and refluxed for 2 h. The e.s.r spectrum of solid is shown in (Fig 29).

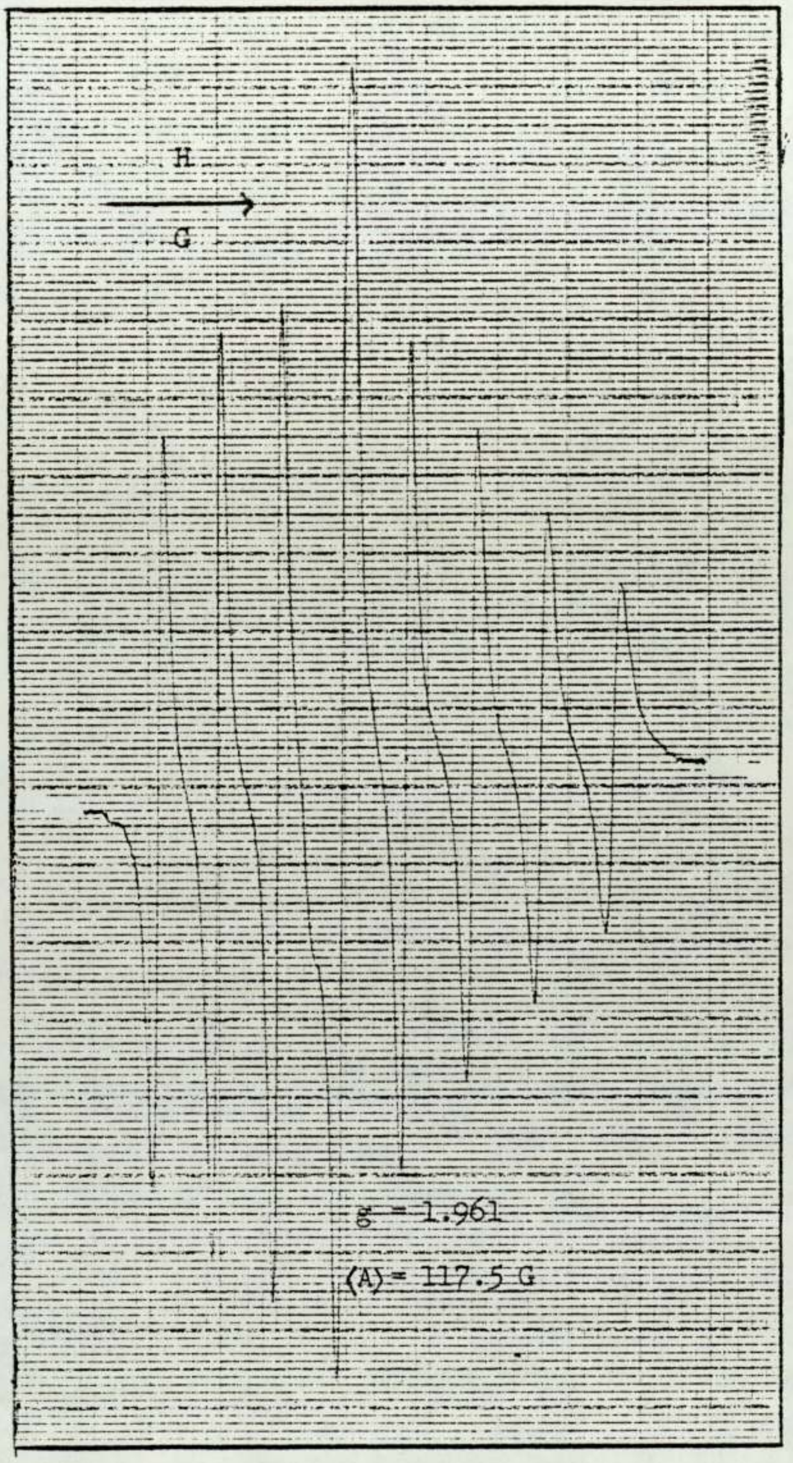
5.2.5: Ammonium metavanadate (1.17 g) was dissolved in concentrated (60%) perchloric acid (100 ml) and then this solution was mixed with kaolinite (10 g) in a polythene bottle and was left for one month. After this time the initial orange colour changed into green. The e.s.r spectrum of solid showed the presence of vanadium(IV) on the kaolinite, but no reduction of the g = 2.0 signal (Fig 30). Then this solid was contacted with distilled water (100 ml) and stirred for 24 h. E.S.R spectroscopy of the washed material showed the presence of vanadium(IV) with less intensity (Fig 31).

5.2.6: Kaolinite (1 g) was added to a mixture of distilled water (35 ml) and 10 percent solution of sodium chloride (5 ml) in a beaker. After addition of sodium dithionite (0.25 g) the mixture was stirred and heated for 15 minutes at 70°C. This procedure was carried out eight times, but it is clear from the e.s.r data (Fig 32) that with the first extraction, the g = 2.0 resonance had disappeared.

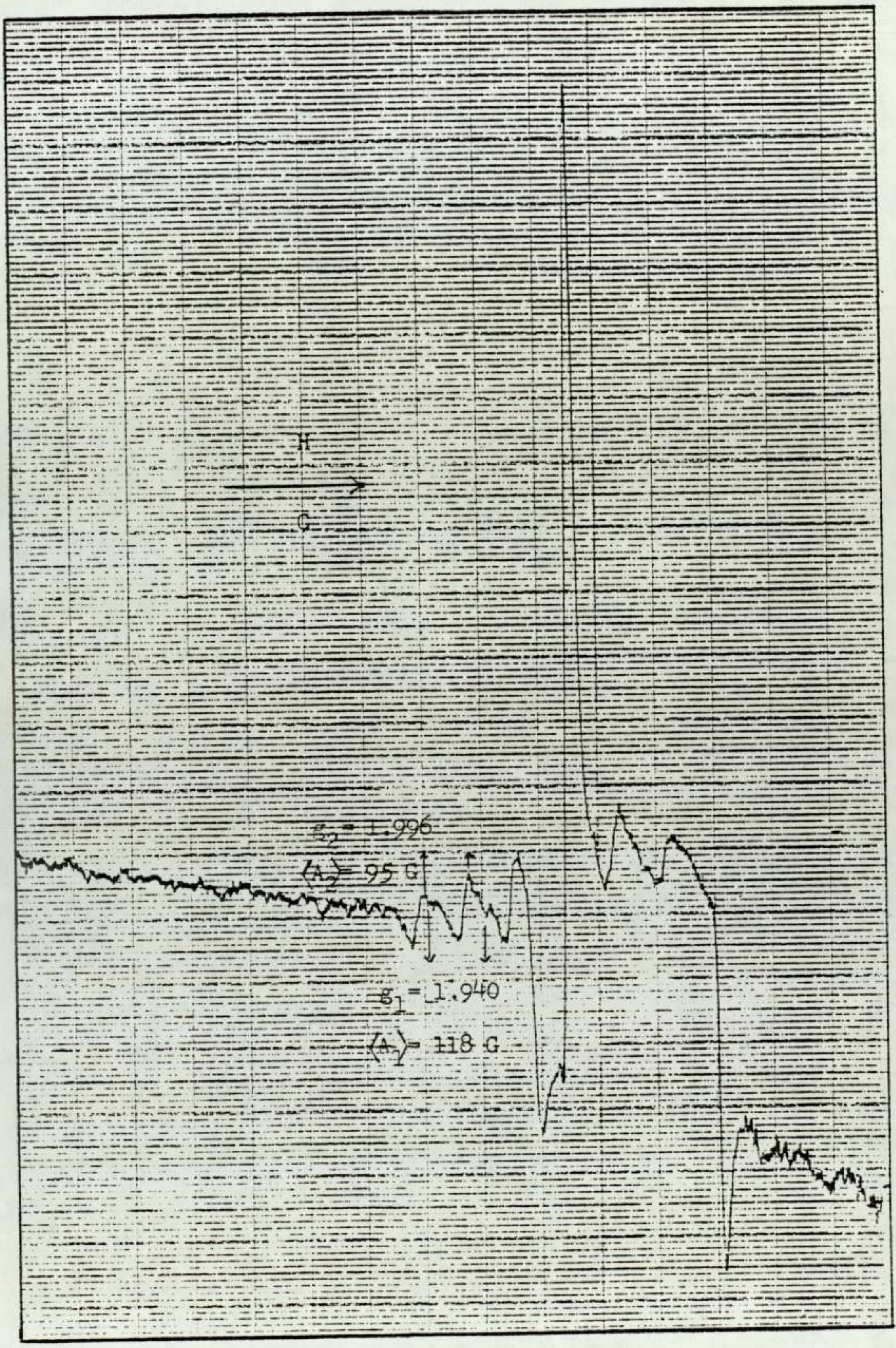
5.2.7: Kaolinite was heated in air for 2 h at various temperatures up to 1200°C. Marked changes in the spectrum occurred for the sample heated at or above, the dehydroxylation temperature (Fig 33). Heating at temperature of 500°C and above causes an elimination of the g = 2.0 resonance, together with a collapse of the low-field resonance to a single line at g = 4.0 . These transitions in the e.s.r spectra coincide with both the collapse of the kaolinite X-ray diffraction[83]



