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**NEW SYNTHESSES OF THE PIGMENTS COPPER PHTHALOCYANINE
AND CERIUM SULPHIDE**

BY

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UNDER THE SUPERVISION OF

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AT THE

UNIVERSITY OF ST. ANDREWS

SUBMITTED 1999



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I would like to dedicate the work in this thesis
to Jeff, Joyce, Heather and Liz

Take the time to make some sense
Of what you want to say
And cast your words away upon the waves
And sail them home with acquiesce
On a ship of hope today

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ABSTRACT

Novel synthetic methods for the production of copper phthalocyanine (CuPc) and cerium sulphide (Ce_2S_3) have been devised. The aims of the new techniques were to produce the pigment in a stable, usable form with the possibility of controlling the particle size.

For the production of CuPc a gas phase synthesis utilising volatile starting materials was attempted. The first obstacle to be overcome was to design a suitable set-up to facilitate such a reaction. The design has to allow easy loading of the starting materials and easy removal of any product. Such a set-up has been built and commissioned see figure 2.1 in chapter 2. A number of volatile copper complexes were synthesised and used in a gas phase reaction with either 1,2-dicyanobenzene or 1,3-diiminoisoindoline, with limited success. It has been shown that such a gas phase method can produce CuPc but in low yields and not pure, also the reproducibility of the results is in doubt.

From solid state reactions the copper complexes react with 1,2-dicyanobenzene and 1,3-diiminoisoindoline to produce CuPc. The CuPc produced is impure.

An aerosol assisted synthesis of copper phthalocyanine was attempted, however, with no success. This was due to a lack of transportation of the precursors into the reaction zone. The introduction of a catalyst to the reaction scheme was studied. From this it was found that the main role of the catalyst was in catalysing the reaction between phthalic anhydride and urea. It is thought that the catalyst plays a role in removing the ligands from the copper complex thus improving the purity of the CuPc produced.

It is unlikely that such a synthetic method, gas phase or aerosol assisted, will be practical or be used in producing CuPc. The chance of producing a sample of high yield and purity and in a suitable form for pigmentation is very low.

Control of particle size is quite important in the pigment industry, as varying particle sizes can result in a different overall colour of the material. Therefore uniform size is important for reproducibility of the pigment.

In materials that have a band structure on controlling the particle size in the 1-10 nm region quantum confinement effects take place. If significant these effects can alter the colour of the material just by altering the particle size.

Particle size control of CuPc was attempted by encapsulating the pigment within the cages of different zeolites. Three different synthetic methods were devised along with using three different zeolites. The resultant material was nearly always green. Analytical techniques used, show that CuPc has been formed and is structurally intact but that some electronic changes have taken place. It is not known whether these changes give rise to the resultant colour or if they result from the material being trapped within a small space or are in fact coating the zeolite by only a few molecules thick.

Despite getting green materials from a number of different syntheses and using three different zeolites the material is not in a suitable form for pigmentation and reproducibility of the exact colour is also a problem.

A low temperature route to produce cerium sulphide was devised using cerium dithiocarbamates and attempting to decompose them in a similar manner to the production of CdS, ZnS and CaS. Cerium dithiocarbamates were synthesised and it was found that they are extremely air sensitive, especially the tris dithiocarbamate salts, $\text{Ce}(\text{S}_2\text{CNRR}')_3$. During the synthetic process air and water must be excluded, even though the products are water stable it is believed that on decomposition of the samples the presence of water causes contamination with oxygen.

The dithiocarbamates, $\text{Ce}(\text{S}_2\text{CNRR}')_3$ and $\text{M}[\text{Ce}(\text{S}_2\text{CNRR}')_4]$ were heated in nitrogen, sulphur and hydrogen sulphide environments to try and produce cerium sulphide and determine a mechanism for the decomposition. In all cases a black or dark brown material was produced. GC-MS studies suggest that the material may be decomposing back to its original starting materials, as CS_2 is evolved upon heating.

CHAPTER 1

INTRODUCTION TO COLORANTS

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1.1.0 INTRODUCTION TO COLORANTS

In everyday life we are surrounded by things that are coloured, the sky, the sun, clouds, plants, grass, cars, clothes, food, drinks, even our skin is coloured. It is due to the nature of the human eye that we can detect and differentiate between a vast number of colours and shades of colour. The light emitted from coloured materials reacts with the retina in the back of the eye sending a message to the brain that the object in vision is a certain colour. These colours come from an incredible number of different colorants many of which are naturally occurring and others synthetically produced.

The term colorant refers to a material that is coloured and includes both dyes and pigments¹. The terms dye and pigment are often falsely interchanged. The major difference between dyes and pigments is their solubility in their application media. Dyes are soluble in the application medium and must have an affinity to the substrate they are colouring. Pigments, however, are characterised by being insoluble in the application medium and are normally attached to substrates by additional compounds.

Nowadays many of the naturally occurring colorants tend to be synthetically produced because it is cheaper and more efficient than extracting a small amount of material from its natural source. The production of colorants is a big industry with over 800,000 tons of coloured materials synthetically produced every year.

Despite the large number of colorants already existing there is still a great deal of research being carried out in this area of chemistry to try and improve the many dyes and pigments and to generate new chromophores.

1.1.1 A BRIEF HISTORY OF COLORANTS

Dyes

Natural colorants, both inorganic, (charcoal, iron oxides, manganese dioxide), and organic, (indigo, turkey red), were used by prehistoric man to dye furs and textiles they

were also used in cave drawings and hieroglyphics¹. However, it was the discovery of Mauve, or Mauvine, by W.H. Perkin² in 1856, whilst studying oxidation reactions of coal tar bases, that marked the start of the synthetic dye industry. Perkin discovered an intense bluish purple coloured solution from the crude bases in methanol. The ability of this material to dye silk a rich purple colour led him to patent the discovery, British Patent No. 1984, and within a year of this, full scale production of mauve started¹.

This result stimulated other chemists to carry out similar experiments leading to the discovery of Fuchsine, by E. Verguin in 1859, and also diazo compounds, by P. Griess in the 1860s. The latter discovery has led to the development of the largest class of synthetic dyes, the azo compounds.

Also in 1856 C.H.G. Williams³ discovered an intensely coloured polymethine dye, cyanine, however, this material was not used as a colorant until later when it was discovered to be very useful for the photographic industry⁴. As a result it initially received very little attention in research and industry.

Over the next few decades a number of significant discoveries both of dyes and their structures were made. In 1868 Graebe and Liebermann described the structure and synthesis of alizarin. After a number of years of work the structure of indigo was formulated by von Baeyer. In the 1890s sulphur dyes were discovered by Vidal. Indanthrone was discovered in 1901, by Bohn, and in 1915 Neolan dyes were produced. Following the second world war Irgalan dyes were discovered in 1949. Reactive dyes, (wool dyes, 1951, cellulose dyes 1956)¹.

Pigments

Pyrrrole pigments are the most abundant naturally occurring pigments⁵, and include haem and chlorophyll. The industrial production of inorganic pigments began in the 19th century, however the production of organic pigments has always formed part of the dyestuff industry. It was not until 1936 that a colorant with a new chromophoric system was developed. This material was copper phthalocyanine, (CuPc), giving rise to the first

organic pigment used industrially to colour materials⁶. This was followed shortly by derivatives of CuPc making them usable as dyestuffs and pigments. The next significant organic pigment to be discovered was quinacridone in 1958 and these were followed in 1984 by the DPP, (diketopyrrolopyrrole) pigments¹.

Organic pigments only account for 4 % of the total pigment production with CuPc contributing to 1 % of the total production of pigments. The most common pigment with over 50 % of the total production of pigments is TiO₂, the most important white pigment. However, since the 1970's research into dyes and pigments has, due too economic and ecological problems, concentrated on optimisation of synthetic methods and manufacturing processes, such as finishing and application of the colorant.

1.1.2 THE COLOUR OF COLORANTS

Colours arise because the material, or a part of the material, absorbs light in the visible region, 400 nm to 700 nm, of the spectrum. It is the position, see table 1.1, shape and the number of absorptions in this region of light that give rise to the specific colours observed. Colours other than black, white and grey are known as chromatic colours and the unit that absorbs the light referred to as a chromophore. Black, white and grey are achromatic colours and materials with these hues absorb either all, none or a portion, respectively, of all the light in the visible region. The shades of grey depend upon the fraction of light absorbed, with lighter greys absorbing less than darker greys¹.

The area where the absorption band is found is the wavelength of light absorbed by the material and the rest of the light is reflected or transmitted giving the material its resultant colour. Table 1.1 lists the expected colours from the range of wavelength absorbed, assuming one major band in the range of 400 nm to 700 nm.

For the solid to appear green in colour then two absorbance maxima must be present in the visible region, one between 400 nm and 450 nm and the second between 580 nm and 700 nm. The shade of the green observed depends upon the relative amounts of light absorbed in the two spectral regions.

Table 1.1 :- Absorbance Maxima and the Expected Colour

λ / nm	400-430	430-480	480-550	550-600	600-700
Colour	Yellow	Orange	Red	Violet	Blue

Due to the varying sensitivity of the eye the colour expected from the visible spectrum is not always the colour observed. The actual colour observed is dependant upon the shape of the band as well as the position and extinction coefficient. The sensitivity of the eye is maximum between 550 nm and 560 nm and therefore the shape of the absorption band for any material is important as any shoulder or tail may be picked up by the eye and exaggerated resulting in the colour differing from that predicted by the visible spectrum alone¹.

The band observed in the visible region has an energy gap which can be directly measured from the absorption maximum. The absorption band occurs when light is absorbed and an electron is excited from the HOMO into the LUMO. According to the Einstein-Bohr frequency condition, equation 1.1, the energy difference from the ground state to the first excited state is inversely proportional to the wavelength of light absorbed thus enabling a minimum energy to be determined.

Equation 1.1 :- The Einstein-Bohr Equation

$$\Delta E = \frac{hc}{e\lambda}$$

Where ΔE is the band gap energy, h is Plancks constant, c is the speed of light, e is the charge of an electron, and λ is the wavelength of light absorbed.

Unsymmetrical absorption bands are the result of the superposition of vibrational processes upon electronic transitions in the ground and excited states.

It is noted that colour can also result from structural formations, a thin layer of crystal or rod like structures, that have a repeating unit separated by a distance that corresponds to

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the wavelength of light observed¹. Examples of these structural colours are in birds and butterflies wings. Colours can also be noticed in oil slicks and also in soap bubbles. In these cases there is no chromophore and upon breakdown to single molecules, unlike pigments and dyes, no colour is observed. The colours are a result of the thicknesses of the films being similar to that of the wavelength of light causing interference in the reflected light.

In 1876 Witt postulated that a compound is coloured due to the presence of certain groups, chromophores and auxochromes. Chromophores are cyclic or linear systems of conjugated double bonds which give rise to the colour of the material. An auxochrome is an electron donating group and an antiauxochrome an electron withdrawing group. The auxochrome and antiauxochromes are thought to influence the intensity of the material and they also provide a site at which chemical bonding to the fabric can occur. In the case of dyes a solubilising group is also present allowing the material to be soluble in the application medium⁷. This occurs in only organic dyes and pigments and in inorganic pigments the colour arises through metal to ligand charge transfer or in the case of compound semiconductors the colour is a direct result of transitions across the band gap, similar to the HOMO to LUMO transition in organic dyes.

The classification of colorants has posed a number of significant problems as many colorants fit into more than one group¹. The Colour Index (C.I.) is probably the most widely used method. The colour index is split into three parts, with part I listing groups of dyes and pigments, methods of application, usage and other simple data. Part 2 gives the structural formulae of the dyes and pigments along with literature references and patents. Part 3 of the colour index lists all the abbreviations used along with generic and commercial names.

In the colour index each coloured compound is given a Generic Name on the basis of the area of application and the method of colouration e.g. indanthrone has a Generic Name of C.I. Vat Blue 4. Each compound is also given a Constitution number in relation to the chemical classification of the material, e.g. C.I. 69800 for indanthrone.

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Under a C.I. Generic Name all commercial dyes or pigments are mentioned which have the same chemical structure. Materials that have the same chemical structure should not be thought of as identical as they may differ significantly with respect to crystal structure, particle size, additives and impurities. As a result a coloured material may have two names and have the same chemical structure. This can occur when a material is used both as a dye and a pigment e.g. flavonthrone, when used as a dye is referred to as C.I. Vat Yellow 1 and its Generic Name as a pigment is C.I. Pigment Yellow 24. If a material has different crystal modifications that are used as separate pigments or dyes then the Generic Name is altered to distinguish the different modifications, e.g. the α form of CuPc is referred to as C.I. Pigment Blue 15. CuPc is also known as C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4, with 15:1 and 15:2 being α stabilised materials and 15:3 the β form with 15:4 being a β stabilised form.

In the case of CuPc where different crystal modifications are used this is known as a crystallochromic effect, showing that the physical form and the crystal structure of a pigment is of primary importance for the application of the material.

1.1.3 PIGMENTS

Colorants can be split into two groups either dyes or pigments which can be subdivided further into inorganic or organic and these can be even further subdivided into natural and synthetic¹. The terms natural and synthetic are rarely used nowadays since many naturally occurring dyes or pigments are synthetically made for economic reasons. As mentioned previously the major difference between dyes and pigments is their solubility in the application medium. Pigments are characterised by being insoluble in the application medium and are normally attached to substrates by additional compounds whereas dyes are soluble in their application medium.

Pigments are used for the colouration of a very broad and diversified number of materials such as,

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- Surface coating, for interior, exterior, automotive and other coatings.
- Paints based on oleoresinous liquids and water emulsions.
- Printing inks for paper and other materials, (metal plates, foils, artists colours, and writing materials).
- Plastics and rubber.
- Textile printing.
- Coloration of man-made fibres by mass pigmentation before fibre formation.

The industrial applicability of a coloured compound depends not only on the position of the absorption band but also on its intensity as a function of concentration¹. The absorbance intensity can be expressed according to the Lambert-Beer law, equation 1.2. For technical dyes ϵ has values ranging from 10^4 to more than 10^5 . The higher the value of the extinction coefficient the more efficient and economical the colorant becomes.

Equation 1.2 :- The Lambert-Beer Law

$$\log \frac{I_0}{I} = E = \epsilon cl$$

Where I_0 is the incident radiation; I is the transmitted radiation; E is the energy; ϵ the molar extinction coefficient; c is the concentration of the sample; l is the path length.

The major distinguishing property of inorganic and organic pigments is their insolubility in the media in which they are used. However, all organic pigments are soluble in one or more of the solvents, chloroform, methanol, DMF, and concentrated sulphuric acid¹.

The small number of solvents in which pigments are soluble renders chemical analysis of pigments more difficult than for dyes.

The tinctorial strength and brightness of organic pigments are higher than those of inorganic pigments. However, their thermo- and photochemical stability tends to be lower. For applications it is important that inorganic pigments are opaque and in

comparison organic pigments are more transparent. Inorganic pigments are usually significantly less expensive.

The attainment of optimum size ranges of pigment particles is referred to as conditioning. Reflectance increases with a decrease in particle size down to the optimum particle size and then decreases with any further particle size decrease.

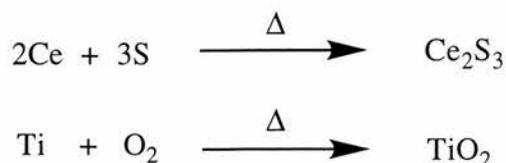
To attain smaller particle sizes grinding techniques, such as ball milling, and acid pasting, which involves dissolving the pigment in acid and then precipitating it out by addition to water, are employed. However, grinding techniques require a considerable amount of mechanical energy and both methods can result in a change of modification.

The detection of impurities is important as they may lead to bleeding i.e. diffusion of slightly soluble coloured byproducts into uncoloured parts of plastic goods.

1.1.4 SYNTHESIS OF PIGMENTS

This section gives a very brief outline of some of the synthetic methods used to produce dyes and pigments, due to the vast number of dyes and pigments that exist, this leads to an extremely large number of synthetic methods that can be used in their production. Chapter 2 outlines the many different ways in which the pigment copper phthalocyanine (CuPc) can be produced and chapter 4 also gives a more detailed description on the methods used in the production of cerium sulphide.

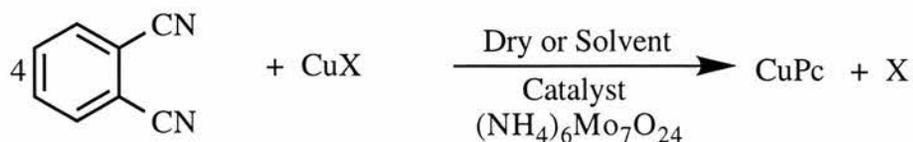
Many inorganic pigments are produced by solid state synthesis, e.g. Ce_2S_3 , TiO_2 . This involves grinding stoichiometric amounts of the starting materials together and then heating to a high temperature, (normally $> 800\text{ }^\circ\text{C}$), to produce a homogeneous mix of the pigment, see scheme 1.1. The temperature at which the materials are heated to is crucial as this dictates the crystal modification produced.