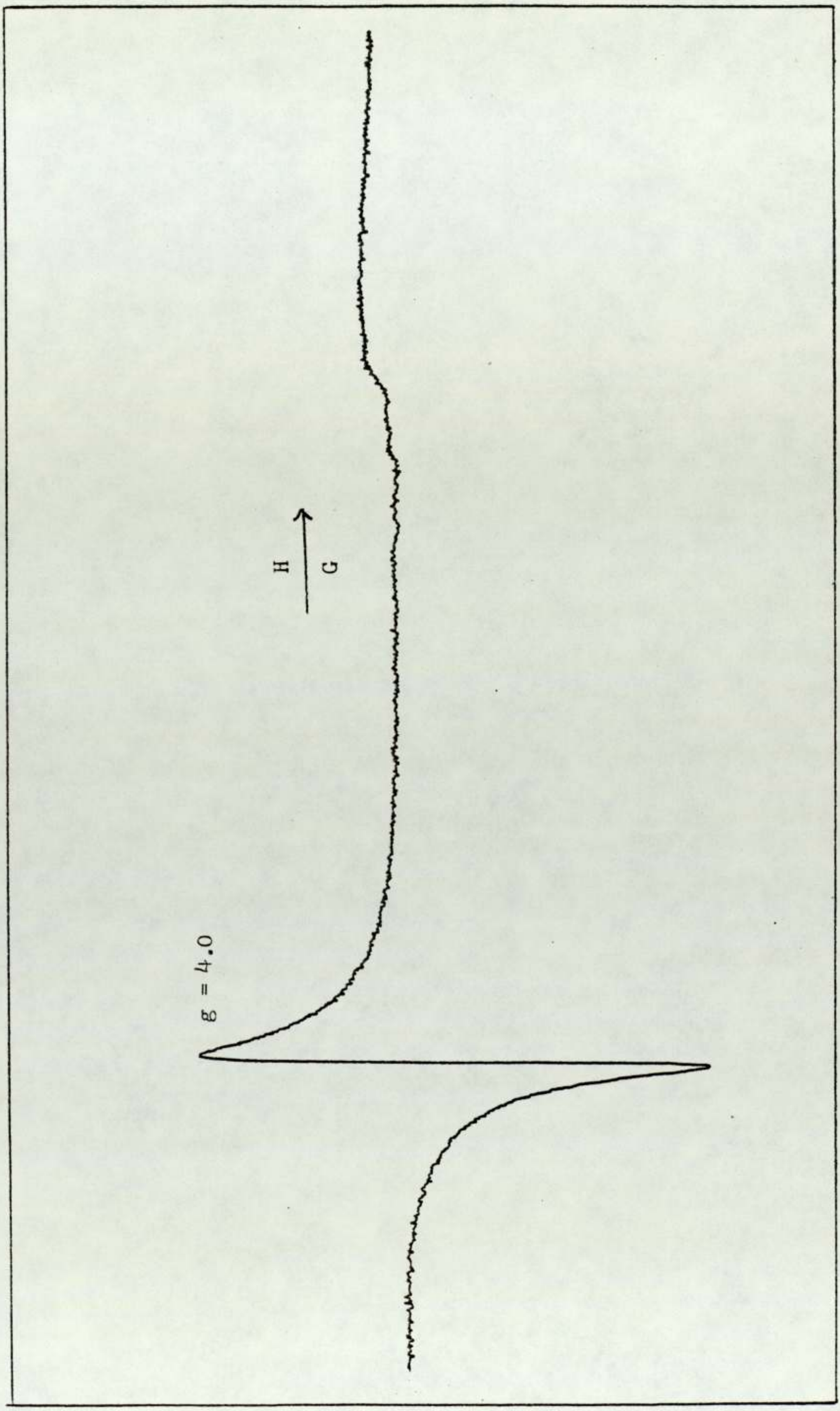
(Fig 29)



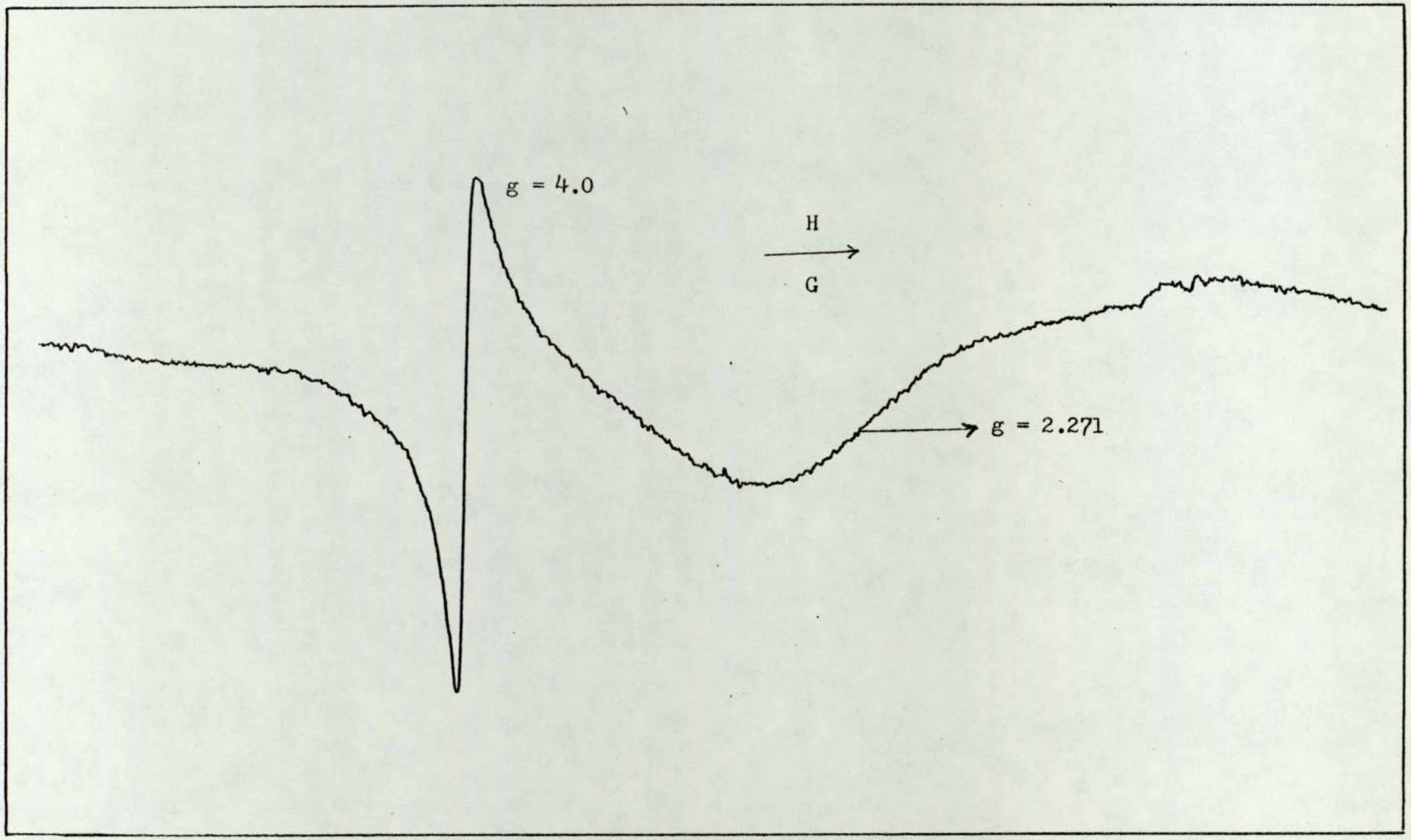
(Fig 30)



(Fig 31)



(Fig 32)



(Fig 33)
E.S.R Spectrum of Kaolinite Heated above 500°C

pattern to the broad, diffuse band characteristic of metakaolin and to the related changes in the hydroxyl bands in the infrared spectrum.

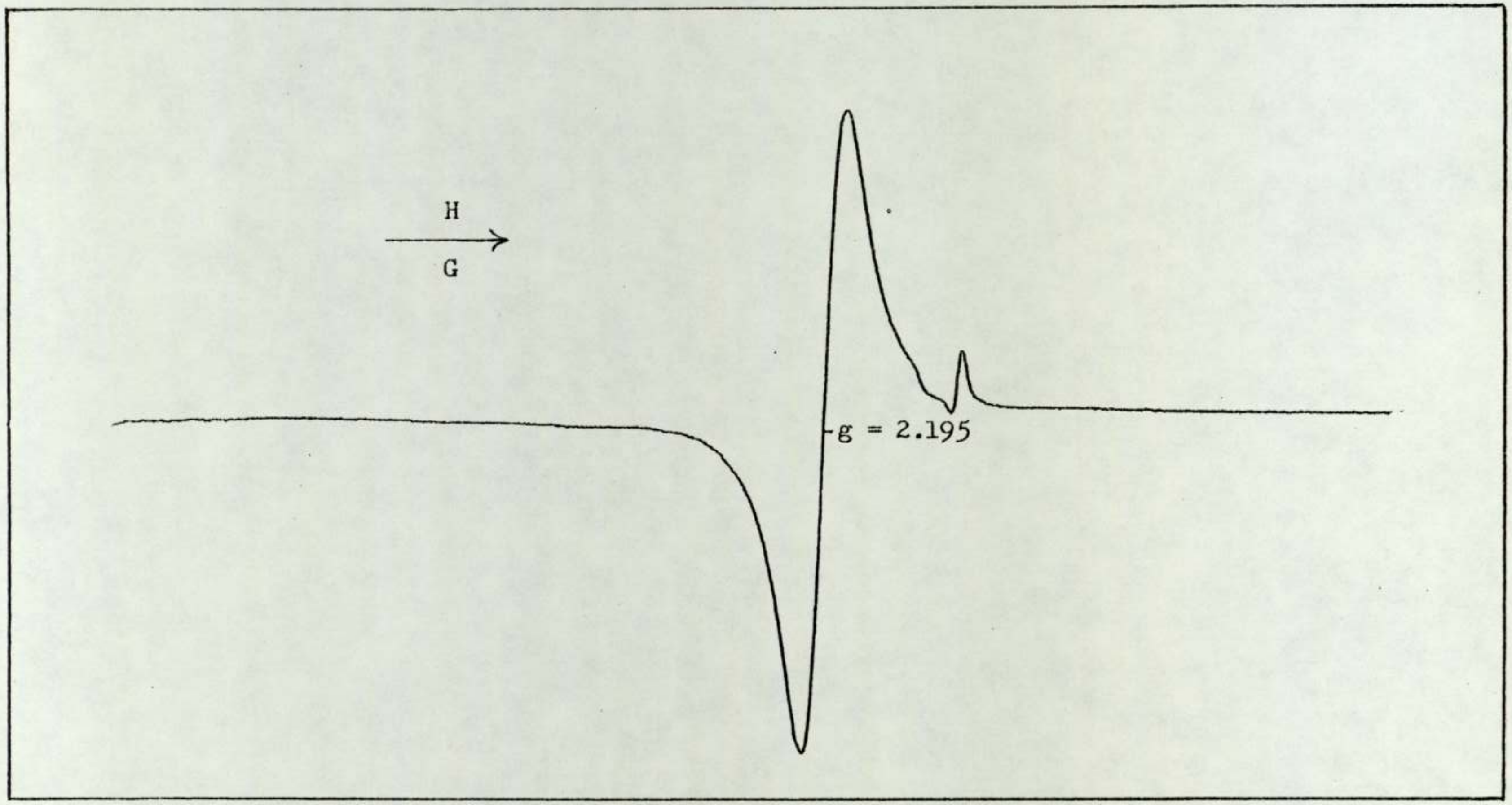
5.2.8: Kaolinite samples (10 g) were covered with an aqueous solution of copper(II) nitrate and copper(II) sulphate (100 ml/0.1M) separately in polythene bottles and were left for one month. After this time a pale-blue solid was separated from the liquid by filtration. E.S.R spectra of these materials are shown in figures (34, 35) respectively. Then these materials were contacted with distilled water (100 ml) and stirred for 24 h. E.S.R spectroscopy of the washed materials showed the presence of copper(II) ions with less intensity figures (36, 37).

5.2.9: A sample of kaolinite was dried at 350°C overnight. A specimen (5 g) of material was covered with a solution of copper(II) nitrate (2.4 g) in methanol (50 ml) and 2-aminopyridine (2 g) was added and stirred for 24 h. A dark-brown solid was separated from solution.

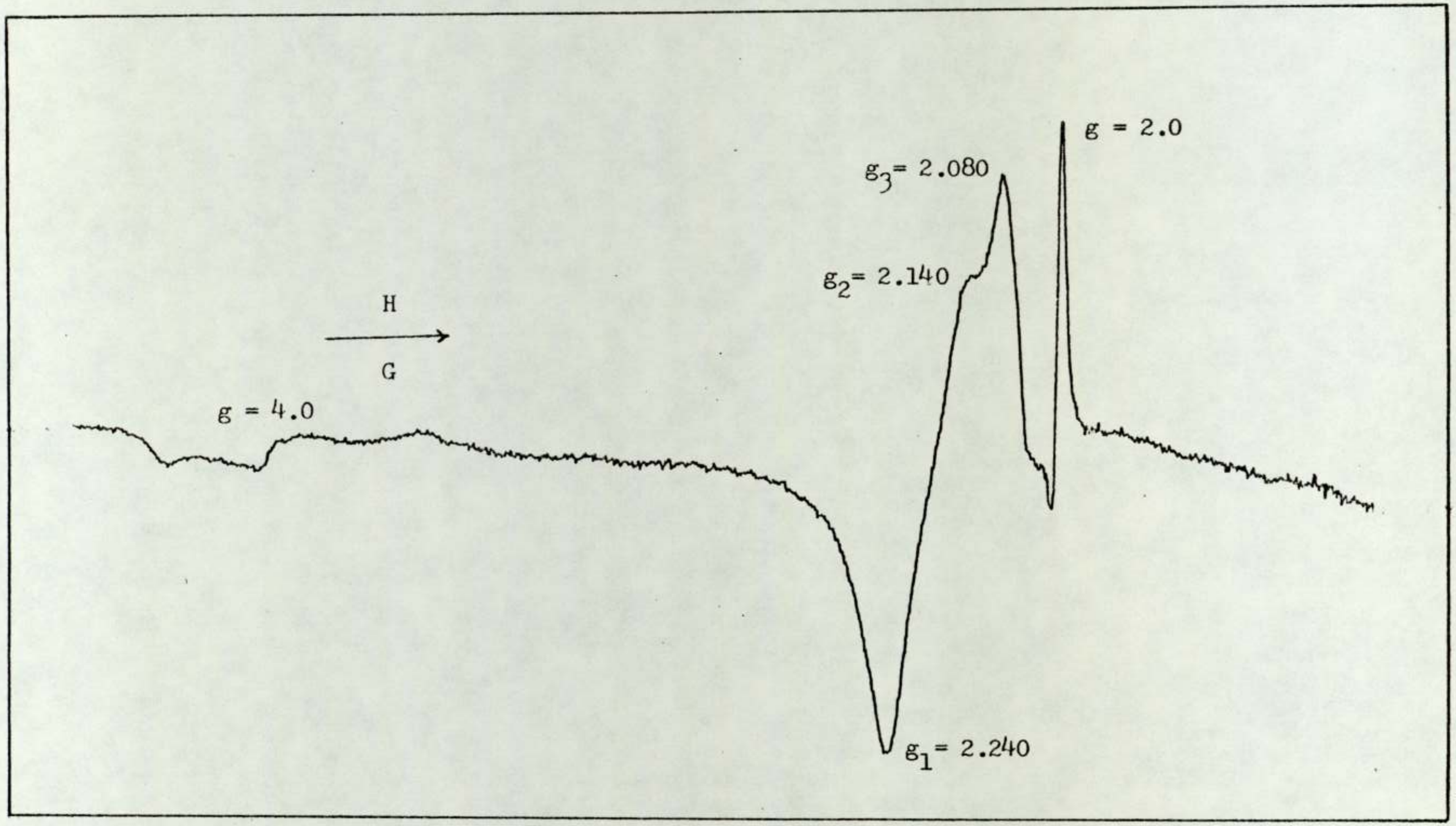
5.2.10: Dry kaolinite (5 g) was covered with solution of copper(II) chloride (1.34 g) in methanol (50 ml) and pyridine (8 ml) was added and stirred for 24 h. A blue solid was filter off.