Scheme 1.1 :- Solid State Reactions to Produce Inorganic Pigments

The synthesis of organic pigments differs depending upon the pigment. A brief outline of the synthesis of copper phthalocyanine and the carbonyl pigment quinacridone and also 1,4-diketo-pyrrolo(3,4-c)-pyrroles (DPP) are detailed below. These three organic pigments have been the discoveries of the 20th century.

Phthalocyanines are obtained in good yields from a variety of ortho substituted benzene derivatives in the presence of a metal source and normally a catalyst as described in more detail in chapter 2.

Scheme 1.2 shows the Phthalonitrile process for the production of copper phthalocyanine⁸. The copper source used in this process is normally copper (II) chloride, however, any copper source can be used. It is noted that if copper (I) salts or copper (0) are used then air must be present during the reaction. The catalyst used in the industrial manufacture of CuPc is ammonium molybdate, however, a wide range of catalysts can be used with similar results⁸.

Scheme 1.2 :- The Phthalonitrile Process for Producing Copper Phthalocyanine

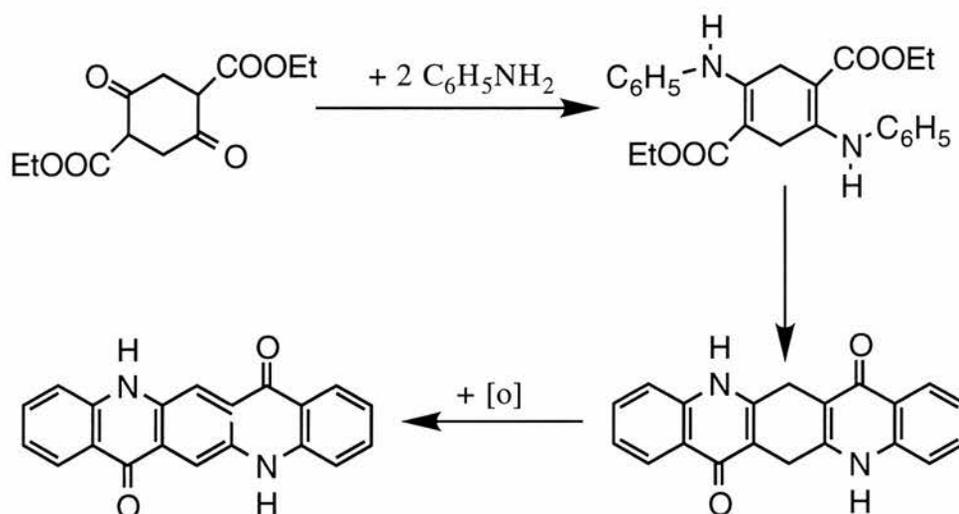
Carbonyl pigments can be categorised into two structurally different groups, those based on quinone or higher anellated rings and those based on quinacridone¹.

Due to the cost and the properties of some the colorants based on quinone they are not frequently used as pigments but mainly as vat dyes. Those based on the quinacridone

structure are more frequently used as pigments as their properties match those required for a good pigment.

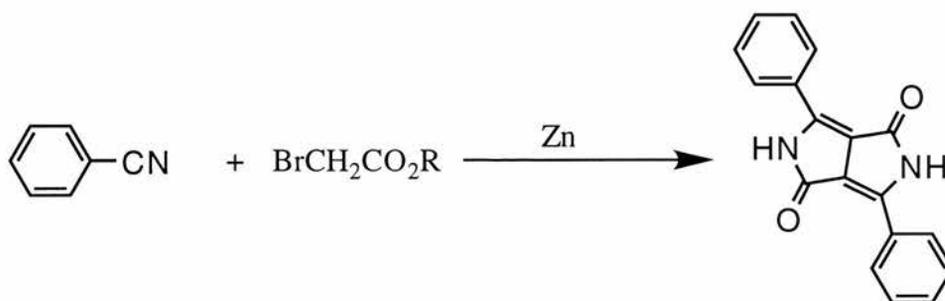
The first step in the industrial synthesis of quinacridone is the dimerisation of diethyl succinate to produce the starting material shown in scheme 1.3. This product then reacts with aniline, as shown in scheme 1.3, and upon heating, in an inert solvent, the product cyclises to produce dihydroquinacridone. In the presence of an oxidation agent, such as *m*-nitrobenzenesulphonic acid, is dehydrogenated to produce the desired product, quinacridone.

Scheme 1.3 :- Synthesis of Quinacridone



There are a number of alternative routes in the production of quinacridone¹ some of which are based on the cyclisation of 2,5-diphenylaminoterephthalic acid⁹.

Discovered by Iqbal and Cassar¹⁰, diketopyrrolopyrrole, (DDP) was synthesised by Farnum et.al.¹¹ when reacting benzonitrile and bromoacetic acid together, scheme 1.4. Iqbal and Cassar repeated this synthesis and found that the product described previously as a red insoluble product, had the properties of an excellent pigment.

Scheme 1.4 :- Synthesis of diketopyrrolopyrrole, (DDP)

Using the reaction above it is impossible to obtain yields that are industrially viable, however, a number of modifications have been made to this synthesis allowing the yield to be significantly increased¹. These include reacting the nitrile with a succinic ester¹² that has tert alkyl alcohols attached through the ester.

1.1.5 ENVIRONMENTAL ISSUES

It is estimated that around 15 % of the total world production of colorants is lost in the synthesis and processing. This corresponds to a release of some 128 tons per day. The main source is to be found in residual liquors because of incomplete exhaustion of dyes (10-20 %) and pigments (1-2 %)¹. The amount of loss for pigments is considerably less than for dyes due to their insolubility in water. The average cost of effluent disposal has increased by a factor of 10 to 15 in the last 20 years.

In order to minimise the possible damages to man and the environment arising from the production and applications of colorants, an international association, ETAD (Ecological and Toxicological Association of the Dyestuff Manufacturing Industry) was founded in 1974. Their purpose is to identify and assess risks caused by colorants and their intermediates with respect to their potential acute toxicity and their chronic effects on human health¹. Pigments tend to have a relatively low acute toxicity presumably due to their low solubility in water and lipophilic systems. The obvious exceptions are the heavy metal pigments.

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There are now a number of laws prohibiting the use of many of the more toxic heavy metal pigments and there is scope for improved nontoxic chromophores.

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CHAPTER 2

GAS PHASE SYNTHESIS OF COPPER PHTHALOCYANINE

CHAPTER 2

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2.1.0 BACKGROUND TO COPPER PHTHALOCYANINE

2.1.1 INTRODUCTION

Since their discovery, in 1928, phthalocyanines (Pc) have become one of the most widely studied single class of compounds¹⁻⁶³. When discovered, Pcs were initially used as pigments as they possess the most remarkable colour properties, all reflecting light in the blue-green portion of the spectrum, with copper phthalocyanine (CuPc) being almost pure blue. Due to its robust properties, high tinctorial strength, good retention of the copper cation and relative ease and low cost of manufacture, CuPc has been the building block for Pc technology¹⁸.

Due to their distinct and unique properties Pcs are commonly used in many applications originating with its use as a pigment, uses now include photosensitisation in solution, photodynamic activity in photodynamic cancer therapy, electrocatalysts for the dioxygen reduction in fuel-cell reactions, photoreductions or photooxidations in photoelectrochemical cells, electrochromic processes as thin films, charge separation in photovoltaic cells, electrophotographic applications, optical information storage systems, catalysts for oxidation reactions, and they are used as gas sensors⁴⁸.

2.1.2 THE DISCOVERY OF A NEW PIGMENT

Before Pc compounds were discovered, ultramarine blue and iron blue were the leading blue pigments being used. Research being carried out at the time was only providing improvements on existing chromophores. In 1928 Dandridge, Drescher and Thomas, working at the Scottish Dyes Works in Grangemouth, discovered traces of a dark blue insoluble complex in the iron vessels which were used to prepare phthalimide from phthalonitrile (1,2-dicyanobenzene) and ammonia¹. This blue solid was noted to have a higher tinctorial strength than any other previous dye or pigment known and could

therefore be used in lower concentrations to produce the same colouring effect. This material was discovered to be iron (II) phthalocyanine and it started the Pc revolution.

It is believed that de Diesbach and Von der Weid discovered CuPc, in 1927, when they described a new blue insoluble compound when attempting to prepare copper complexes from copper (I) cyanide and 1,2-bromobenzene in pyridine. They did not determine the nature of the dark blue solid they produced assuming it to be the copper pyridine salt they were investigating assigning the formula $[\text{Cu}(\text{C}_6\text{H}_4(\text{CN})_2)_2\text{Py}_2]$ ⁸. This blue solid is most likely to be CuPc.

After their discovery Dandridge, Drescher and Thomas realised the potential of the blue solid as a new chromophore and filed the first of many patents in 1929¹. From their investigations they found they could synthesise several different Pcs from reacting ammonia with phthalic anhydride, phthalamide or phthalimide in the presence of a metal source and all the Pcs formed had excellent tinctorial strength.

In November 1935 at an exhibition in London, seven years after its discovery, CuPc was introduced to the pigment trade and manufacture and trade of the pigment followed early in 1936⁸. Since then Pcs and their derivatives have been used and are still widely used as pigments in industry today.

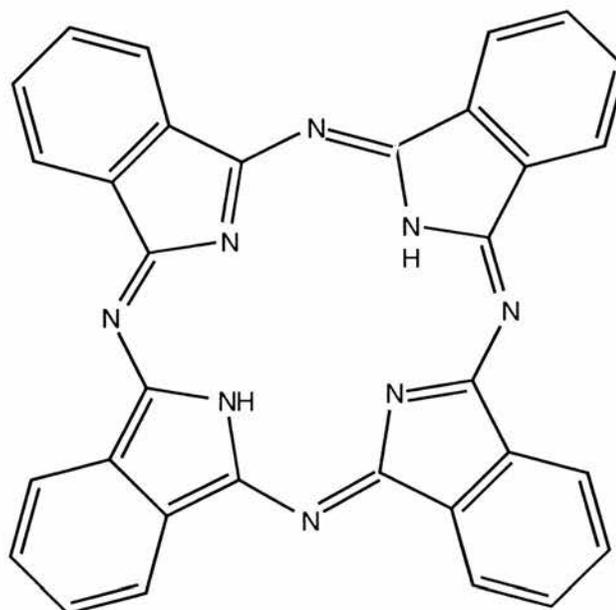
2.1.3 THE STRUCTURE OF PHTHALOCYANINE

Despite Pcs being discovered in 1927/1928 the structure was not determined until 1934 when Linstead and his co-workers², were asked by Dandridge, Drescher and Thomas to elucidate the structure and determine its properties. They did this by using a number of simple chemical techniques and deductions based on the behaviour of the complexes and suggested the structure for MPc to be tetrabenzotetraazaporphyrin as shown in figure 2.1. This structure was corroborated by Robertson³ who studied the complex using X-ray diffraction.

The Pc ligand is a rigidly planar aromatic molecule made from three isoindole units and an o-quinoid linked by four aza nitrogen atoms. Due to the aromaticity of the ligand the o-

quinoid and the three isoindoles are indistinguishable from each other. The hydrogen atoms are placed opposite from each other based on the calculations carried out by Robertson³.

Figure 2.1 :- The Structure of Metal-Free Phthalocyanine (H_2Pc)

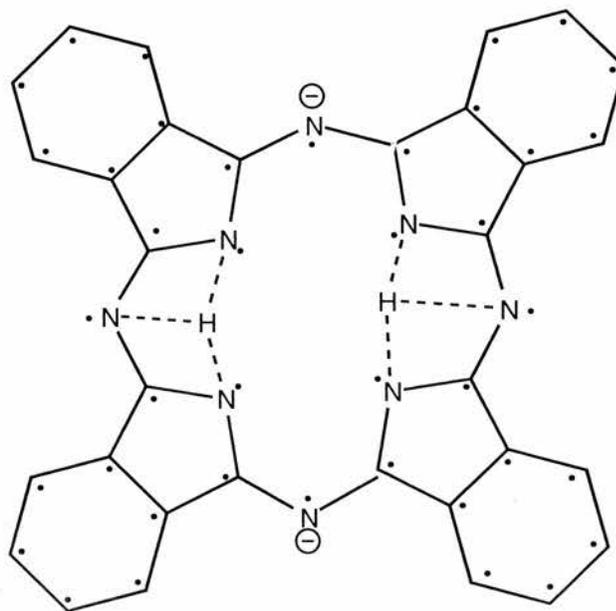


Berezin²⁹ proposed a similar structure, figure 2.2, where the π electrons are represented by dots and two circles represent the ionisation electrons. This representation better explains the equal bond lengths of the C-N bonds and the C-C bonds linking the benzene nuclei. In this case the hydrogen atoms are coordinated by three nitrogens, two isoindoline and one of the aza nitrogens, therefore the hydrogen atoms in metal-free Pc have to be opposite each other.

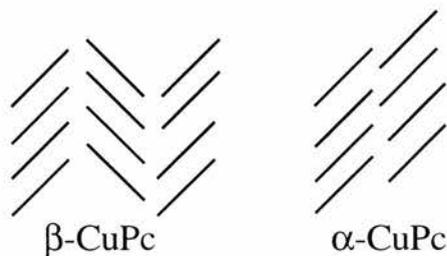
On removal of the two inner hydrogen's a hole with a radius of about 1.35 \AA is left, into which a wide range of metal ions can fit⁴. The metal ion is held in a square planar configuration, even for beryllium and cobalt, by co-ordination to the isoindole nitrogen's, which are either electrovalent or covalent in nature depending upon the nature of the metal, e.g. alkaline and alkaline earth metals form electrovalent M-N bonds whereas most other metals tend towards covalent bonds. Most complexes have the central metal ion in

an oxidation state of +2 and coordinate one Pc ligand. In the case of the alkali metals, two metals can be coordinated in the centre of the Pc ring in a similar manner to the hydrogen atoms in the metal free derivative. There are a number of larger metals, mainly the lanthanides and actinides, that can coordinate two or even three Pc units, with the metal being out of the Pc plane.

Figure 2.2 :- Berezins Structure of Metal-Free Phthalocyanine (H_2Pc)