From the infrared spectra which were obtained for each case, it was deduced that copper complex was formed on the clay. Some small frequency shifts were observed which was not thought to be consistent with a mixture of crystal of complex and clay, but is consistent with absorption of the complex.

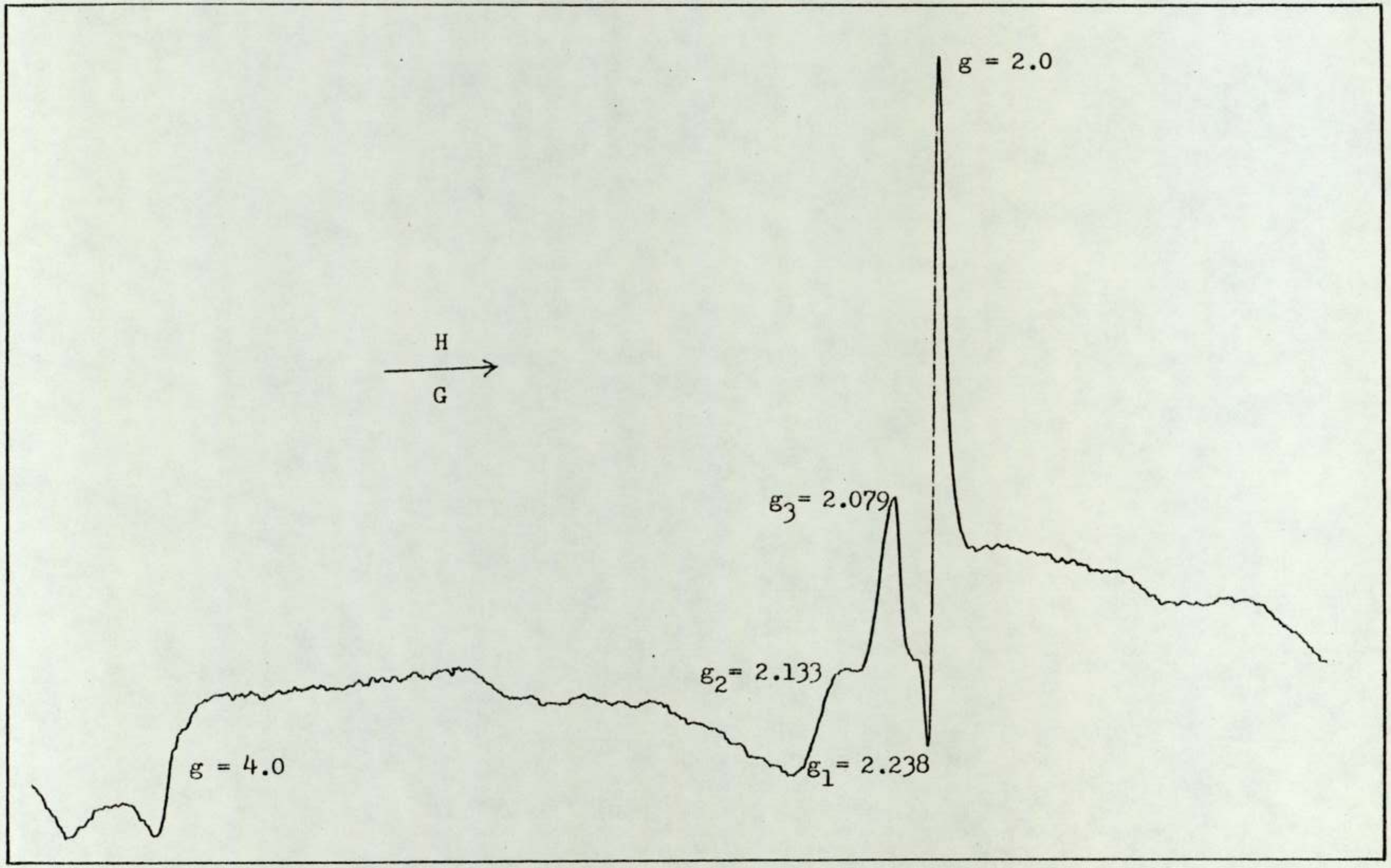
E.S.R spectra of these copper complexes on the clay were



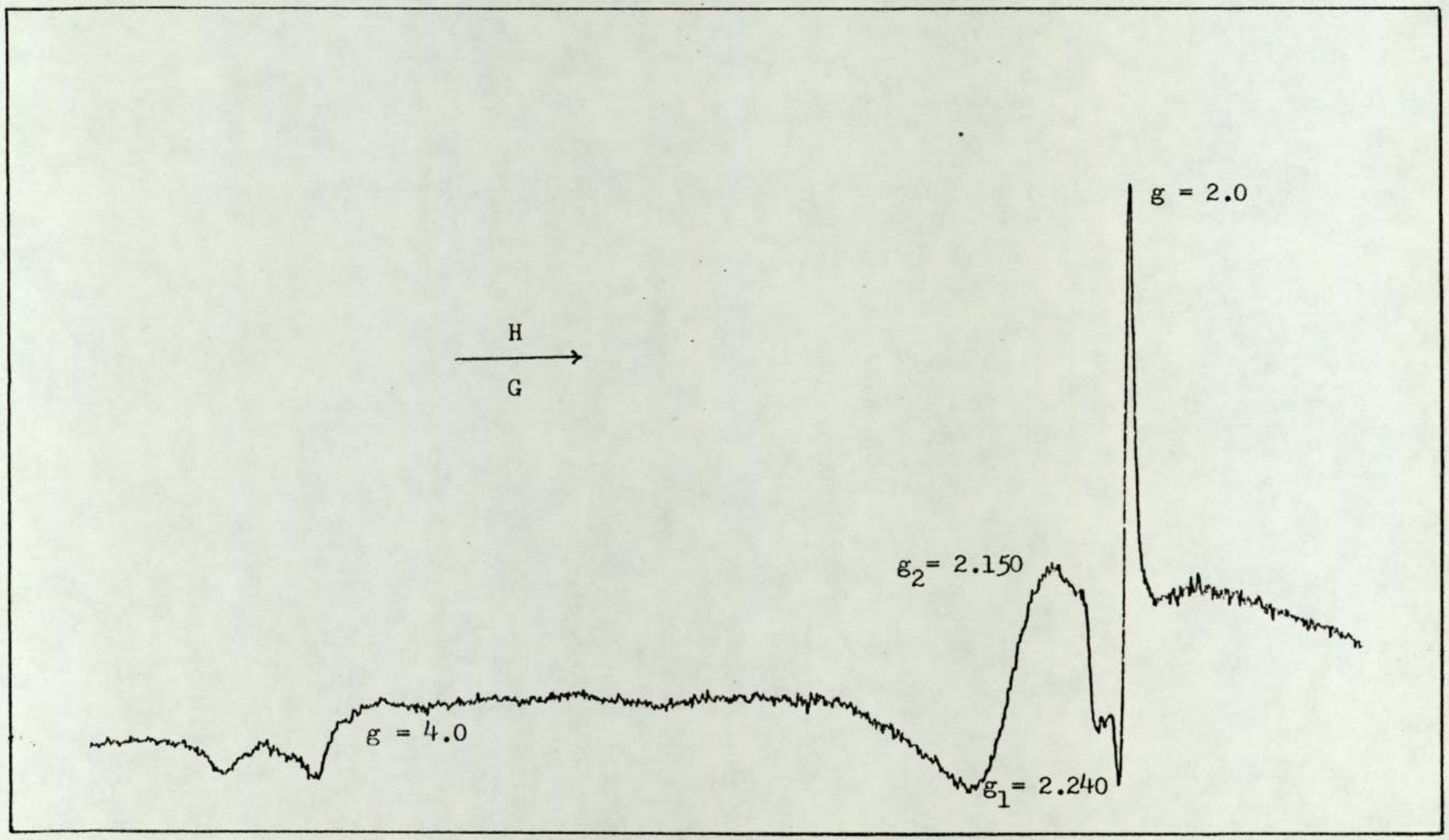
(Fig 34)



(Fig 35)



(Fig 36)



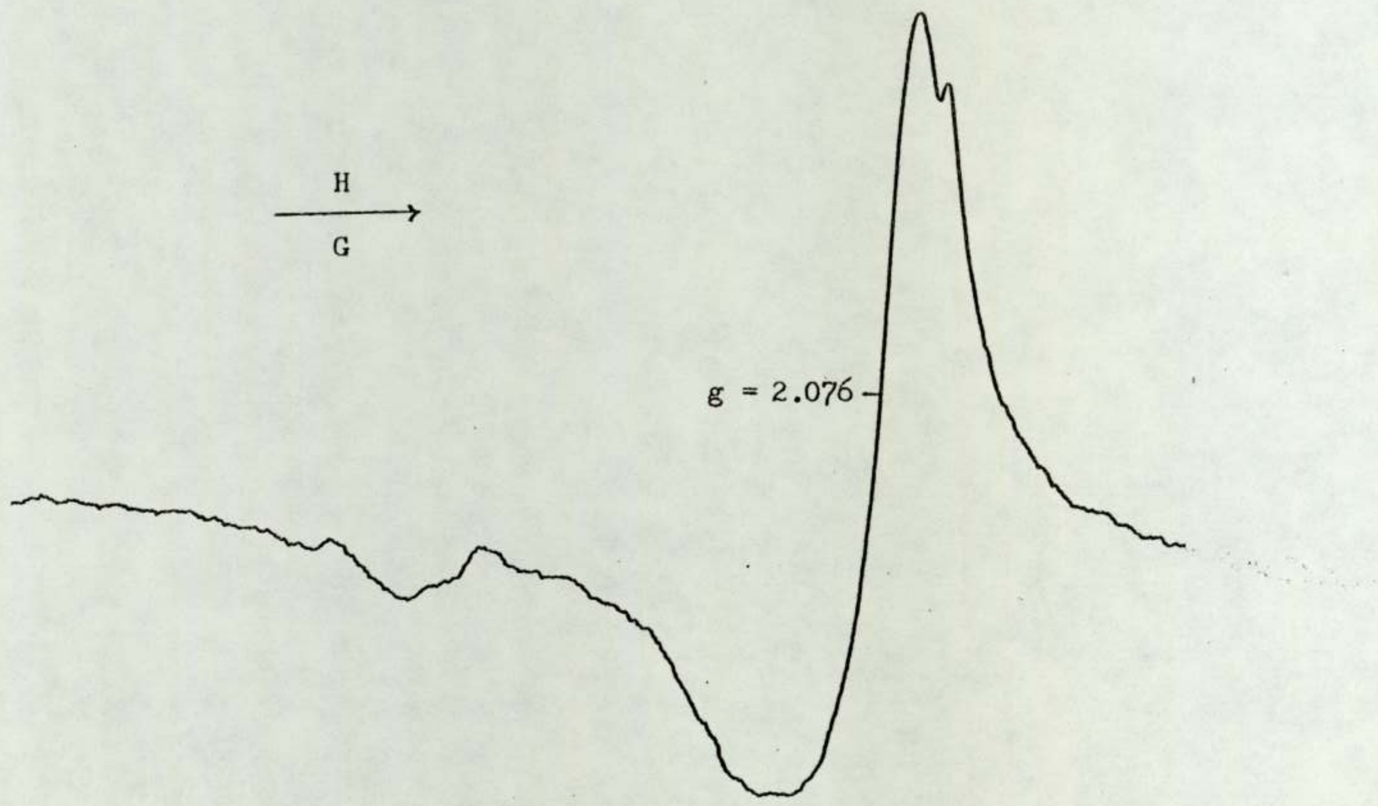
(Fig 37)

measured. These spectra are shown in figures (38, 39) respectively.

Elemental analysis for percent of copper in the complexes which were formed on the clay were performed by mixing clay plus copper complex (0.5 g) in boiling concentrated nitric acid. The solid was filtered and dried in an oven at 40°C. The difference between weight of clay plus complex before and after treatment with acid was due to weight of complex on the clay. The acid solution was diluted with distilled water to (250 ml), then (5 ml) of this solution was diluted with distilled water to (100 ml) and titrated with EDTA (chapter II section 2.9.1). Elemental analyses for percent of C H N also were performed by the microanalytical laboratories of the chemistry department. X-ray powder diffraction was used to determine the (001) basal spacing of the silicate layer after absorption of copper (II) complexes. Data are given in table (33).

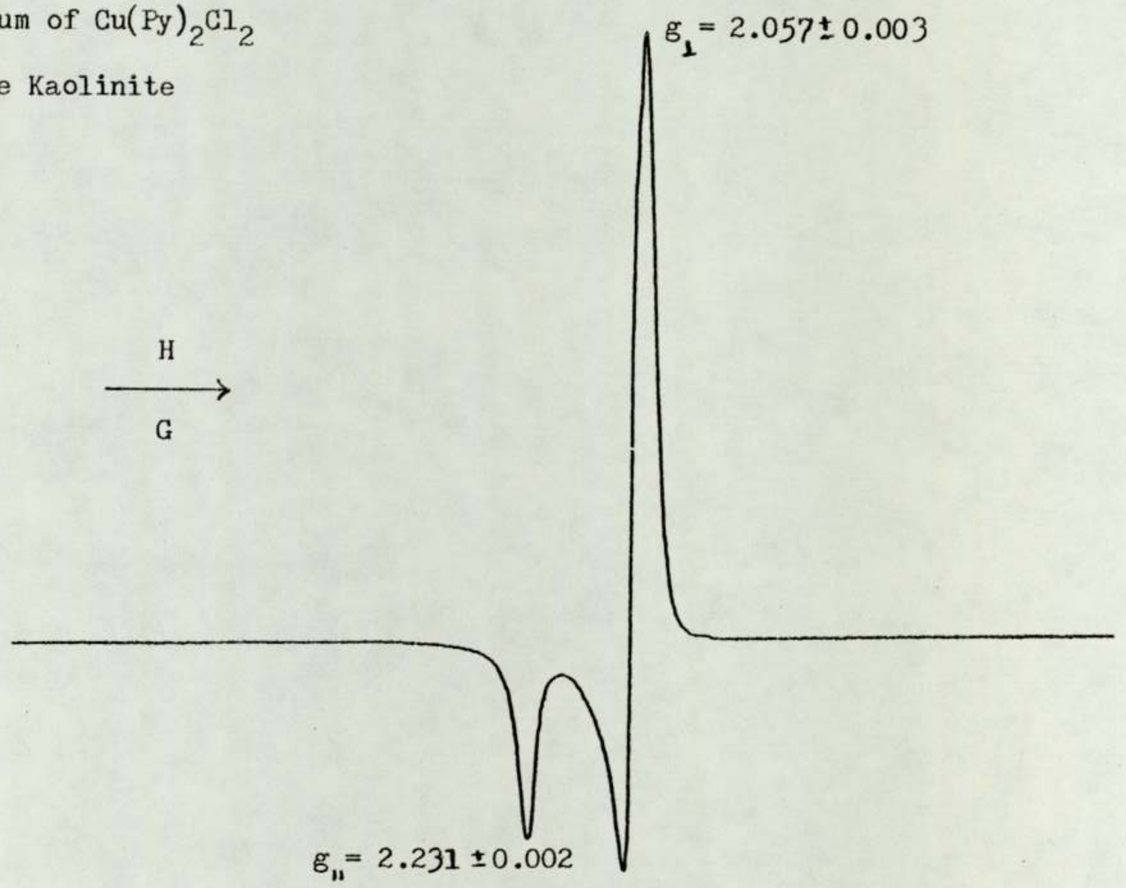
5.2.11: Kaolinite (10 g) was placed in a polythene bottle and covered with an aqueous solution of chromium(III) nitrate (100 ml/2000ppm) with $pH \simeq 2.0$ and shaken for one day to fourteen days. Solid was separated from solution and dried at room temperature in air. The amount of chromium remaining in the solution was determined using atomic absorption spectroscopy. The solid was then covered with distilled water (100 ml) and shaken for 24 h. An e.s.r spectrum was obtained from the solid, but because of the kaolinite signal it was difficult to determine the signal due to chromium(III). A graph showing the variation in concentration of chromium in solution with time is given in (Fig 40).