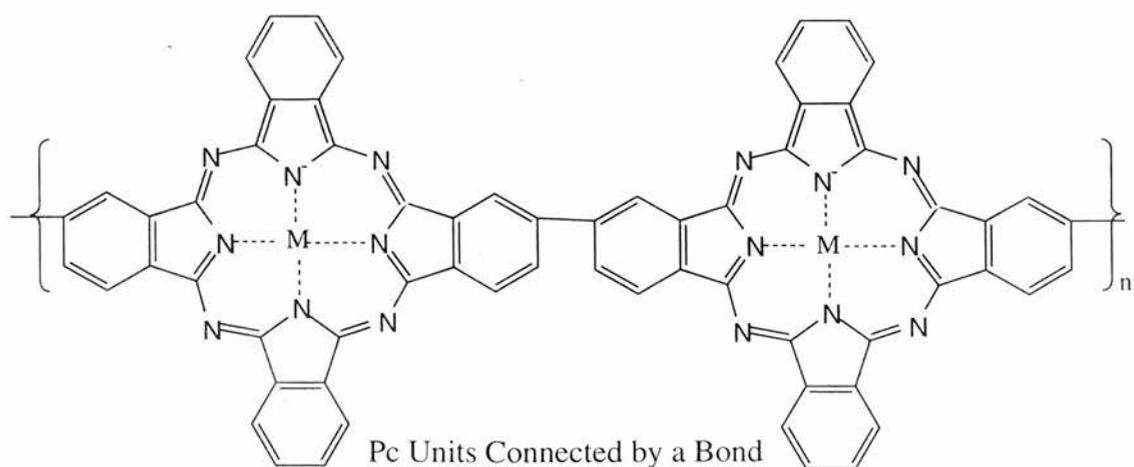


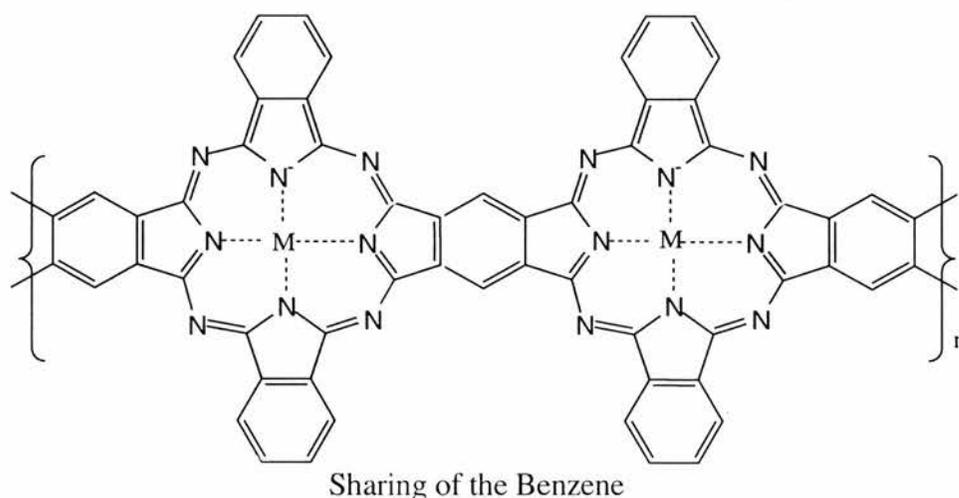
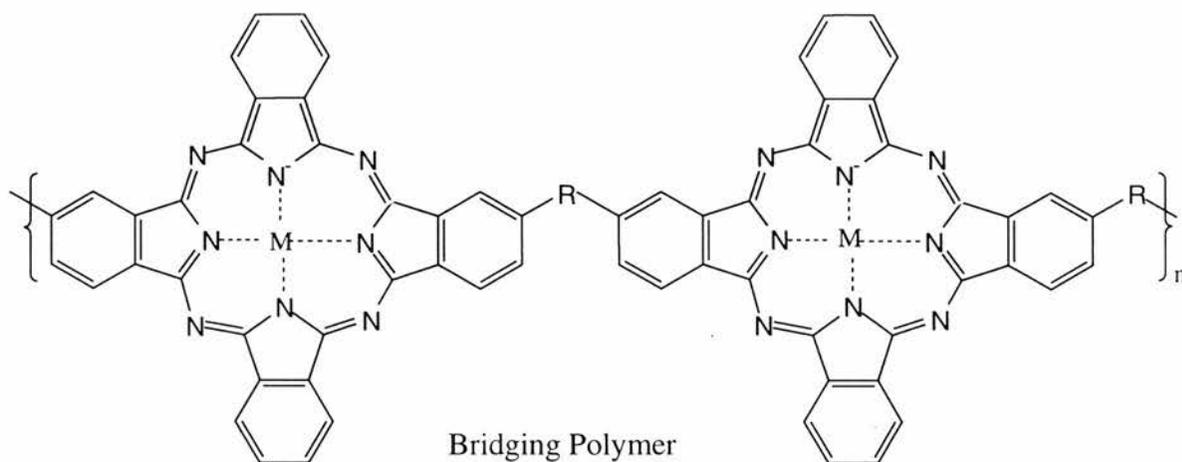
Pcs exist in polymorphic forms, CuPc exhibiting five different polymorphic forms (α , β , γ , δ , ϵ), which can be distinguished by infrared and/or X-ray diffraction. In most cases the most stable form is the β -phase which forms rod shaped crystals, figure 2.3(a). The α -phase is the next most stable forms and this forms brick shaped crystals, figure 2.3(b). The other forms of CuPc are structural intermediates between the two main forms and are less stable. The polymorphic forms of Pc differ slightly in shades of colour due to the different stacking arrangements, known as the crystallochromic solid-state effect⁶⁴. Reliable predictions of crystal packing and thus pigment colour from the topology and structure of an isolated dye molecule is not however possible.

Figure 2.3 :- The α and β Polymorphs of CuPc

It appears that the main difference between the various polymorphic forms of Pc is the co-ordination of the metal to the different nitrogen atoms of neighbouring rings, this results in different packing arrangements between rings and hence different crystal structures²⁰. The different structures can be detected by powder X-ray diffraction as each polymorph has a different packing arrangement and therefore will produce a different powder pattern. In order to produce any given polymorphic form, it becomes necessary to block in some way the nitrogen atoms that are not required to coordinate.

Polymeric Pcs also exist and in general there are four types of Pc polymer¹⁸ three of which are depicted in figure 2.4.

Figure 2.4 :- Three of the Possible Polymeric Structures of MPc



The Pc unit can be joined by a single bond between a benzene ring on one Pc and the benzene ring on another Pc. The Pc units can be linked by a bridging group, R. A third method of polymerisation involves the sharing of a benzene ring between two Pc units. A less common form of polymerisation is the connection of the rings through the central atom either by a metal metal bond or a bridging group.

The polymers of Pcs are darker in colour than their corresponding monomers being dark blue-green to greenish black powders¹³.

2.1.4 PROPERTIES OF PHTHALOCYANINES

Pcs tend to be nontoxic and have excellent thermal stability, in general they do not have an accessible melting point but decompose at elevated temperatures. The more stable Pcs,

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such as CuPc, NiPc, PtPc, can be sublimed, intact, at temperatures above 400 °C and sublimation is often used as a method of purification or separation of Pcs.

Many of the Pc compounds are resistant to atmospheric oxidation even at elevated temperatures. Oxidation of the complexes tends to be reversible except under drastic conditions, for example, in the presence of strong oxidising agents, such as hydrogen peroxide in an acid medium. Exposure to chlorine, bromine, and oleum lead to electrophilic substitution in the benzene rings²⁹. Reduction is more common and can occur at any of the sixteen peripheral carbon atoms on the benzene rings leading to a substituted product. Reduction may also occur at the central metal atom depending on the number of valency states attainable by the metal atom¹⁸.

Pcs are extremely insoluble in water and most organic solvents but have slight solubility in higher boiling aromatic solvents such as quinoline, chlorobenzene, and chloronaphthalene. Various functional groups can be introduced onto the benzene nuclei thereby altering the solubility properties. The addition of eight alkyl or alkoxy substituents, two onto each of the four benzene rings, enhances solubility in organic media²⁹. The addition of sulphonate groups to the outer benzene rings brings about solubility in water⁶⁵. The addition of functional groups also has an affect on the colour of the Pc. Highly chlorinated (15 Cl atoms) CuPc is a brilliant green colour compared to the brilliant blue colour of pure CuPc.

Virtually all the Pcs are soluble in concentrated sulphuric acid; some such as CuPc, NiPc are reprecipitated upon dilution with water, whereas others, such as CaPc and Na₂Pc, are demetallated and the resulting metal free Pc slowly decomposes in the acidic medium. When CuPc is dissolved in concentrated sulphuric acid and then diluted with water this is known as acid pasting, which is widely practised in the dye industry to produce a suitable pigment form. The more stable MPcs are stable to molten potassium hydroxide and boiling hydrochloric acid, however all are decomposed by nitric acid producing phthalimide and metal salts.

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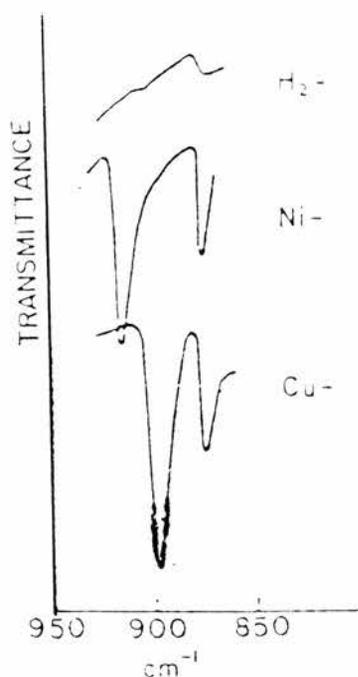
All Pcs are intensely coloured and because of this they have become dominant in the blue to green area of the pigment trade. CuPc is of great interest as it is almost pure blue absorbing almost all the red and yellow portions of the spectrum⁸.

MPcs are characterised by an intense absorption in the visible region at around 600-700 nm, dependent upon the metal atom⁵¹, called the Q band. There may also be one or two weaker bands near the Q band, these are attributable to vibrational overtones of the Q band³². For CuPc the band maximum is at 678 nm in 1-chloronaphthalene. There is also another band around 300-400 nm region, known as the Soret or B band. The absorption spectra remain the same from solvent to solvent except that the Q band is shifted in energy depending upon the nature of the solvent²⁹. The bands in the UV-Visible area are predominantly associated with the $\pi-\pi^*$ transitions in the ring, and Pcs have been shown to exhibit semiconductor type behaviour⁶⁵ that will be discussed further in chapter 3.

One of the major methods of distinguishing the various polymorphs of MPcs is the use of infrared spectroscopy. Table 2.1 and figure 2.5 show some of the main characteristic infrared bands for the β modifications of metal free, nickel and copper phthalocyanine.

Table 2.1 :- Infrared Data of H₂Pc, NiPc and CuPc

H ₂ Pc / cm ⁻¹	NiPc / cm ⁻¹	CuPc / cm ⁻¹
498	521	509
559	578	575
-----	645	640
715	-----	-----
726	731	728
765	770	770
775	780	779
870	876	875
-----	915	898
999	-----	-----
1065	1075	1064
1089	1086	1087
1101	1098	1099
1115	1120	1118
1150	1164	1162
1295	1288	1285
1338	1333	1330
1433	1426	1415
1495	1503	1500
1610	1605	1603

Figure 2.5 :- Infrared Spectra of H₂Pc, NiPc and CuPc

Due to the aromaticity of the Pc ligand, there are a vast number, approximately 50, bands in the IR, many of which are in the fingerprint region. There are a large number of bands which are characteristic to the molecule as a whole and some of these bands are altered by the different crystal packing arrangements therefore allowing IR to be used to determine the modification of Pc obtained. Most of the bands found in the IR are characteristic of the ligand, however, each MPc has its own characteristic bands particular to the metal. It is believed that the characteristic M-N stretch is in the range 888-919 cm^{-1} ; 915 cm^{-1} in the case of nickel and 898 cm^{-1} for copper²¹. There is no corresponding band in the spectrum of the metal free Pc. However, it does have a band at 999 cm^{-1} which corresponds to N-H stretch and does not occur in the MPcs.

2.1.5 METHODS OF PREPARATION

The metallic complexes of Pc differ from other organic coordination compounds since they are not usually prepared from the parent metal free compound. The fundamental reaction is that of an ortho benzo derivative reacting with a metal source to produce a MPc. It is believed that the metal is encapsulated at the same time as the Pc unit is formed, therefore acting as a template for its formation⁴.

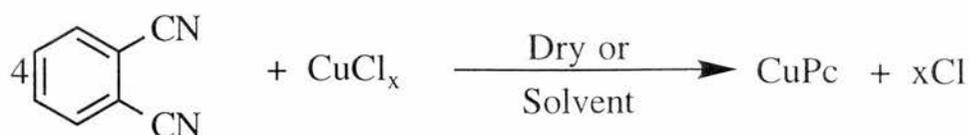
The synthesis of metal phthalocyanine (MPc) complexes can be carried out under a wide variety of conditions and there are three main routes which are detailed below.

The Phthalonitrile (1,2-Dicyanobenzene, DCB) Process

This is the simplest process for the production of CuPc, with the basic reaction consisting of mixing phthalonitrile (1,2-dicyanobenzene, DCB) and copper (I) or copper (II) chloride in a 4:1 mole ratio and heating the mixture until the reaction begins. Yields of CuPc greater than 95 % can be obtained by this method.

This reaction can be carried out without solvent either by grinding the powders whilst heating in a ball mill or by heating the DCB and the copper chloride to form a melt. The mixture is heated to between 200-250 °C and left for a minimum of 2 h, until the mixture has turned a deep blue/black colour, before being washed. It is noted that if copper (I) chloride is used then there is a possibility of forming chlorine radicals which may then attack the the CuPc to form chlorinated CuPc.

Scheme 2.1 :- The Phthalonitrile Reaction



The reaction may also be carried out in a range of solvents, such as, nitrobenzene, methanol, ethylene glycol, glycerol, phenol and naphthalene solvents. Inorganic sulphonic or carboxylic acids, molybdic oxide and other metal oxides can be employed as catalysts¹⁷, however they are irretrievable from the product mixture, adding to the impurities of the pigment. One improvement on the basic scheme is the addition of urea to the system⁶⁶, possibly acting as a chlorine radical scavenger, reducing the formation of chloro substituted Pcs, which is the main side reaction that occurs. The role of the catalyst and the urea is not fully understood.

Once the reaction is complete the product is then washed with methanol, mixed with 5% hydrochloric acid, filtered, washed acid free with water, washed with methanol and acetone, and dried at 100 °C. Slight variations are used depending upon the method of synthesis used e.g. nitrobenzene and sodium hydroxide may sometimes be employed in the washing of the CuPc. The CuPc is then converted into a usable pigment form by a known finishing method, see reference 17 for examples.

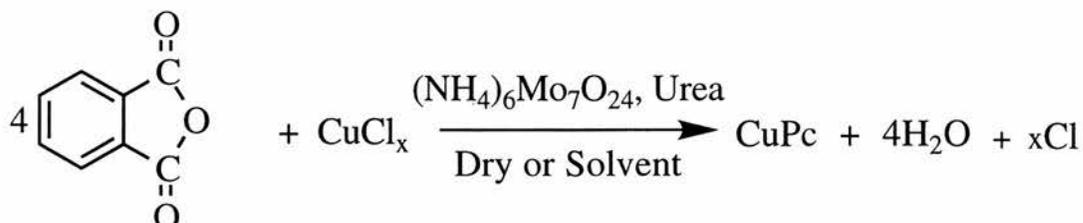
The Phthalic Anhydride-Urea Process

This process for making CuPc is still a very useful one due to the low cost and abundance of the starting materials. The phthalic anhydride reacts with urea in the presence of a catalyst, normally ammonium molybdate, to form an isoindoline derivative, as an intermediate, which then reacts, with the copper complex to produce CuPc, as described in the next process.

As with the phthalonitrile process the synthesis of CuPc from phthalic anhydride and urea can be carried out with no solvent eg. as a "melt", commonly known as the Wyler process. The reaction can also be carried out utilising a high boiling organic solvent as the reaction medium. The yield in the presence of solvent is up to 10-15 % higher than in the fusion process¹⁷ possibly due to solvent involvement in the mechanism or the viscosity of the medium allowing the reactants to flow more easily. The yields for the phthalic anhydride-urea process tend to be lower than for other methods, probably

because of extra reaction steps required to produce an isoindoline derivative which then directly reacts with the copper source.

Scheme 2.2 :- Phthalic Anhydride-Urea Reaction



Wyler⁵ disclosed the first melt process by melting a mixture of urea and boric acid at 150 °C to which a mixture of phthalic anhydride and anhydrous copper (II) chloride is added. The reaction mass is then heated at 200 °C until colour formation is complete (the mixture turns a deep blue colour). The product is then cooled, ground and mixed with dilute sodium hydroxide, filtered, mixed with 5 % sulphuric acid, filtered and dried.

It is believed that the boric acid catalyses the reaction between phthalic anhydride and urea forming 1,3-diiminoisoindoline (DIII) or an other isoindoline derivative. There have been many catalysts used, such as boric acid, chromic acid, ammonium chloride, zinc oxide and molybdc oxide and many more, however ammonium molybdate produces the highest yields¹⁷ and is most commonly used at present. It is also reported that sulphur containing compounds can be used catalysts in the production of DIII⁶⁷. Some of the molybdate, or any catalyst used, is irretrievable from the product being incorporated within the CuPc.

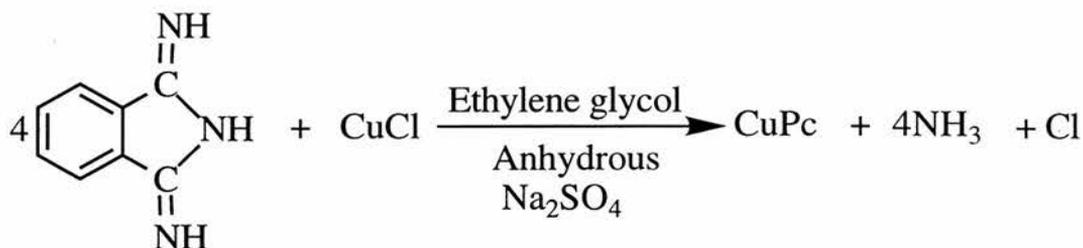
The Diiminoisoindoline (DIII) Process

This process is not as commonly used as the previous two, because the DIII is a more expensive starting material. It is synthesised by the reaction of phthalic anhydride with

urea and then purified. This process produces higher yields than the phthalic anhydride-urea process and gives higher purity CuPc than other processes.

DIII and copper acetate in ethylene glycol react in the presence of adiponitrile or 2-chlorobenzonitrile at 60-70 °C for 1 h and then at 120 °C for 2 h to form the finely divided pigment, CuPc.

Scheme 2.3 :- The Diiminoisoindoline Reaction



CuPc can also be made by milling DIII, copper (I) chloride, anhydrous sodium sulphate and ethylene glycol for 3 h at 100-110 °C. The sodium sulphate is removed by mixing the product in water and filtering. It is then mixed in 1 % hydrochloric acid followed by dilute sodium hydroxide. The product is suitable then for use as a pigment, but not in solvent systems.