ESR Spectrum of $[(2\text{-ampy})_2(OCH_3)CuNO_3]_2$ on the Kaolinite



(Fig 38)

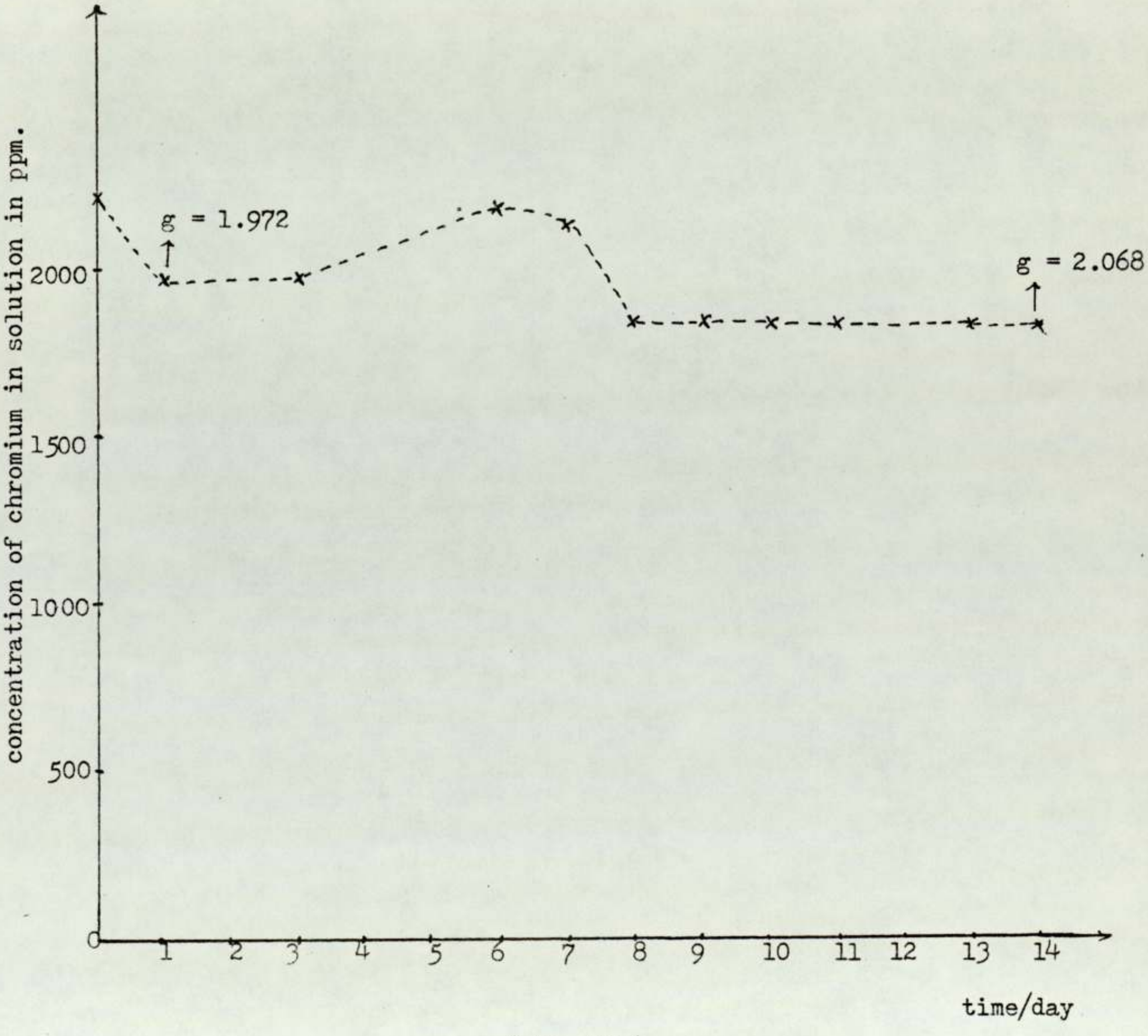
ESR Spectrum of $Cu(Py)_2Cl_2$ on the Kaolinite



(Fig 39)

Compounds		Kaolinite + $Cu(Py)_2Cl_2$		Kaolinited	Kaolinite + $[(2\text{-ampy})_2(OCH_3)CuNO_3]_2$	
		Found%	Required% $C_{10}H_{10}Cl_2CuN_2$		Found%	Required% $(C_{11}H_{15}CuN_5O_4)_2$
Analytical data	C	39.30	41.30	——	35.13	38.30
	H	3.27	3.41		3.99	4.50
	Cu	22.31	21.70		21.30	20.30
	N	9.71	9.57		18.63	18.40
E.S.R data		$g_{\parallel} = 2.231 \pm 0.002$ $g_{\perp} = 2.057 \pm 0.003$		$g_{\parallel} = 2.052 \pm 0.007$ $g_{\perp} = 2.002 \pm 0.002$	$g = 2.076 \pm 0.002$	
X-ray data (001)d spacing Å		7.35		7.26	7.31	

Table (33)


concentration of chromium in solution in ppm.
2000
1500
1000
500
0
g = 1.972
g = 2.068
1
2
3
4
5
6
7
8
9
10
11
12
13
14
time/day

(Fig 40)

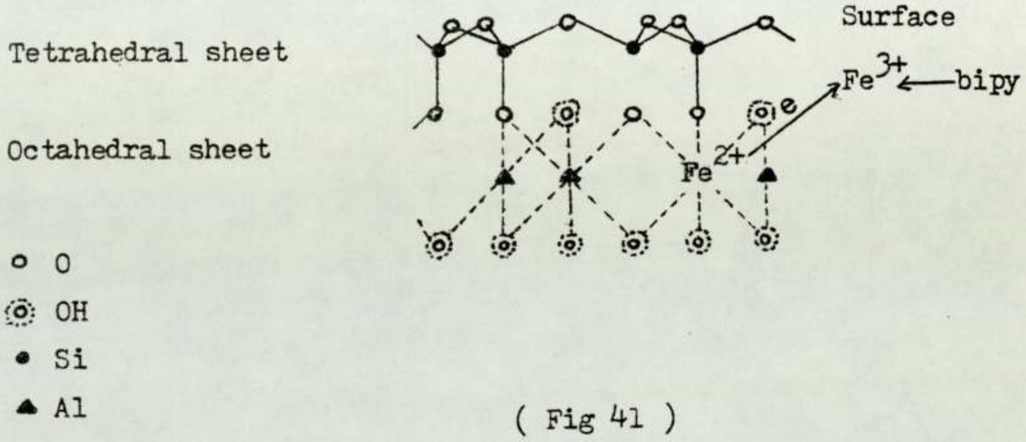
5.3 Discussion

Carter[24] reported a rhombic e.s.r spectrum which three g-factors were calculated for a sample of kaolinite which had been in contact with a copper(II) solution. Recently, Angel and Hall[25] (1972) studied the e.s.r spectra of a number of kaolinites from a variety of sources, which were both untreated and subjected to a variety of physical and chemical treatments. They concluded that the principal features of the kaolinite spectra were attributable to both iron(III) ions and defect centres within the kaolinite lattice. Kaolinites from this wide variety of locations were found to contain paramagnetic impurities which produce contributions to the e.s.r spectrum.[84] In this work kaolinite used was supplied by English China Clays Ltd. The sample exhibited resonances A and C (Fig 26) which are centred at $g = 2.0$ and $g = 4.0$ respectively. The resonance at $g = 4.0$ is composite and can be unequivocally assigned to two iron(III) species in different sites, and the resonance A may be attributed to a defect which can be produced by X-irradiation and is stabilized by magnesium(II) or iron(II).[85] These resonances, which are characteristic of all kaolinites, were not affected by treatment with nitric acid. This material was then treated with 2,2'-bipyridyl and the surface colour was seen to change to pink. This pink colour is attributed to tris[2,2'-bipyridyliron(II)] cation. Re-examination of the e.s.r spectrum showed that in addition to the unchanged resonance centred on $g = 2.0$ and $g = 4.0$, a new signal at $g = 2.115$ had materialized. The room temperature Mössbauer spectrum of this specimen (Fig 28) has two well resolved peaks as well as a less intense unresolved central region of absorption . If the two outer peaks are taken to be both parts of a quadrupole split doublet then $\delta = +1.04$ mm.s^{-1} with respect to natural iron and $\Delta = 2.07$ mm.s^{-1}. These parameters are consistent with the presence of distorted high spin octahedral iron(II). These peaks should be of equal intensity but commonly are not in minerals because of texture in the absorber giving some preferential orientation. The percentage resonance absorption is very small compared to the average counts per channel (the spectrum took one week to accumulate) so computation of the data is difficult, hence resolution of the central region into its components is also difficult. The similarity between this spectrum and the one reported by Tricker[86] et.al is very great. After computation the results indicated that there were two iron sites: $\delta = 0.35$mm.s^{-1} , $\Delta = 0.92$ mm.s^{-1} and $\delta = 1.53$ mm.s^{-1} , $\Delta = 2.57$ mm.s^{-1}. The first site is consistent with iron(III) in an octahedral environment. The second site is consistent with iron(II). Heating at temperatures of 500°C and above causes elimination of the $g = 2.0$ resonance, together with a collapse of the low-field resonance to give a more intense and isotropic spectrum at $g = 4.0$ (Fig 33). These transitions in the e.s.r spectra coincide with both the collapse of the kaolinite X-ray diffraction pattern to the broad, diffuse band characteristic of metakaolin and to the related changes in the hydroxyl bands in the infrared spectrum. Also one new feature, a broad band centred on $g = 2.271$ was observed in the e.s.r spectrum.

A similar observation on heating the sample to 1200°C was obtained which agrees well with the report of Angel and Vincent.[87] No change in the X-ray diffraction pattern and e.s.r spectrum was observed for the sample when heated to 400°C for 2 h. Heating above

500°C caused a decrease in intensity of the $g = 2.0$ resonance and above 650°C metakaolin was formed and the $g = 2.0$ peak vanished. After heating at 1200°C mullite was detected. E.S.R spectroscopy showed that the resonance at $g = 2.0$ is stable at temperatures up to about 400°C. At temperatures above 500°C the collapse of the signal on dehydroxylation suggests that the paramagnetic species is more closely associated with the octahedral layer than the tetrahedral layer, which is virtually unchanged on dehydroxylation.[15] At the same time the single-line resonance at $g = 4.0$ exhibits a corresponding increase in intensity. It has been suggested[88] that this is consistent with an increase in the number of ferric ions occupying distorted tetrahedral configurations after the change in aluminium(III) coordination from six to four.

It was anticipated that any surface iron contaminant would be affected by chemical treatment of the kaolinite which would either modify or remove the iron species. In this work when kaolinite was treated with nitric acid no removal of iron was observed. Similar results have been reported by Tricker[86] et al for some other kaolinite specimens. The presence of iron in the surface particles was confirmed by 2,2'-bipyridyl treatment which produced the familiar red colour of $[Fe(bipy)_3]^{2+}$; however, Mossbauer evidence gave no sign of $[Fe(bipy)_3]^{2+}$, therefore the concentration of surface iron is considered to be low with respect to lattice iron as revealed by Mössbauer spectroscopy. The presence of a new signal at $g = 2.115$ was detected by e.s.r spectroscopy after acid/2,2'-bipyridyl treatment. This probably arises from the change in magnetic properties of the surface iron contaminant. $[Fe(bipy)_3]^{2+}$ possibly may be formed as a result of a redox reaction. This can be explained as an electron transfer across a layer of oxygen atoms in kaolinite as represented diagramatically in (Fig 41).



(Fig 41)

If this is so, then the amount of surface iron contaminant must be small because lattice iron(II) can still be seen by Mössbauer spectroscopy, but $[Fe(bipy)_3]^{2+}$ is not observed (see Fig 28). It is postulated that dehydroxylation of kaolinite at 500°C is accompanied by oxidation of lattice iron(II) to iron(III) which causes an increase in the intensity of the now isotropic resonance at $g = 4.0$. This observation is accompanied also by the removal of the resonance at $g = 2.0$ (see above) and the growth of a broad resonance at $g = 2.271$, which has also been seen by others[87] when surface contaminated kaolinites are heated. This is attributed to a change in the surface iron, possibly to magnetite, (Angel)[87]. Angel's[28] explanation was accepted for the resonance at g = 2.0, however it was considered desirable to examine the possibility that organic radicals could be responsible for the signal. Interaction with galvinoxyl leaves the resonance at g = 2.0 unaffected, and this is taken to indicate that the signal does not result from organic radicals.

An investigation of the effect of reducing agents, in particular sodium dithionite, which was designed to remove surface and free iron oxide and hydroxide, failed to remove the g = 4.0 signal; however in one experiment the sharp g = 2.0 signal was lost. This experiment was not reproducible, but Angel[87] removed the resonance at g = 2.0 by heating the clay in hydrogen at 500°C and also observed the isotropic line at g = 4.0 to increase in intensity. Thus the specimen in this work also may be changed by reducing agents. Finally it was decided to consider hydrazine as a reducing agent (see page 139) and the e.s.r spectrum is shown in (Fig 29). No effect on g = 2.0 was seen, but some change in g = 4.0 was noted. It has been suggested that the g = 4.0 signal may result from two iron(III) sites, hence it appears probable that the iron(III) in one of these sites is more rapidly reduced than the other.

In conclusion, it appears that the specimen of kaolinite, used in this work, is broadly similar to those studied by Angel. Angel's view of the origin of the g = 2.0 and g = 4.0 e.s.r signals is accepted, but differences of detail in other aspects of the behaviour of the specimen in the present work are noted. However, we are in a position of having a reasonable understanding of our kaolinite and may now move to a discussion of its behaviour in the presence of solution of metal ions.

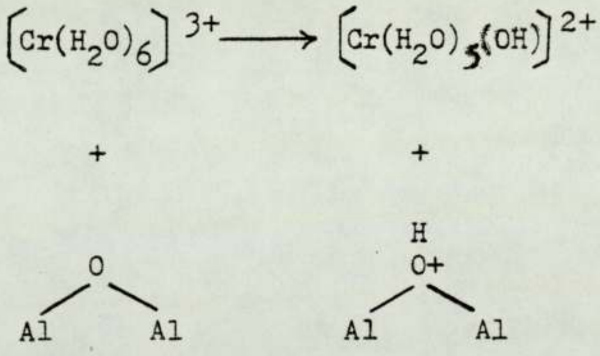
5.3.1 Sorption of Chromium(III) by Kaolinite

It has been reported[89] that hydrolytic reactions may occur before or after the sorption of metal ions by clay minerals. e.g. copper(II) may be taken up as "$\overset{II}{Cu}(OH)^+$". It is difficult to clearly resolve whether the hydrolytic species are formed in solution or produced in situ after sorption of the hydrated ion at specific sites. To consider this phenomenon chromium(III) is potentially useful because of the slow reaction behaviour (kinetically inert). For these experiments kaolinite was covered with an acidic solution of chromium(III) ($pH \simeq 2$) and stirred from one day to fourteen days after which the chromium(III) remaining in the solution was determined by atomic absorption. E.S.R spectroscopy was also used to detect the sorption of chromium(III) onto the clay. When the "exchanged" kaolinite was in contact with distilled water for 24 h some of the chromium(III) was released into the solution as shown by atomic absorption analysis. An analysis for iron by atomic absorption showed that very small quantities of iron were also released.