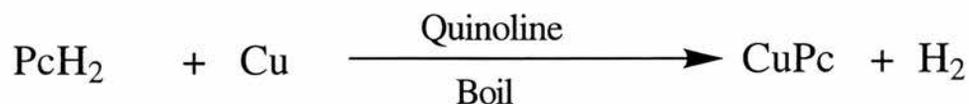
There are many other methods of MPC formation, two of which, synthesis from the metal-free Pc and also metal substitution, are detailed below but these are less commonly used.

Synthesis from the parent ligand

This reaction is analogous to the synthesis of most other metal chelating compounds. In this case the metal free Pc is synthesised first and then reacted with the metal or metal source. It is found to be easier and increased yields are obtained if the Pc subunits are reacted with the metal which acts as a template for ring closure and formation of the Pc

ligand rather than using the synthesis of metal free Pc and then reacting it with a metal source.

Scheme 2.4 :- Reaction of Metal Free Phthalocyanine and Copper

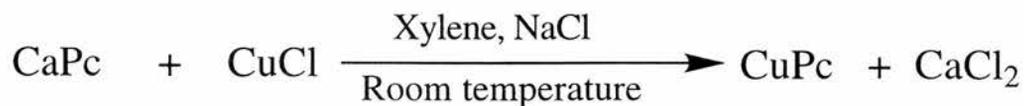


Metal free Pc may be converted to the copper complex by heating it with copper powder in quinoline, chloronaphthalene or pyridine, evolving hydrogen gas, scheme 2.4 above.

Metal substitution

In many respects this method is the same as for the reaction involving the parent ligand. Instead of substituting the two inner hydrogen's, the central metal(s) is replaced by a metal with a stronger covalency to the Pc ligand. CuPc is the most stable of the Pcs so most other metals can be replaced by copper. Labile MPcs such CaPc, Na₂Pc, Li₂Pc, MgPc are most commonly used. As indicated above it is easier to form MPcs from the subunits directly in a reaction with a metal or metal salt than from the parent ligand or by metal substitution.

Scheme 2.5 :- Reaction of Calcium Phthalocyanine and Copper Chloride



CaPc may be converted directly to the β-CuPc pigment by ball milling it with sodium chloride, copper (I) chloride, and a small amount of xylene.

Many variations are used in the production of MPcs, (for examples see references 17 and 19), particularly in industry, to obtain an economic yield. Phthalic acid, phthalamide,

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phthalimide, and other benzo derivatives are often used but the results are often more erratic due to the use of aminating agents in producing an isoindoline derivative.

CuPc has been made from *o*-cyanobenzamide and copper or a copper compound, and from *o*-chlorobenzonitrile or *o*-chlorobenzamide, copper (I) cyanide and pyridine in a sealed tube. Heating *o*-dihalobenzenes with potassium copper cyanide is also said to produce CuPc¹⁹. The method using pyridine or quinoline as a solvent medium for the reaction of *o*-dichlorobenzene with copper (I) cyanide is similar to the de Diesbach and von der Weid method. All the reactions described can be carried out using the metal, metal oxides, or more commonly with metal salts.

In the synthesis of CuPc the use of copper (I) chloride has generally replaced copper (II) chloride for several reasons, firstly it is easier to obtain and keep in the anhydrous form, it is less expensive, it has less tendency to produce chlorination in the Pc ring, and the yield of CuPc produced is improved. However, it is believed that the best results are obtained for CuPc, when a mixture of copper (I) and copper (II) salts are used in a ratio of 9:1⁶⁶, reducing the amount of substituted Pcs.

As it has been shown there are a significant number of ways in which MPcs can be synthesised, despite giving high yields, most MPc methods usually leave intractable impurities including substituted Pcs, and often free ionic copper. A technique of purification or exploitation of an improved or a novel synthetic process would be gratefully received by the pigment industry³⁵.

2.1.6 MECHANISM OF PHTHALOCYANINE SYNTHESIS

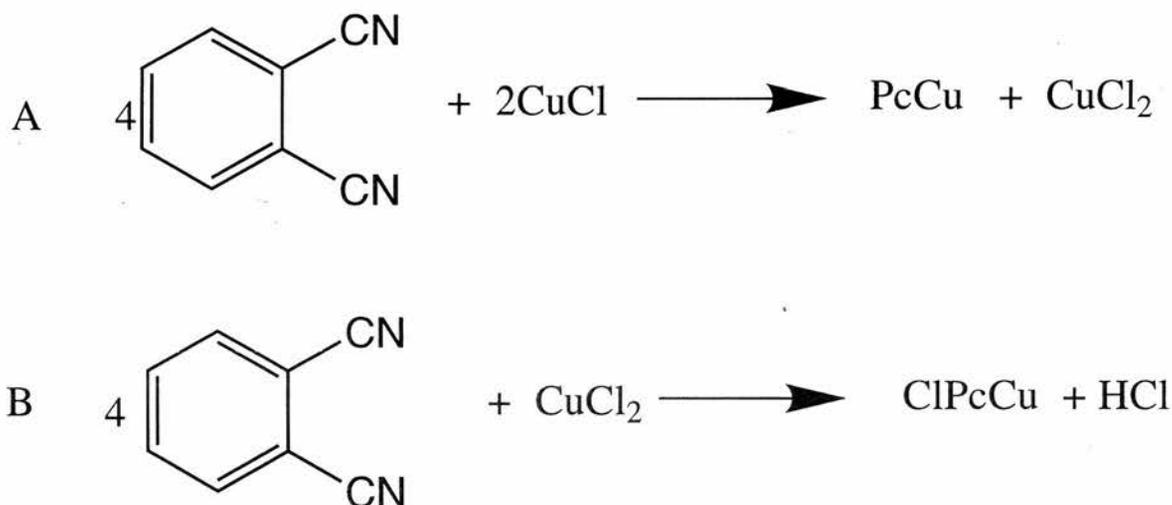
The mechanism for MPc production is not fully understood since there are many possible intermediates which may be formed from so many different methods of synthesis. The formation of Pc from DCB has been shown to proceed through reactive precursors condensing to reactive oligomeric intermediates which, as a result of ring closure reactions, cyclise to give the conjugated macrocyclic product³⁹.

Linstead et.al.² reported that equimolar amounts of CuPc and the monochloro derivative are formed when copper (I) salts are used with a temperature above 200 °C, as shown in scheme 2.6. When copper metal and copper (I) salts are reacted with DCB production of CuPc only takes place in the presence of air whereas copper (II) salts react in inert atmospheres, suggesting that copper (II) is a reactive species.

However, it is thought that chlorine radicals are produced in the reaction which points towards Cu (0) being present.

During the reaction to produce CuPc the ligand, or the organic precursor must be reduced to produce an anionic ligand and the copper must be as copper (II). Therefore when copper (II) is used a reducing agent is required but when copper (I) is used it can act as a reducing agent.

Scheme 2.6 :- Reactions of Copper (I) Chloride with 1,2-Dicyanobenzene

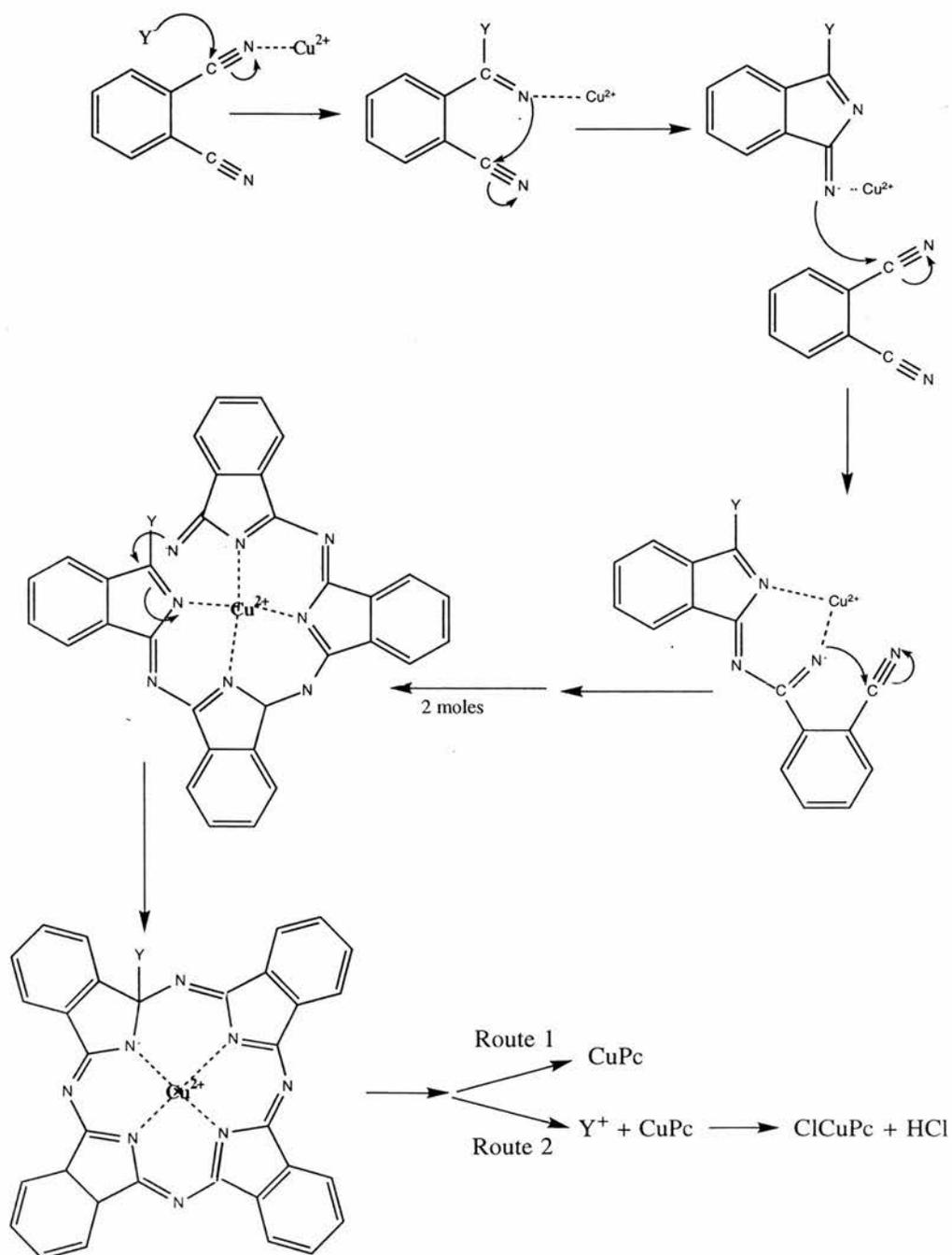


A mechanism proposed by Oliver and Smith³⁹ and also separately by Christie and Deans⁴¹, a combination is shown in scheme 2.7. This mechanism shows how coordination with the Cu²⁺ ion might play a role in retaining the structure in a conformation favourable for ring closure by intramolecular nucleophilic attack.

This explains why copper metal and copper (I) salts only react in the presence of air, as a small amount of copper (II) is required for the reaction to proceed. It has been noted that,

in solution, the solvent molecules might actively participate in the reaction since the formation of the MPc was observed in the presence of an appropriate protic solvent e.g. alcohols³⁴. The alcohol nucleophilically attacks the DCB and when no solvent is used then another organic precursor or a ligand from the copper complex can act as the nucleophile which is shown as Y in scheme 2.7.

Scheme 2.7 :- Reaction Mechanism for Production of CuPc



Although the template reaction is thought to play a key role in the cyclisation reaction leading to the macrocyclic Pcs, electrochemical studies found that this may not be the case. As previously mentioned the organic ligand must be reduced and the copper remain as or be oxidised to copper (II). Electrolysis of DCB in ethanolic solution took place at a potential of -1.6 V irrespective of the metal ion present²⁸. It can therefore be said that the metal ion is not involved in the electrochemical reaction thus suggesting an importance of anion radicals in the cyclisation and not metal templating for the formation of MPc. Therefore in the electrochemical reaction if the metal is acting as a template it is after the reduction of the DCB.

Many catalysts have been used in the syntheses of MPc¹⁷. Their role is not fully understood but it is thought that they catalyse the production of an isoindole derivative. It would be advantageous if the role of the catalyst could be understood.

2.1.7 WHY A GAS PHASE REACTION

From the introduction to CuPc, 2.1.0 - 2.1.6, it has been shown that it can be easily synthesised and in high yields. In many of the reactions in the production of CuPc impurities are formed and due to their nature, low solubility and volatility, they are extremely hard to remove from CuPc. The most common form of purification of CuPc is sublimation, however if the impurity is a substituted Pc then it becomes hard to separate even by sublimation.

The majority of the Pcs used in industry have to 'finished' before they can be used as pigments. This process is time consuming and can result in a loss of yield.

It is therefore hoped that a new method of synthesis of, initially, CuPc would result in a process with good yields and the pigment produced in a form suitable for pigmentation, therefore removing the finishing process. A gas phase synthesis of CuPc may produce such a result. The idea is that a gas phase copper source will react with a gas phase organic precursor and precipitate out CuPc. If the precursors can be introduced and

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product removal be carried out easily then such a reaction could also provide a continuous production.

It was also hoped that additives could be added in the gas phase which could result in a control of the particle size and the pigment form produced. The control of the particle size of CuPc will be discussed in further detail in chapter 3.

2.2.0 RESULTS AND DISCUSSION

2.2.1 GAS PHASE SYNTHESIS OF COPPER PHTHALOCYANINE

PART I

A gas phase reaction to produce CuPc poses two problems, firstly the reactants must be in the gaseous form before reaction; a chemical or physical problem. Secondly a suitable set-up is required to facilitate such a reaction; a chemical engineering problem.

The first problem can be overcome by using volatile precursors and subliming them into the gaseous state prior to reaction.

Due to an expanding interest in Chemical Vapour Deposition (CVD), there has been significant research into the design of volatile copper complexes⁶⁸⁻⁷². Many are relatively easy to synthesise and are reasonably air stable. Some of the more volatile ones were synthesised and are listed in table 2.2, with sublimation temperature and pressures if reported, the other two complexes were found to be suitably volatile for a gas phase reaction.

Table 2.2 :- Volatile Copper Complexes Synthesised

Copper Complex	O.S.	Temp./ °C	Pressure / mmHg
[Cu(η^2 -2-butyne)(hfac)] (A)	I	40	0.1
[Cu(hfac) ₂] (B)	II	100	1.0
[Cu(7-tBuO-NBD)(hfac)] (C)	I	75	0.1
[Cu(acac) ₂] (D)	II	170	1.0
[Cu(PEt ₃) ₂ Cl] (E)	I		
[Cu(COD)(hfac)] (F)	I		

O.S. is the oxidation state of the copper

The letters in the brackets are used in future as a reference to the complex

In four out of the six copper complexes synthesised the hfac ligand (1,1,1,5,5,5-hexafluoroacetylacetonato) is present. This ligand greatly increases the volatility of the copper complexes thus increasing the amount of precursor in the gas phase.

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As previously mentioned in 2.1.4 there are a vast amount of organic precursors that can be used in the synthesis of MPc. Phthalic acid, phthalamide, phthalimide, o-cyanobenzamide, DCB (phthalonitrile), DIII and many other ortho benzo derivatives can be reacted with a copper source to produce CuPc. However, many require the presence of urea or another aminating agent to form an isoindole derivative as an intermediate in producing the MPc. In these cases the precursor will have to be reacted with the aminating agent and then sublimed or the aminating agent sublimed along with the organic precursor. In the later case the isoindole unit would have to be formed before being able to react with the copper source. It was therefore decided that the organic precursors DCB and DIII would be selected since no aminating reagents are required, both are also used in industrial processes.

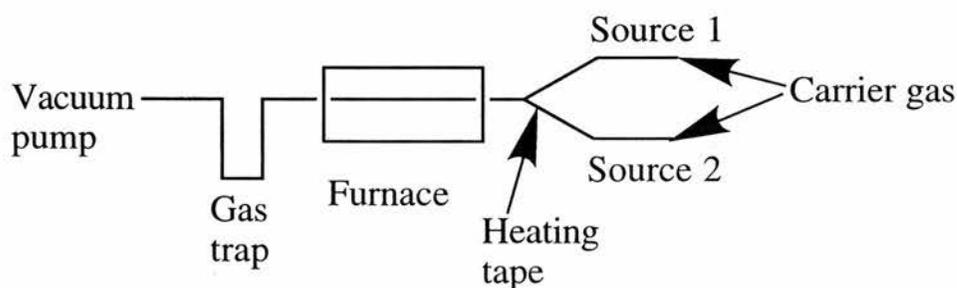
Experiments to find out approximate sublimation rates and temperatures for the two organic precursors chosen were carried out. These reactions involved placing a known weight of the precursor in a Schlenk tube attached with a cold finger and then heating. Approximate rates were found to be 0.32 g h^{-1} at $130 \text{ }^{\circ}\text{C}$ for the DCB, which is slightly higher than that found by Pace⁵⁶, and 0.23 g h^{-1} at 150°C for the DIII, under a dynamic vacuum. In practice it was found that the rates of transportation through the reactor were lower than these values measured under ideal conditions even when increased temperatures were used. The lower rates are a result of some of the precursor precipitating out on cold spots, namely at the loading site, when being transported into the reaction zone.

The second problem is how to sublime and transport the precursors into a reaction zone. Previous work carried out on the attempted gas phase synthesis of CuPc⁵⁶ involved the copper source being placed in a quartz boat within the reaction zone and the organic precursor, (DCB), being placed in a heated tube and the vapour being transported over the copper source and into the furnace by a carrier gas, nitrogen. The majority of the CuPc produced in these reactions was found within the quartz boat and the yields were very low, 2-5 %. It is believed that the CuPc formed is from gas phase DCB reacting with solid copper complex.

The requirements for apparatus to facilitate a gas phase reaction to take place had to be met in the designing of the set-up. Separate and easy loading of the precursor is required to prevent any prereaction. Sublimation temperature has to be controlled along with choosing a carrier gas to allow transportation of the subliming materials into the reaction zone. Control of the reaction temperature is important along with being able to trap any product and unreacted starting materials for recycling. The use of a dynamic vacuum is essential to allow the precursors to be able to be sublimed and transported, as all require reduced pressure to volatilise them.

From ideas based on the literature work on CVD, work carried out by Pace⁵⁶, and the requirements listed above, the apparatus, shown in figure 2.6, was designed.

Figure 2.6 :- Reaction Set-up Used in the Gas Phase Synthesis of CuPc Part I



The apparatus design consists of a glass Y piece attached to sources 1 and 2 which have a carrier gas inlet and join together at the outlet allowing the gaseous precursors to flow into the reaction zone. The reaction zone consists of a quartz tube, 46 cm long and 2 cm diameter, which is placed in a carbolite MTF 12/38/η00 tube furnace. A gas trap, (cold trap), is fitted at the end of the furnace to trap out any unreacted starting material or product. To this a dynamic vacuum pump is attached to facilitate the sublimation of the precursor. The precursor is loaded into the source by removing a glass stopper and then placing the precursor into the tube. Heating tapes are then wrapped around the apparatus, one for each source, giving control of the individual source temperatures. A thermocouple is placed between the heating tape and the glass tube at the source to

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monitor the actual temperature. A carrier gas, nitrogen or air, is passed through a flow meter, (approximately $4 \text{ dm}^3 \text{ hr}^{-1}$), and then over the subliming precursors.

Once the two initial problems, finding precursors and designing apparatus, had been overcome, crude gas phase reactions were carried out to find out whether CuPc could be produced in the gas phase. Table 2.3 lists the reaction combinations tried.

Table 2.3 :- Results from Gas Phase Reactions

Copper Complex	Organic Precursor	Carrier Gas	Reaction Temp./ °C	Product
A	DCB	Nitrogen	250	None
A	DCB	Nitrogen	250	None
A	DCB	None	250	None
A	DCB	Air	500	Colourless Liquid
A	DIII	Air	500	Blue Solid
A	DIII	Nitrogen ^a	600	None
B	DCB	Nitrogen	500	None
B	DCB	Air	500	None
B	DCB	Nitrogen	450	None
B	DCB	Nitrogen	450	None
C	DCB	Air ^{a,b}	300	None
C	DIII	Air	500	Blue Solid
C	DIII	Air ^a	600	None
C	DIII	Air ^{a,b}	600	None
D	DCB	Air ^a	500	None
E	DCB	Nitrogen ^a	500	None
F	DCB	Nitrogen ^a	400	None
G	DIII	Nitrogen	500	None

^a Glass wool was placed in the quartz tube

^b The organic precursor was placed in a quartz boat inside the furnace

For the first few reactions only one heating tape was used to heat both the precursor sources and the heating tape temperature was set at approximately 200 °C, hot enough to sublime both precursors. It was hoped that at this temperature high rates of sublimation would be achieved. It was found that at this temperature the copper source sublimed more

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rapidly, transporting and depositing in the cold trap before the organic precursor appeared to be subliming. Copper complexes A and C showed signs of decomposition depositing copper metal on the glass surface this is due to the high temperature used.

It was discovered that the actual temperature of the glass at the sources varied depending upon how tightly the heating tape was wrapped around the apparatus. The heating tape was wrapped as tightly as possible to the apparatus and temperatures adjusted to allow the precursors to sublime. All heating tape temperatures reported are those measured near where the sample is placed, by using a separate thermocouple. It is still believed that actual temperatures inside the glass tube is 10-20 °C less than reported.

The furnace, reaction, temperature was initially set at 250 °C, at this temperature the solid state reactions are normally highly exothermic and rapid production of CuPc ensues. At this temperature no precipitate was being deposited in the reaction zone and the starting materials were passing through into the cold trap. On increasing the temperature to 300°C, 350°C or 400 °C similar results were obtained. When higher reaction temperatures, 500-600 °C, were used then some of the starting material decomposed in the hot zone leaving a black deposit on the walls of the tube which is believed to be carbon, it could also be copper oxide, very little of this material could be scraped off to analyse. In some instances metallic copper was deposited on the walls along with the black solid both of which were very hard to remove and took vigorous heating with concentrated nitric acid. It is thought that the black solid is more likely to be carbon deposits rather than copper oxide because the solid formed when air and nitrogen environments are used and when cleaning the tube with nitric acid no colour change was observed as would be expected with copper oxide.

The first reaction listed in table 2.3 is that of copper complex A, with DCB and nitrogen carrier gas. The precursors were heated under a dynamic vacuum and the carrier gas passed over at approximately 4 dm³ h⁻¹ to transport the vapour into the reaction zone, which was set at 250 °C. After 15 minutes it was noticed that a small amount of the copper complex had passed through the furnace unreacted and very little DCB had passed through. It was noted that both starting materials had crystallised out on cold spots near

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the loading site. The cold spots occur near the loading site because of a design fault in the apparatus, the site is on a curve and it is therefore impossible to heat the whole area equally. After 30 minutes a noticeable amount of both precursors had been transported through the furnace unreacted. No CuPc was formed and no material was deposited within the furnace. One bonus from this result is that the unreacted starting material can be retrieved and recycled. It is also noted that a small amount of the copper complex touching the glass surface, at the source, had decomposed, depositing metallic copper. This is due to the high temperature used with the heating tape.

This reaction was repeated several times with slight variations. The precursors were heated until sublimation occurred before the carrier gas was passed over, this was tried to increase the amount of precursor vapour being transported. To prevent decomposition of the copper complex the heating tape temperature was reduced, however this reduced the amount of vapour transported. The flow rate was altered to either increase residence time, in the reaction zone, by lowering the rate or to increase the amount of precursor in the furnace by increasing the flow rate. Similar results were obtained, to that of the first reactions, with more or less unreacted starting material having passed through the furnace. The reaction was tried using no carrier gas to try and increase the residence time of the precursors, however, little or no precursor was transported into the hot zone, with the precursors depositing on cold spots between the source and the furnace. It is therefore necessary to have a carrier gas to facilitate transportation.

The reaction between copper complex A and DCB in air at 500 °C produced a small amount of a colourless liquid. However, on repeating of the experiment no liquid was obtained. It is thought that the liquid is most likely to be solvent, (dichloromethane), from recrystallisation of the copper complex and not having pumped on the complex long enough to dry it fully. An FTIR of the liquid was obtained but no conclusive data could be gained due to the broadness of the bands. No other data could be gained due to the small amount of the sample obtained.

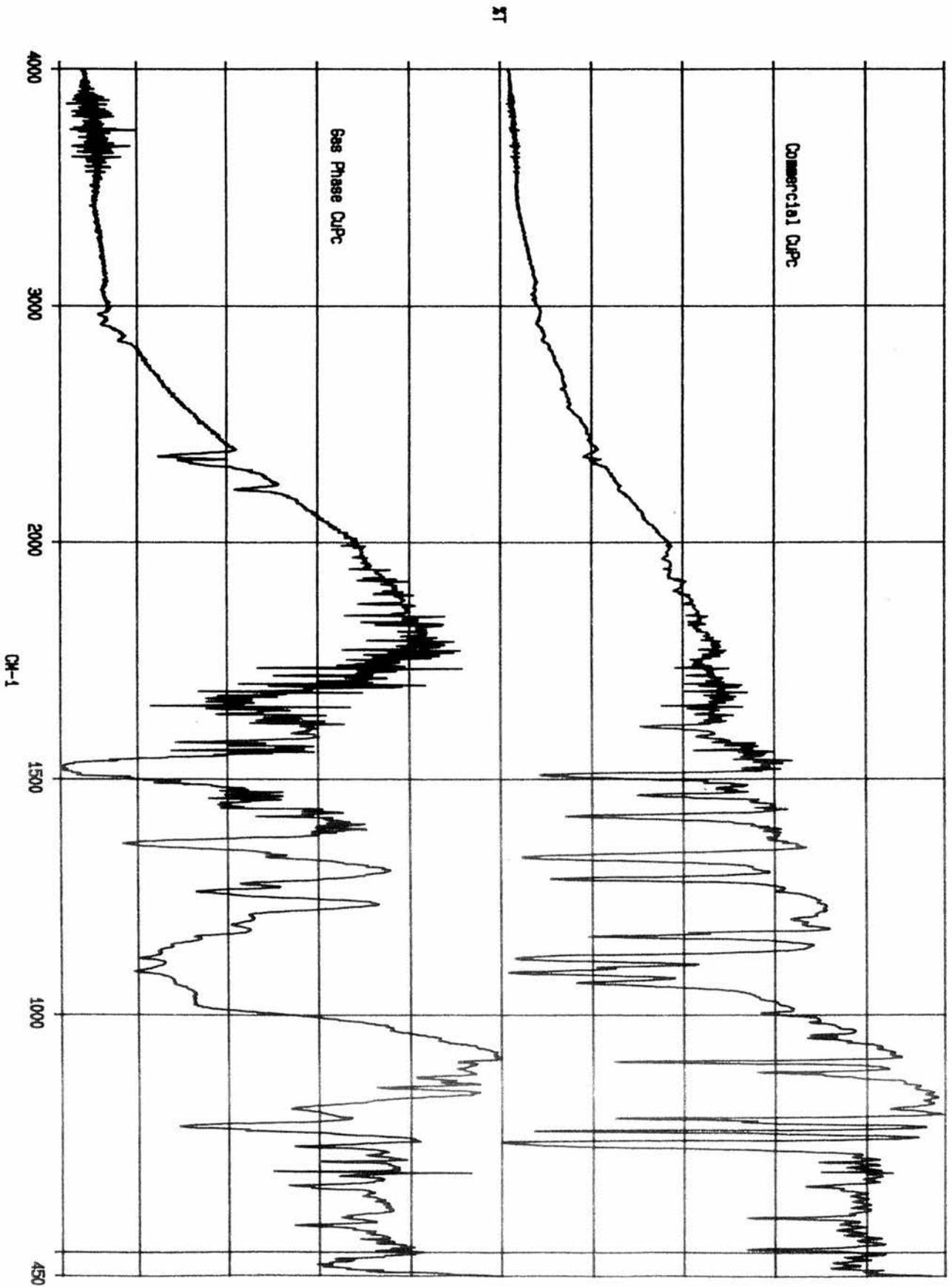
The reaction between A, [Cu(η^2 -2-butyne) (hfac)], and DIII in air at 500 °C, yielded a small amount of a blue solid along with some black carbon deposits. In this reaction the

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solids were sublimed before the carrier gas was passed over, this was done to allow the DIII to sublime to produce a higher concentration of vapour before transporting it into the reaction zone. The blue solid produced was not easily retrievable by scraping it from the tube with a spatula. When the tube was washed with solvents the solid was washed away. On repeating the experiment only a very small amount of a blue solid was noted and due to its position in the tube it was not retrievable using a spatula. The tube was this time washed with a small amount of concentrated sulphuric acid, the blue solid and some of the black deposit on the tube appeared to be removed by the acid. The acid did not go a characteristic yellow/green colour, as when CuPc is dissolved in the acid, suggesting that the blue solid was not a CuPc. On addition to water no precipitate was detectable. This would suggest that the solid was not CuPc but possibly the result of some side reaction or an intermediate to CuPc which was not stable to concentrated sulphuric acid. Due to the difficulty in retrieval of such a small amount of product the blue solid could not be characterised. The presence of a blue precipitate was encouraging and proved that a reaction could take place under these conditions, however, not consistently.

The copper complex [Cu(7-tBuO-NBD)(hfac)], (C), when reacted with DIII in a flow of air and a reaction temperature of 500 °C produced a small amount of a blue solid, similar to that produced before but with a slightly deeper colour. Enough of the solid could be removed by scraping with a spatula to analyse the crude product. The tube was then washed with solvents, (dichloromethane, ethanol, acetone and diethyl ether), and then washed with water, but the blue solid still remained. To remove the solid a small amount of concentrated sulphuric acid was added, the solid dissolved in the acid and gave the characteristic yellow/green colour of CuPc dissolved in concentrated sulphuric acid. On addition of the acid solution to a small amount of ice a blue colour prevailed. On filtration of the product it soaked into the filter paper used and was irretrievable. The fact that the solid dissolved in concentrated sulphuric acid and then a blue precipitate formed on addition to ice suggests that CuPc, or a Pc derivative, is likely to have been synthesised. The crude product that was scraped off was analysed by FTIR, figure 2.7, and table 2.4

Figure 2.7 :- FTIR Spectra of Commercial CuPc and the Gas Phase Sample



lists the peaks of the sample in a KBr disc and compared with literature values²¹, and also a commercial sample obtained from Fluka Chemicals. There is definitely CuPc present in the sample, however, it is not pure with broadening of some of the bands that are representative of CuPc. There a great number of other bands present, some of which are representative of CuPc, and some of which are due to an impurity.

Table 2.4 :- FTIR Bands of the Gas Phase, Literature and Commercial CuPc

Literature	Commercial CuPc	Gas Phase Sample
509	506	507
575	573	573
640	640	640
728	730	722
753	755	755
770	-----	-----
781	779	-----
875	879	886
898	901	901
-----	1003	-----
1064	1068	-----
1087	1090	1092
1099	1101	-----
1118	1120	1120
1162	1166	1166
1285	1288	1278
1330	1334	1334
1415	1420	1417
1500	1508	1503
-----	1522	1522
-----	1541	1540
-----	1560	1560
-----	1570	1571
1603	1610	1604

It is also noted that the Cu-N stretch is weak, suggesting that the impurity may be the major product. Purification of the sample is virtually impossible due to the amount obtained.

The UV-Visible spectrum of the blue solid in 1-chloronaphthalene shows an absorption maximum at 679 nm which is remarkably close to that of the commercial sample of β -CuPc (678 nm) and the spectrum is characteristic of CuPc, with two smaller peaks to the higher energy side, attributable to overtones of the Q band.

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This result suggests that either the impurity has no bands in the Visible region or has an absorption maximum extremely similar to that of CuPc. For the maximum to be in a similar region of the visible spectrum then it is likely that a substituted Pc is being formed during the reaction.

If the impurity is coordinated directly to the copper centre then a hypsochromic (blue) shift in the UV-Visible spectrum would be expected²⁹. This is not the case. Therefore the assumption would be that substitution has occurred on the ring itself. There are a number of possible combinations that may occur to form a substituted CuPc. The hfac ligand may have substituted onto the outer benzene rings, analogous to that of the copper (I) chloride reaction. Another possibility is the decomposition of the hfac ligand to release fluorine which may attack the ring. A third scenario is the attachment of either a hfac ligand or another isoindole derivative joining at the bridging carbons of the indole group, forming a type of leuco CuPc, similar to that synthesised by Barnhart¹¹. The leuco CuPc compound is supposed to be a colourless or relatively colourless solid, which would fit with the UV-Visible spectra. However, the Leuco CuPc is reported to decompose to produce CuPc at elevated temperatures and therefore it is not likely to form in the gas phase where the temperature is 500 °C.

A similar material to the leuco CuPc, designated the CuPc precursor, was synthesised by Brooks¹⁴, the precursor contains six isoindole units coordinated around the copper ion. Again this material is relatively colourless and would leave the UV-Visible spectrum unchanged from that of CuPc. The CuPc precursor is also reported to produce CuPc at elevated temperatures and since the furnace temperature is at 500 °C it is unlikely that it would be formed. It is also not that likely to be either the leuco CuPc or the CuPc precursor since they require six molecules of the organic precursor to react with one molecule of copper and since it is hard enough to get five molecules to react at reduced pressure it is even less likely that seven molecules would react.

The blue solid is unlikely to be metal free Pc because this would produce a double absorption in the visible spectrum and only a single band at 679 nm is found.