A plot of uptake of chromium(III) against time (Fig 40) agrees well with that reported by Carter[24]. Thus an initial fairly rapid uptake is followed by a period in which chromium is released to the solution after which a new equilibrium appears to be established. Much of the chromium taken up is labile as demonstrated by the fact that it is released into pure water. This observation is considered to result from simple sorption onto the surface of kaolinite crystals. Previous workers have indicated that most of the "exchange" capacity of kaolinite arises from broken bonds at the edges of crystals,[14] but others have more recently obtained data to suggest that much of the sorption occurs on the crystal surfaces.[13] The small release of iron detected by atomic absorption may arise from the surface contaminant detected in the previous section. Indeed this contaminant may play an active role in the uptake of metal ions since one of our group has demonstrated[90] quite remarkable affinities for cations to exist for various hydrated iron oxides of the type found in some geological environments. From these results we can probably accept Carter's[24] explanation of absorption of chromium(III) by kaolinite. The initial rapid adsorption occurs on the surface of the kaolinite. Chromium(III), as the $[Cr(H_2O)_6]^{3+}$ species, will be efficiently adsorbed because of its high charge. When the chromium(III) ion is attached to the clay mineral, deprotonation of the hydrated ion may occur, in which a hydrogen ion is lost from one of the water molecules acting as ligands. The effect would be to reduce the charge in the chromium, thus making the ion less competitive for occupation of exchange sites. A reduction in the rate of adsorption of chromium(III) can thus result after a period of time. Indeed new equilibria will have to be established and the curve shown in (Fig 40) becomes understandable in these terms.

The e.s.r spectrum initially showed an extremely broad signal at $g = 1.972$. A g-factor of 1.976 has been reported[91] for $[Cr(H_2O)_6]^{3+}$ species. The environment of the chromium(III) ions thus is obviously similar on the clay surface to that in $[Cr(H_2O)_6]^{3+}$, the isotropic signal may indicate a solution-like environemt on the clay, but the breadth of the line suggests that the chromium ions may not be well separated, this would of course be the case if the surface iron compounds were involved in the sorption process. With time, the g-factor changed to 2.068 (14 days see fig 40), hence we may deduce that some change in the chromium environment has occurred. This is entiraly consistent with Carter's view that hydrolytic reactions may occur on the clay. Also use of the kinetically inert species supports the view that this might be generally the case. There would certainly be no shortage of proton acceptor sites on the clay and this might enhance the essential deprotonation step :

e.g.



After this dimers and oligomers may rapidly form accounting for both the enhanced breadth of the e.s.r signal and also for the shift in g-factor.

In accordance with the previous considerations, the attempted use of vanadate(V) as an oxidising agent to remove g = 2.0 failed. It was thought that if g = 2.0 is due to a free electron this would reduce vanadium(V) to vanadium(IV), as shown in the following equation :

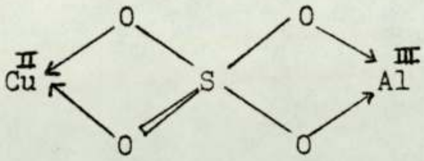
$$V^{V} + e \longrightarrow V^{IV}$$

The formation of vanadium(IV) was confirmed by e.s.r spectroscopy, but the resonance at $g = 2.0$ was unaffected. The same result was also obtained in the absence of kaolinite, hence reduction is not due to a free electron. Since vanadium(IV) was detected by e.s.r spectroscopy, it can be used to probe exchange sites in the kaolinite. When kaolinite was covered with vanadate(V) solution after one month e.s.r measurement of solid showed a strong isotropic signal, which was due to the formation of vanadium(IV) adsorbed by kaolinite. The observed spectrum arises from the flipping of the unpaired electron of the ionic $3d^1$ configuration and has eight fairly well resolved components, corresponding to a nuclear spin of 7/2 for ^{51}V. The g-value and hyperfine constant for this material was calculated and found to be $g = 1.961$ and $\langle A \rangle = 117.5$ G, in excellent agreement with the g-value and $\langle A \rangle$ measured in the aqueous vanadyl solution.[92] There is no need to consider the formation of a vanadium complex, because perchlorate is a weak ligand. When this material was washed with distilled water the signal intensity greatly reduced compared with the signal for kaolinite at $g = 2.0$. The residual signal however seems to consist of two isotropic signals (Fig 31) with $g_1 = 1.940$ and $\langle A_1 \rangle \doteq 118$ G ; $g_2 = 1.996$ and $\langle A_2 \rangle = 95$ G . It is reasonable to deduce that g_1, $\langle A_1 \rangle$ is due to an aqueous vanadyl species, but g_2, $\langle A_2 \rangle$ implies vanadium(IV) in a different environment. In the case of g_1, $\langle A_1 \rangle$ the aqueous vanadyl ion is freely tumbling and presumably sorbed onto the surface of the kaolinite. The second signal g_2, $\langle A_2 \rangle$ which is also due to freely tumbling species might arise from sorption of aqueous vanadyl ion on the broken edges of the crystalline plates. Another explanation is that, as we have previously shown, some iron surface contamination is present on the kaolinite (page 157). Such iron oxide species are effective substrates for sorption of metal ions, hence we must consider that "surface" sites may in reality be associated with the iron oxide. McBride[93] has also used e.s.r spectroscopy to investigate kaolinite sorption sites. He concludes that the popularly held view of edge adsorption is not valid at least at acid pH. If this is accepted, then the two sites observed in the present work are likely be located on the larger surface areas of the crystals. One (g_2, $\langle A_2 \rangle$) as stated above may be associated with iron oxides on the surface, the other (g_1 $\langle A_1 \rangle$) may well be a pure kaolinite exchange site. Also, in agreement with McBride, we note that under normal humidity conditions, all exchange sites seem to offer solution type environments to the metal ion.

5.3.2 Sorption of Copper(II) ions

The sorption of copper(II) nitrate and copper(II) sulphate by kaolinite was considered by using electron spin resonance spectroscopy. Kaolinite was covered with copper(II) nitrate and copper(II) sulphate separately and left for one month. E.S.R measurement of the solids showed an isotropic spectrum for copper(II) nitrate which can be due to $[Cu(H_2O)_6]^{2+}$ species. The anisotropic signal found for copper(II) sulphate might be due to sorption of a sulphato-complex on the edge of crystals. When these materials were washed with distilled water, a complex signal was observed for copper(II) nitrate which could be an anisotropic resonance with ($g_1 = 2.238$, $g_2 = 2.133$, $g_3 = 2.079$). Alternatively it may arise from the two overlaping isotropic signals of copper(II) ions sorbed in two distinct sites similar to that observation for aqueous vanadium(IV) and following the view of McBride[93]. In the case of copper(II) sulphate a broad signal with a shoulder was observed. Possibly this can be explained following the nitrate argument, or it could be specific edge sorption encouraged by the sulphate anion. We have previously discussed such matters for montmorillonite (page 122) and may utilise the same argument here. Thus SO_4^{2-} has the correct stereochemistry to interact with the crystal edge :

i.e.



The copper(II) may now have an enhanced affinity for the edge as shown in the above figure.

In conclusion the main advance seems to be the use of VO^{2+} to identify two sorption sites on kaolinite. Copper(II) data is more difficult to interpret, but good agreement for nitrate was observed with the above considerations. As with the montmorillonite study, the detailed behaviour of copper(II) seems to be a function of the counter anion. Finally, Carter's[24] data using e.s.r to investigate copper(II) must be re-interpreted, however her results on the uptake of metal ions appear to be acceptable, because good agreement between her chromium data and that presented here is noted.

5.3.3 Formation of Copper(II) Complexes on the Kaolinite Surface

An attempt was made to synthesise copper complexes supported by kaolinite, from the physical data it was deduced that this was successfully achieved. Elemental analysis of the anchored complexes showed good agreement between expected and observed figures (table 33). The infrared spectrum showed some small frequency shifts which were not thought to be consistent with a mixture of crystals of the complex with clay, but is consistent with adsorption of the complex on the surface. The X-ray diffraction pattern showed no change in (001) basal spacing of kaolinite after treatment with copper complexes, therefore it can be deduced that the complexes were not formed between the silicate layers. The presence of copper complexes on the surface was also confirmed by e.s.r spectroscopy. An anisotropic spectrum was observed for dichlorobispyridinecopper(II) on the kaolinite surface with $g_{\parallel} = 2.231 \pm 0.002$ and $g_{\perp} = 2.057 \pm 0.003$, $G = 4.05$. A comparison between these values and those obtained for the bulk complex (see chapter three page 82) indicate much less evidence for the presence of exchange coupling (i.e. G 4.0).[55] From this observation it can be concluded that dichlorobispyridinecopper(II) has formed as a monomer on the kaolinite surface. In the case of the 2-aminopyridine complex an isotropic spectrum was obtained with $g = 2.076$ which is close to that value for free complex $g = 2.063$.

In conclusion, as was expected, kaolinite can not expand and support the copper(II) complexes in interlamellar positions, hence kaolinite was not considered to be as suitable as montmorillonite for the purpose of the work described in chapter three, because the complexes are likely to be too labile.

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