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A reaction between the hfac ligand and the DIII may have taken place and if so such a reaction may produce a blue coloured solid. However, on reacting Hhfac and DIII together at 180 °C in the absence of a solvent a buff brown coloured solid is produced. The FTIR spectrum of the solid is not similar to that of the gas phase sample and it is therefore not likely to be the impurity present.

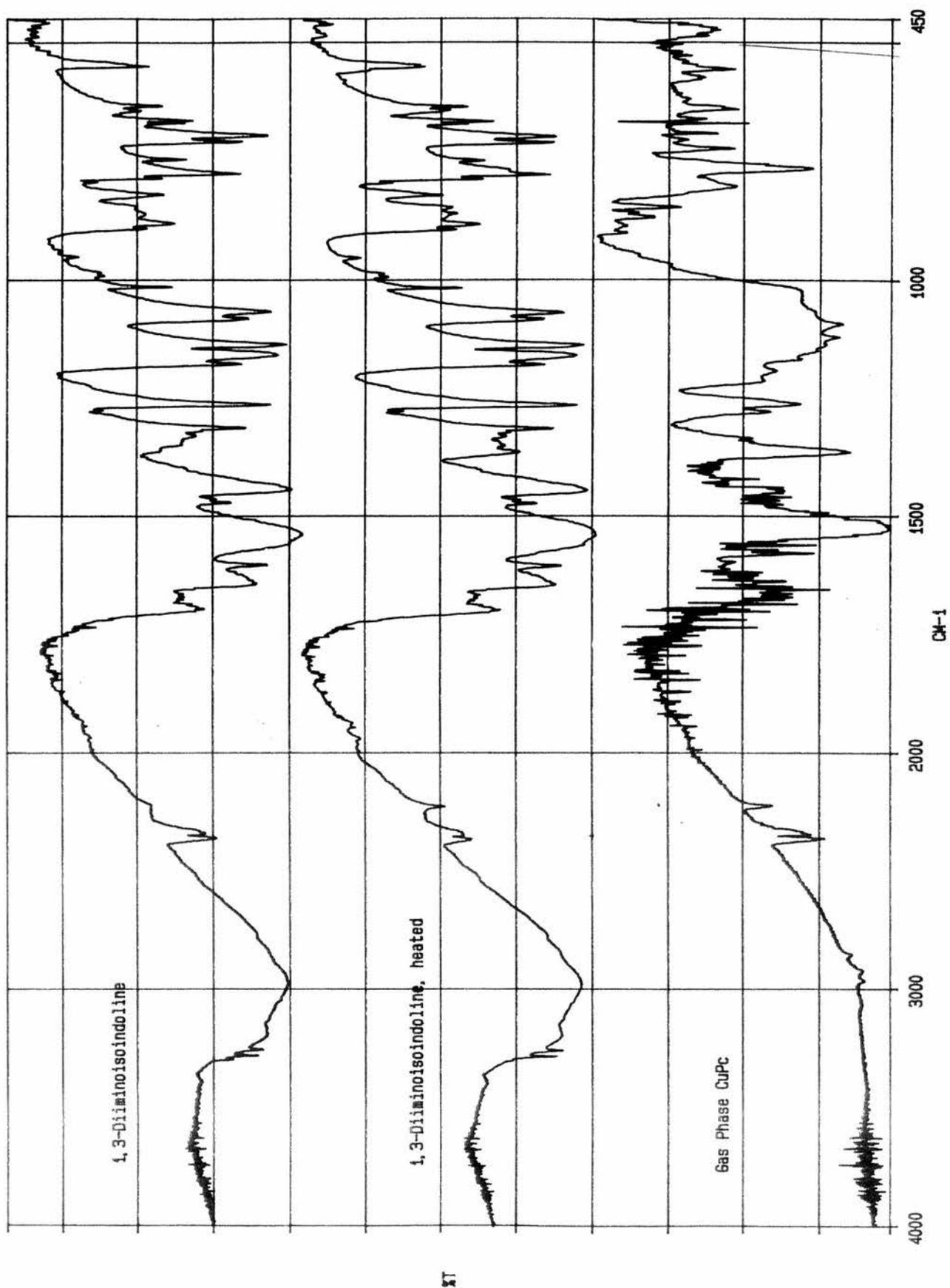
A final possibility is that two or more molecules of the DIII precursor have reacted together to form a blue solid. A blue solid is produced upon heating the DIII at elevated temperatures. The FTIR spectrum, figure 2.8, is similar to that of the gas phase sample but there are still a number of discrepancies. The colour of the solid of the DIII oligomer is a lighter blue than the solid obtained in the gas phase.

The reaction, $[\text{Cu}(7\text{-tBuO-NBD})(\text{hfac})]$, (C), and DIII, was repeated to try and improve the yield to enable the impurity to be better characterised. Unfortunately only extremely small amounts, if any, of a blue solid were formed which was extremely difficult to be retrieved. As before when a small amount of blue solid was found a small amount of concentrated sulphuric acid was used to wash the tube. On addition to ice only a very faint blue precipitate formed and on filtration the filter paper went slightly blue and the solid was therefore inseparable from it. As there is only a very small amount of blue solid being formed in each reaction it means that characterisation is virtually impossible. Several modifications were tried to improve the yield with little success.

One possible explanation of these results is these DIII may be reacting with itself and precipitating out in the reaction zone and then the gas phase copper is passing over and reacting with this precipitate to form CuPc and some unreacted DIII oligomer. It would be impossible to determine if this or a genuine gas phase reaction to form the CuPc is occurring.

In a number of reactions the organic precursor was placed in a quartz boat which in turn was placed at the start of the furnace. These reactions are similar to the work of Pace⁵⁶ with the organic precursor being placed at the start of the furnace instead of the copper source. These reactions were carried out because it was found that the organic precursors were less volatile than the copper complexes.

Figure 2.8 :- FTIR Spectra of DIII, DIII heated, and Gas Phase CuPc



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Glass wool was placed in the reaction tube next to the quartz boat in an attempt to determine if a gas phase reaction is occurring it will also be easier to remove the product by just removing the glass wool.

Small amounts of CuPc were formed using this method, unfortunately the CuPc formed was within the quartz boat and none was detectable on the glass wool. It is a possibility that the organic precursor vapour is reacting with the copper vapour and then precipitating out into the quartz boat. If this was the case then some of the product, even a very small amount, would be transported by the carrier gas and precipitate out on the glass wool. This did not happen. It is therefore likely that a solid gas reaction is taking place. The CuPc that formed in the quartz boat produced a layer covering the surface of the organic precursor preventing any further sublimation and reaction.

Due to a difficulty in product retrieval, mainly due to the small amount of and the position within the reaction tube, glass wool was placed in the reaction tube. It was hoped that any product would be deposited on the glass wool which can be removed more easily than scraping the solid from the side of the reaction tube or from solvent washing of the tube. The glass wool could then be placed in a suitable solvent, such as 1-chloronaphthalene, to dissolve any CuPc and then the solvent removed to leave the product to be analysed.

At the higher temperatures used, 600 °C, parts of the glass wool touching the quartz tube turned a black colour. At this temperature glass starts to melt so it is most likely that the glass wool is decomposing rather than that any precursor decomposition is occurring. Therefore a lower temperature has to be used when using glass wool. When the glass wool was used the same black solid that had been observed previously was deposited. This solid was only removed from the quartz tube on addition of concentrated nitric acid, when the glass wool was added to the acid the black solid remained in contact with it. No CuPc was deposited on the glass wool only the black carbon deposits. Previous reactions that had produced a blue solid were repeated using the glass wool however no blue solid formed when the glass wool was present. It is thought that the glass wool interferes with the gas phase reaction by reducing the chance of a collision between the gaseous copper and organic precursor molecules therefore reducing the chance of a reaction occurring.

In all the reactions tried only a very small amount of solid, if any at all, was ever deposited within the furnace. Most of the solid transported goes straight through the reactor and into the cold trap. The reason that no CuPc is forming is the difficulty of assembling all five molecules together in the hot zone at the same time.

As a result of this a number of modifications to the apparatus were attempted to try and increase the vapour flow. All attempts resulted in a small amount of the precursors being transported. No CuPc was formed using these modifications and it is believed that for a gas phase reaction to occur the carrier gas may have to be bubbled through the solid so that a reasonable amount of precursor can be transported.

2.2.2 SOLID STATE SYNTHESIS OF COPPER PHTHALOCYANINE

In view of the gas phase results obtained, solid state reactions were carried out to make sure that the copper complexes react with the organic precursors to produce CuPc. It was also hoped that any impurities present could be characterised and thus help in the selection of a better copper source and/or organic precursor and also gain some insight into the possible mechanism for the synthesis of CuPc.

As previously mentioned, in section 2.1.4, reactions to produce CuPc can be carried out in the presence or the absence of a solvent. In an attempt to recreate a similar environment to that of the gas phase reactions the solid state reactions were carried out without solvent and in air or nitrogen environments.

The two precursor solids were ground together and placed in a flask that was then evacuated. The gas, air or nitrogen, was then bled into the flask which was then heated. Reaction flasks were heated in oil baths and not isomantles. The isomantles tend to heat the flask very rapidly to the required temperature causing decomposition of the precursors and producing a black solid.

Due to the volatility of the precursors and the exothermic nature of the reaction causing an increase in the temperature above that intended, yields produced were low, as a

significant amount of the precursors had sublimed to the top, the coldest part, of the flask and remained unreacted.

The first set of reactions carried out were those of the copper complexes A to E reacted with either DCB or DIII in air. Table 2.5 shows the combinations and the results obtained. As was expected the copper complexes chosen do react with DCB and DIII in air to produce CuPc. A comparison of the FTIRs, figure 2.9, with that of pure CuPc shows that CuPc has definitely formed, with the characteristic copper nitrogen stretch falling around 898-901 cm^{-1} .

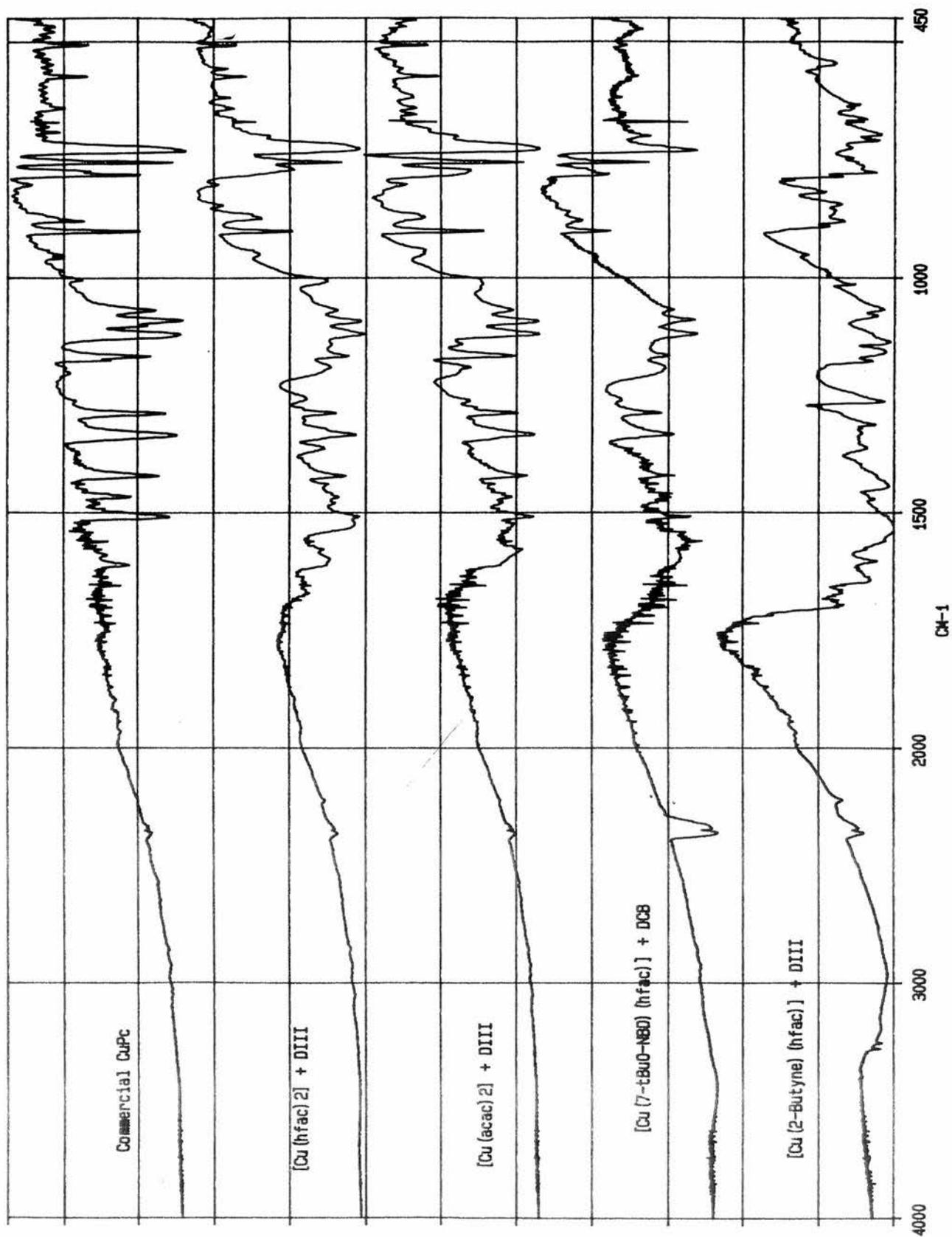
Table 2.5 :- Results Obtained from Solid State Reactions in Air

Copper Complex	Organic Precursor	Oxidation State	CuPc Produced
A	DCB	I	YES
A	DIII	I	YES
B	DCB	II	YES
B	DIII	II	YES
C	DCB	I	YES
C	DIII	I	YES
D	DCB	II	YES
D	DIII	II	YES
E	DCB	I	YES
E	DIII	I	YES
CuCl	DCB	I	YES
CuCl ₂	DCB	II	YES

In most of the spectra there is a broad shoulder to lower frequencies of the band at 1064 cm^{-1} . In a number of samples there is broad band between 1550-1600 cm^{-1} . There are also a number of other broadened bands present in the spectra. The presence of an impurity maybe due to the crudeness of the method used, but this method was used as it is most likely to represent what is likely to happen in the gas phase.

Under a nitrogen atmosphere a different set of results was obtained, only the copper (II) salts reacted to give CuPc as has been reported by Linstead². In the reactions where CuPc

Figure 2.9 :- FTIR Spectra of the Solid State Reactions Carried Out in Air



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was not formed it is unknown what the products are but it is most likely that some reaction possibly producing CuPc intermediates is occurring, however the separation of the mixture and characterisation of the product is extremely difficult.

Table 2.6 shows the combinations and results obtained from the solid state reactions carried out in a nitrogen environment.

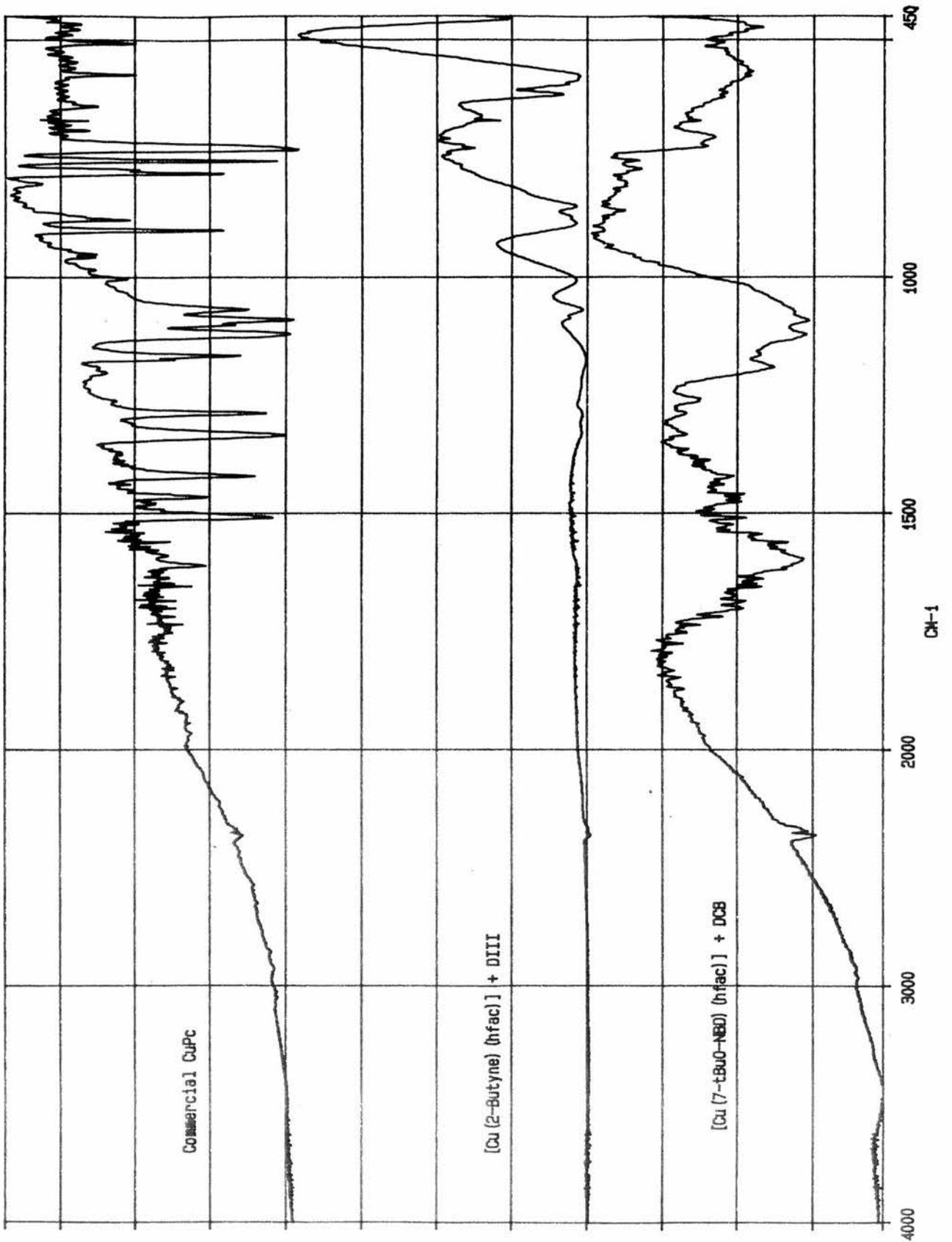
Table 2.6 :- Results Obtained from Solid State Reactions Under Nitrogen

Copper Complex	Organic Precursor	Oxidation State	CuPc Produced
A	DCB	I	NO
A	DIII	I	NO
B	DCB	II	YES
B	DIII	II	YES
C	DCB	I	NO
C	DIII	I	NO
D	DCB	II	YES
D	DIII	II	YES
CuCl	DCB	I	NO
CuCl ₂	DCB	II	YES

It is noted that some of the copper (I) salts, mainly the copper (I) chloride, did produce a small amount of CuPc in a nitrogen environment. When the copper (I) salt was purified prior to use no CuPc was formed when reacted with DCB or DIII. It is likely that a small amount of the copper (I) salt may have oxidised producing copper (II). This catalytic amount of Cu (II) may then trigger the formation, or play an active role in the formation of CuPc^{39,41}. From the FTIR, figure 2.10, of the reactions of copper (I) salts and either DCB or DIII it is not known what the products are.

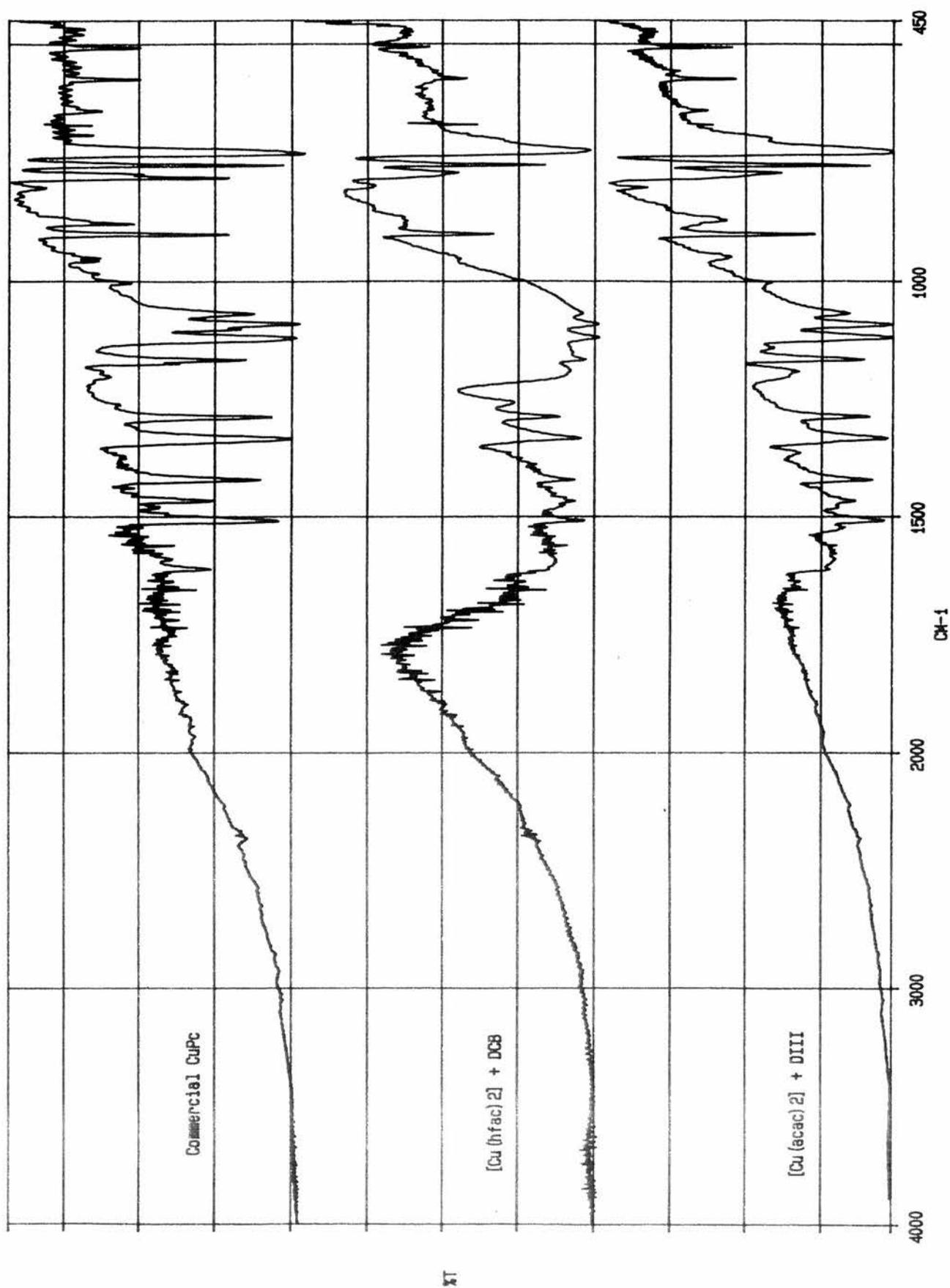
From the FTIR spectra, figure 2.11, it is shown that CuPc is produced when copper (II) salts are used in the solid state but again it is not pure. In a nitrogen environment the bands in the FTIR are broader than for the samples produced in air reasons for which are not clear.

Figure 2.10 :- FTIR Spectra of Copper (I) Salts Reacted in Nitrogen



%T

Figure 2.11 :- FTIR Spectra of Copper (II) Salts Reacted in Nitrogen



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Linstead² suggested that the readiness with which the various compounds of copper react appears to be determined by the ease with which they can supply the metal. He supplied no evidence for this. For this statement to be true then in the case found here the copper complexes must be more stable under nitrogen than air. This is what would be expected. Thus, in air the copper complexes decompose more rapidly releasing the copper allowing it to act as a template for the reaction. In a nitrogen atmosphere the higher stability of the complexes leads to slower decomposition and a higher chance of a side reaction taking place. It would therefore appear that Linstead's statement is correct.

It is noted that copper (II) chloride in a nitrogen environment produced a chlorinated CuPc. The evidence for this is a doublet band in the FTIR around 730 cm^{-1} . When reacted in air there is no evidence for a chlorinated CuPc. Again evidence suggesting that the copper is released more easily in air than nitrogen.

It appears that the same impurity occurs for all the copper complexes used in the solid state reactions both in air and nitrogen. There are a number of possibilities that could be the culprit leading to the impurity.

Firstly, since most of the copper complexes contain the hexafluoroacetylacetonato ligand this may either be reacting with the organic precursor or producing a substituted CuPc. It is believed that $[\text{Cu}(\text{hfac})_2]$ when heated at elevated temperatures may decompose to form copper (II) fluoride⁵⁶ which reacts to form CuPc and possibly a fluorinated CuPc, a reaction similar to that with copper (II) chloride. There is no evidence in the FTIR spectrum of a C-F stretch and therefore the product is not likely to contain fluorine.

A second and more likely possibility is the formation of an isoindole derivative. The isoindole derivative can either form an oligomer, it may form a Schiff base with the hfac or react with the copper. Reactions to produce such a Schiff base were carried out. There appeared to be no reaction between the hexafluoroacetylacetonone (Hhfac) and DCB, some of the DCB had sublimed to the top of the reaction flask but the rest remain unreacted. A reaction did take place between the DIII and Hhfac to produce brown buff coloured compound. Since the product did not have the characteristic FTIR peaks shown by the impurity the product was not further characterised.

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It is most likely that the impurity has come from the partial reaction between the organic precursor and the copper complex. This would account for the same impurity being present in all of the reactions attempted.

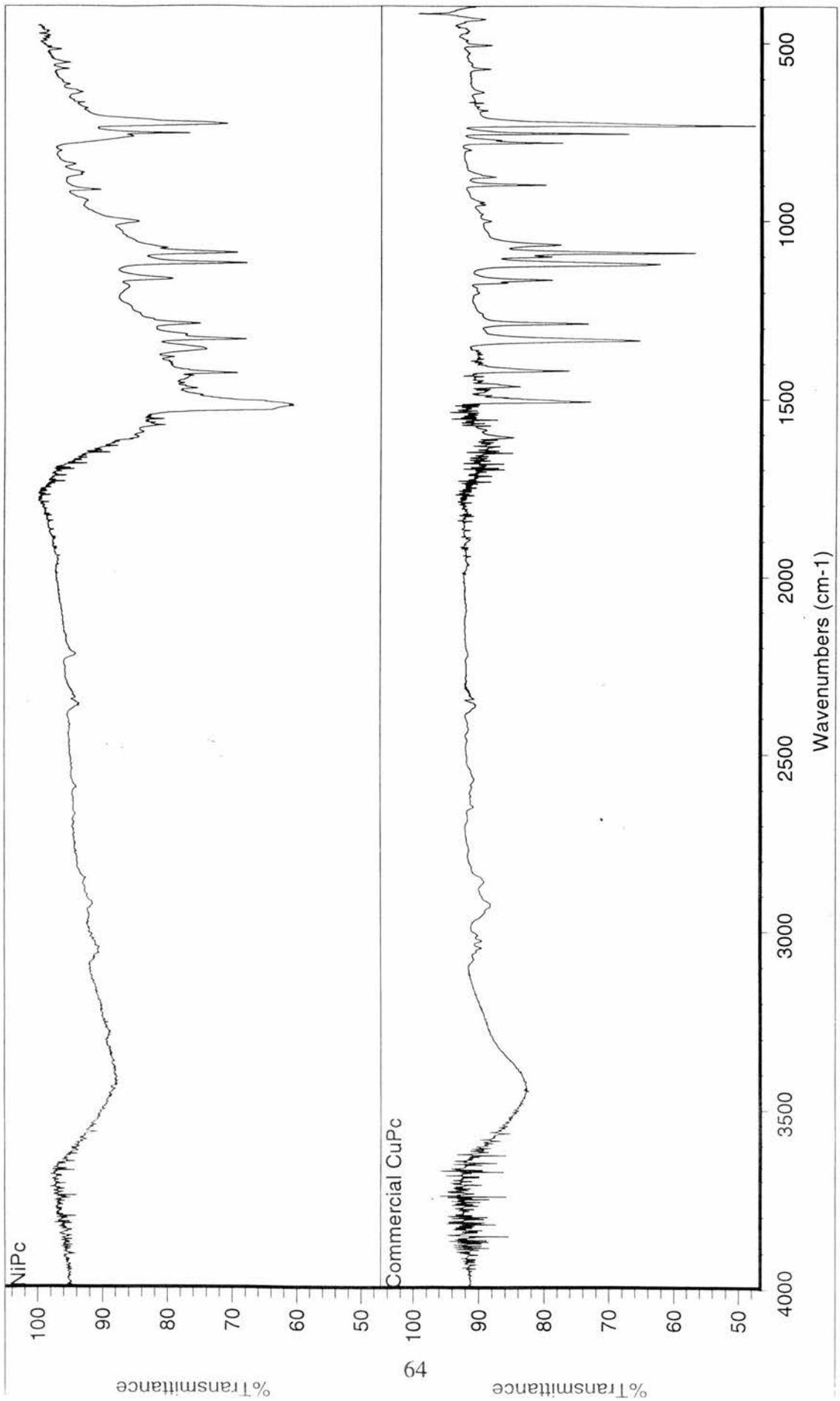
CuPc is difficult to characterise fully and, due to its paramagnetic nature, NMR studies cannot be easily carried out. To gain more information about the nature of the impurity NiPcs were synthesised so that NMR data could be obtained. It is thought that the complexes of nickel will react in a similar manner to those of copper. Nickel (II) acetylacetonate, ($[\text{Ni}(\text{acac})_2]$), and nickel chloride were used enabling a comparison to be made with the results obtained using copper acetylacetonate and copper (II) chloride respectively. The reactions between the nickel complexes and either DCB or DIII were carried out in air using the same solid state conditions used with the copper complex.

The FTIR spectrum, figure 2.12, of NiPc is compared to CuPc. From the FTIR spectrum it is believed that the nickel complex has reacted similarly to the copper complex with the characteristic Ni-N band at 916 cm^{-1} .

It is noted that in most cases DIII reacts more cleanly than DCB. This is because there are fewer reaction steps involved. The DCB must cyclise to form an isoindole derivative which then further reacts with the metal complex.

NMR data were obtained for both of the products, in deuterated sulphuric acid. The spectra obtained when DIII is reacted with the $[\text{Ni}(\text{acac})_2]$ suggests that NiPc has been formed.

The UV-Vis spectrum, in 1-chloronaphthalene, of the sample shows the characteristic spectrum for MPcs but the $\lambda_{\text{max}} = 685\text{ nm}$, is slightly higher than expected. The literature⁷³ value is $\lambda_{\text{max}} = 671\text{ nm}$. This shift in the position of the band maximum may possibly be due to the impurities present. The nickel may be in pyramidal geometry with a ligand coordinated axially to the metal. This would result in a red shift which is detected. This would also still give NMR signals as the metal is diamagnetic. If the nickel was octahedral then it would become paramagnetic and the NMR peaks would be significantly broadened.

Figure 2.12 :- FTIR Spectrum of NiPc Compared with Commercial CuPc

Such a complex may be forming when copper is used but due to Jahn Teller distortions a red shift is not detected in solution.

2.2.3 AEROSOL ASSISTED SYNTHESIS OF COPPER PHTHALOCYANINE

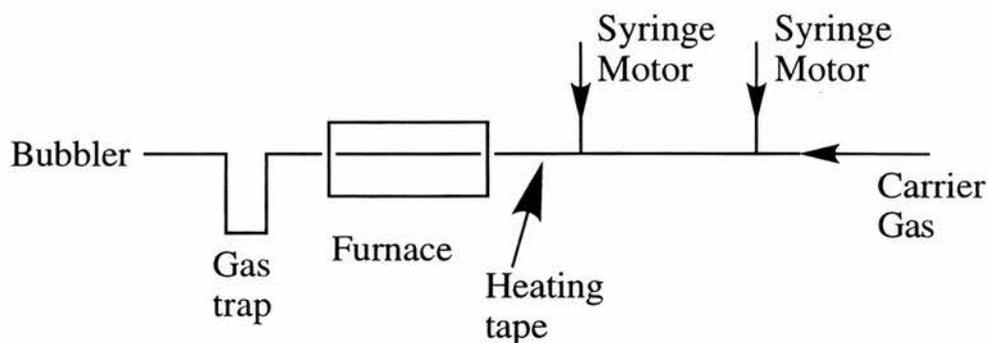
In attempting a gas phase reaction a number of obstacles were encountered. The biggest being the lack of precursor being transported in the gas phase into the reaction zone, and the different sublimation rates. One method to eliminate this problem is the use of aerosol assisted chemical vapour deposition (AACVD). Instead of passing a carrier gas over the subliming solid or liquid, the precursors are dissolved in a solvent and then sprayed to form fine droplets which can be continually evaporated and the precursor transported into the reaction zone⁷⁴. This method also allows two or more precursors to be delivered in one solution the stoichiometry being controlled by the relative solution concentrations. It is also possible to have two separate solutions being injected at controlled rates to obtain the correct stoichiometry. The precursor can be delivered at atmospheric pressure, no vacuum pump is required for vaporising.

This method is commonly used for the deposition of semi-conductors⁷⁴⁻⁷⁷ but has never been used to produce CuPc, however Hendrickson⁴² has patented a method by which CuPc can be dispersed by a liquid medium thereby producing ultrafine particles of pure CuPc. The system involves the vaporising of the pigment in the presence of a gas stream and the particles are then transported to a liquid dispersing medium and deposited as ultrafine particles. If CuPc can be synthesised by using this method then it may be possible to subsequently pass it through a liquid dispersing medium to produce a suitable form of the pigment.

As before with the gas phase synthesis of CuPc the aerosol synthesis poses chemical and engineering problems that must be overcome before a reaction can take place.

Figure 2.13 shows a schematic of the apparatus designed for this technique. One or two syringes can be set up to inject the solution(s), controlled by a Vickers Medical Treonic IP5, digital syringe pump, with an injection rate set at between 20-0.2 cm³ h⁻¹.

Figure 2.13 :- Apparatus Used for the Spray Synthesis



The solution is sprayed into a glass tube with a diameter of 5 mm, with the temperature controlled by a heating tape. The carrier gas, controlled as before using a flow meter, is passed through the tube transporting the evaporating materials into the reaction zone. It is important that the carrier gas is heated prior to coming into contact with the injecting solution, otherwise it will act as a coolant and cause the precursors to precipitate. The glass tube is heated for 6 cm before the carrier gas reaches where the syringe needle enters the apparatus. The reaction zone is set up as for the previous gas phase reactions. The apparatus was designed so that if two solutions are used the precursors will only meet in the furnace and are not able to react in the glass tube.

Reactions were carried out at atmospheric pressure, no vacuum can be applied as the solution is pulled rapidly from the syringe depositing the precursors on the glass tube and removing the solvent. No glass wool was used in these reactions as it is thought to hinder the reaction.

The temperature of the glass tube, into which the solution is injected, is crucial. If the temperature is too hot then on hitting the hot environment the solvent will evaporate before leaving the syringe needle thus precipitating the precursor solids in the syringe needle and blocking it. If the temperature is not hot enough to evaporate the solvent and

precursors rapidly then the solution will drip onto the glass tube and then the solvent is likely to boil off and leave the two solids which may then react or remain intact.

The concentration of the solution also plays an important role in the aerosol syntheses. A concentrated solution can lead the solids to precipitate out on reaching the hot carrier gas, leading to a blocked syringe or the precipitation of the precursors onto the glass tube directly below the needle. A weak solution may lead to a lack of precursor vapour present on evaporation and therefore less chance of reaction. If there is a reaction the amount of product obtained would be so small that it may not be detectible in such a large reaction zone.

For the initial reactions both precursors were dissolved in either ethanol or THF and then placed in the syringe. The precursors tried were reasonably soluble in both solvents. It was thought that these solvents would be suitable as they have low boiling points and would evaporate quickly leaving the reactants in the gas phase. Solution concentrations were set at $0.025 \text{ mol dm}^{-3}$ with respect to the copper complex and 0.1 mol dm^{-3} with respect to the organic precursor. These concentrations were used as they gave the desired ratio of 4:1, and were not too concentrated also any product should be detectible in the apparatus used.

The glass tube was initially heated to $100 \text{ }^{\circ}\text{C}$, via the heating tape, a flow rate of $4 \text{ dm}^3 \text{ min}^{-1}$, of air, and an injection rate of $20 \text{ cm}^3 \text{ h}^{-1}$.

Unfortunately no CuPc was produced using this method. In most cases the two precursors were deposited on the glass tube, directly below the syringe needle having not evaporated, and the solvent transported into the cold trap. It appeared that the solution was dripping onto the glass tube and the solvent was then boiling off and being transported into the cold trap.

The temperature of the glass tube was altered to try and combat this problem of precipitation. An increase in the temperature resulted in the precipitation of the precursors in the syringe needle, causing it to block and preventing any further injection of the solution.

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Reactions involving direct injection of the solution into the furnace were carried out in an attempt to get the precursors to volatilise and then react in the gas phase. In these reactions a dark blue solid that was CuPc was found, however, it was directly below the end of the syringe needle. It would appear, as before, that the two precursors have been deposited on the quartz tube and not volatilised due to the high pressure, with the solvent boiling off and being trapped in the cold trap. The two solids have then reacted to produce an impure sample of CuPc.

After several discussions with Dr P. Wright⁷⁸ it was discovered that there were a number of reasons that could be leading to the results obtained. Firstly the solvents chosen were not suitable because their boiling point was too low and as a result the solvent boiled off too rapidly precipitating the precursors on the glass tube. Higher boiling point solvents, such as toluene, pyridine, xylene, mesitylene, and 1,2,4-trimethylbenzene, were studied in the hope that they would evaporate less quickly but still rapidly enough to volatilise the precursors. In using these solvents DIII was not suitable for reaction due to its insolubility, DCB was found to be suitably soluble in all solvents chosen. The copper complexes were sparingly soluble in these solvents.

The rate of injection was considered to be too fast, thus injecting too much liquid into the hot tube and not allowing time for evaporation. The injection rate was therefore reduced to $0.6 \text{ cm}^3 \text{ h}^{-1}$ and the flow rate was also reduced to $2 \text{ dm}^3 \text{ min}^{-1}$ to increase the residence time of the precursors. The furnace temperature was kept at $400 \text{ }^\circ\text{C}$ as this has no effect on the injection of the solution.

The diameter of the syringe needle was also reduced to try and reduce the size of the droplets entering the hot zone. It had also been suggested that the end of the needle be crimped, this was attempted but was hard to be consistent from needle to needle.

The combinations, of copper complexes B and F with the higher boiling solvents, slower injection rate, lower flow rate are shown in table 2.7.

The concentration of the solution was the same as that used in the previous experiments. As before the temperature of the heating tape was altered between $130 \text{ }^\circ\text{C}$ and $160 \text{ }^\circ\text{C}$ to

try and determine an optimum temperature for the evaporation and transportation of the precursors.

Table 2.7 :- Combinations Tried Using the Aerosol Assisted Synthesis

Copper Complex	Solvent	Heating Tape Temp./ °C
B, F	Pyridine	130
B, F	Pyridine	140
B, F	Toluene	130
B, F	Toluene	140
B, F	Toluene	150
B, F	Xylene	130
B, F	Xylene	140
B, F	Xylene	150
B, F	Mesitylene	140
B, F	Mesitylene	150
B, F	Mesitylene	160
B, F	1,2,4-Trimethylbenzene	150
B, F	1,2,4-Trimethylbenzene	160

Again no CuPc was formed using these changes in conditions and solvents. Once again, the major problem was precipitation of the precursors directly below the syringe needle in the glass tube preventing transport into the furnace. This, as described before, can be caused by a number of factors; the temperature of the heating tape either being too high or low, the speed of the syringe, the concentration of the solution. The speed of the syringe motor was varied from 20 cm³ h⁻¹ to 0.2 cm³ h⁻¹. The lower end of this range is believed to be suitably slow enough for such a spray technique.

The temperature of the heating tape has been varied from between 100-160 °C with little success. The concentration of the solution was 0.025 mol dm⁻³ for the copper and 0.1 mol dm⁻³ in the organic, which is as low as can be used, otherwise no product would be detected.

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The apparatus had been designed so that two solutions could be injected simultaneously if required. Since when one solution was used no transportation of the precursors occurred then it was decided to use two separate solutions.

[Cu(hfac)(COD)] has been used in AACVD previously by Roger et.al.⁷⁴ and we have shown that it is transported into the reaction zone when dissolved in toluene, the DCB is also transported when in toluene. However, when both of these solids are placed in the same solution and injected, no transportation occurs. It is unknown why this should happen, maybe some prereaction is occurring in the solution preventing the precursors from evaporating.

To combat this two separate solutions were then used and injected separately thus allowing the precursors to transport into the reaction zone. The conditions used were as before, a flow rate of $2 \text{ dm}^3 \text{ min}^{-1}$, an injection rate of $0.6 \text{ cm}^3 \text{ h}^{-1}$, and a furnace temperature of $400 \text{ }^\circ\text{C}$. The use of two separate solutions allowed the concentrations to be increased without causing any problems in transportation. The concentrations used were 0.05 mol dm^{-3} for the copper complex and 0.2 mol dm^{-3} for the DCB in toluene.

These modifications were also unsuccessful in the production of CuPc. The precursor solution placed in syringe one always resulted in transportation of the precursor into the cold trap. The solution in syringe two however was not always transported and was normally deposited directly below the needle. There are two possible reasons for this result both of which would require a modification of the apparatus. Firstly the temperature at injection is lower for the second solution than it is for the first. This is due to it's entering an internal tube with the carrier gas of the first solution being passed between it and the heating tape. Two heating tapes were used so that a temperature gradient could be obtained, with the hotter end nearer the furnace and solution two. This failed to have the desired effect and gave the same results as observed previously. Another problem occurs because it is not possible to heat the carrier gas prior to it's making contact with the solution therefore adding to the problem with the heating tape.

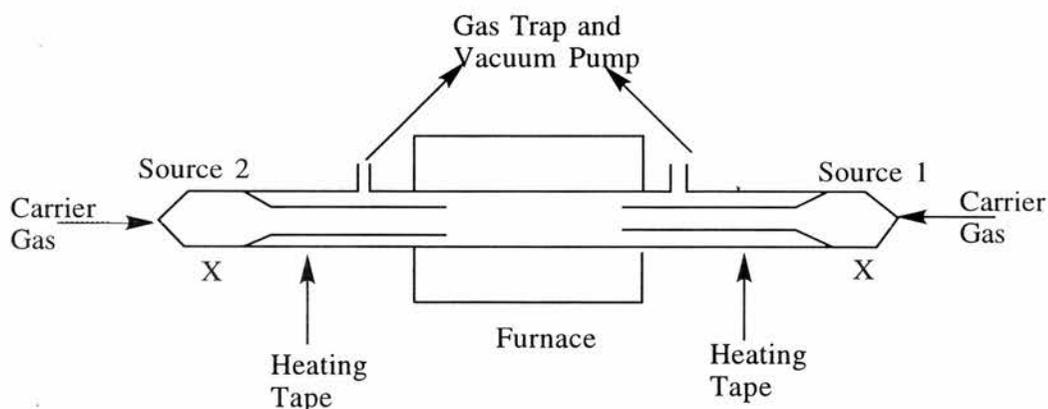
For a gas phase reaction to occur via an AACVD technique the apparatus will have to be modified to allow two separate solutions to be injected and two sources of carrier gas to be applied and heated.

2.2.4 GAS PHASE SYNTHESIS OF COPPER PHTHALOCYANINE

PART II

From the results obtained from the gas phase and aerosol syntheses of CuPc, the problem appears to be with the design of the apparatus set-up. In both set-ups the transportation of the precursor gases into the reaction zone posed a big problem. A new set up was devised, figure 2.14, which allows separate sublimation of the two precursors and with a slight modification could allow two solutions to be injected simultaneously. All the previous conditions for a gas phase synthesis were met.

Figure 2.14 :- New Gas Phase Apparatus



This set up allows the two solids to be sublimed separately at opposite ends of the furnace allowing a dynamic vacuum to be applied at both ends helping sublime and transport the precursors. As before the design allows easy loading of the precursors and in this case there are no cold spots prior to the reaction zone. The heating tape can be wrapped more tightly around the glass tube than previous thus allowing a more equal and accurate temperature from the source to the furnace. There are glass tubes from the

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sources that enter into the furnace so that the vapour is passed and can mix in the hot zone. This prevents mixing of the precursors before the hot zone. The carrier gas is applied at both ends. In some of the reactions the quartz tube within the furnace is replaced by a coiled quartz tube to try and increase the residence time of the precursors.

Gas phase reactions were carried out at a furnace temperature of 450 °C, a gas flow rate of 2 dm³ min⁻¹. The source temperatures used were between 120-170 °C depending upon the copper complex and 140 °C and 180 °C for the DCB and the DIII respectively. Table 2.8 lists the combinations tried using this new apparatus.

Table 2.8 :- Gas Phase Reactions Using Apparatus Set-up in Figure 2.14

Copper Complex	Organic Precursor	Carrier Gas
B	DCB	Nitrogen
B	DIII	Nitrogen
B	DIII	Nitrogen
B	DIII	Air
C	DCB	Air
C	t-BuDCB	Air
C	DIII	Air
D	DCB	Nitrogen
D	t-BuDCB	Air
D	DIII	Air

Tertiarybutyl DCB was used as a precursor in an attempt to increase the volatility of the organic precursor and increase the amount of vapour transported into the furnace.

The set up can be modified for the aerosol synthesis by injecting the solutions at point X at both of the sources and the reaction carried out as before with the removal of the vacuum pump to prevent the solutions being sucked out of the syringes.

As with the previous attempts with the gas phase syntheses, no CuPc was produced. In all the reactions small amounts of the precursors were found unreacted in the gas trap. Some of the organic precursor had decomposed at the end of the glass tube that entered into the furnace. It is noted that this solid has similar bands in the FTIR to that of the

impurities found earlier, however it only occurs when DIII is used and not when the DCB or tBuDCB are used. When the DIII was used a blue/green deposit was normally found which is a result of the precursor reacting with itself at elevated temperatures. The same product is also noted when DIII is heated at elevated temperatures in a Schlenk flask. This solid was not found within the quartz tube in the furnace and therefore did not react with the copper source.

No success was gained when the aerosol technique was used with this set up, resulting in some of the precursors depositing in the cold trap or in the tube before entering into the centre of the hot zone. It is noted that in this case transportation occurred, however, the solution concentration is very low and therefore a reaction is not likely.

2.2.5 CATALYTIC SYNTHESIS OF COPPER PHTHALOCYANINE

Gas Phase Reactions

In many syntheses of CuPc catalysts are employed. With the results obtained it was decided to employ a catalyst to try and improve the chance of reaction. There are a great many catalysts that can be used in the production of CuPc¹⁷. Their role is not fully understood. The most common catalyst used in the commercial syntheses of CuPc is ammonium molybdate. It was decided to look at using ammonium molybdate as a catalyst in the gas phase. Since the molybdate is not very volatile, a volatile molybdenum source in molybdenum hexacarbonyl, was also studied in the attempt to produce CuPc in the gas phase. The apparatus in figure 2.14 was used for the reactions carried out, a quartz tube not the coiled tube, was used with a flow rate of 2 dm³ min⁻¹ of air passing over both precursors. Due to its involatility the ammonium molybdate was placed in a quartz boat in the furnace and heated to 400 °C. It was hoped that the precursor vapour would pass over the catalyst and react.

When molybdenum hexacarbonyl is used, a small amount of the catalyst is ground together with the precursor, preventing it from evaporating away before the precursor

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vapour reaches the reaction zone. As the precursors vaporises the catalyst should also be transported with the precursor vapour into the reaction zone. It is noted that the hexacarbonyl decomposes at 150 °C and therefore on reaching the reaction zone will decompose and therefore may not be able to catalyse the reaction. It is not known if molybdenum hexacarbonyl will catalyse the synthesis of CuPc, but it is hoped that it will. Table 2.9 shows some of the reaction combinations carried out in air and the results obtained.

Table 2.9 :- Gas Phase Reactions Using a Molybdenum Catalyst

Copper Complex	Organic Precursor	Catalyst	Product
A	DCB	(NH ₄) ₆ Mo ₇ O ₂₄	None
A	DIII	(NH ₄) ₆ Mo ₇ O ₂₄	None
A	DCB	Mo(CO) ₆	None
A	DIII	Mo(CO) ₆	None
B	DCB	Mo(CO) ₆	None
B	t-BuDCB	(NH ₄) ₆ Mo ₇ O ₂₄	None
B	DIII	(NH ₄) ₆ Mo ₇ O ₂₄	YES
C	DCB	(NH ₄) ₆ Mo ₇ O ₂₄	None
C	t-BuDCB	Mo(CO) ₆	None
C	DIII	(NH ₄) ₆ Mo ₇ O ₂₄	None

Only one of the reactions tried using catalysts produced a small amount of blue solid in the furnace, the reaction between [Cu(hfac)₂], (B) and DIII with the molybdate as the catalyst. It is not sure if the catalyst played any role in the reaction. The blue solid was found near the vacuum outlet and from the FTIR it is not likely to be CuPc. It is most likely that the reaction occurring, is that of DIII reacting with itself forming a blue solid, this has been noticed in other reactions.

The ammonium molybdate catalyst used turns from a white powder into a grey one most likely due to the elevated temperatures used the molybdate is decomposing. In the cases where the molybdenum hexacarbonyl is used it is likely that it is too volatile and is pulled off by the vacuum. It is not certain that it does act as a catalyst.

Solid State Reactions

In most cases of CuPc syntheses organic precursors other than DCB or DIII are used and many of them require aminating agents. The Wyler process, phthalic anhydride urea, was the first major process in the production of CuPc and it uses ammonium molybdate as a catalyst.

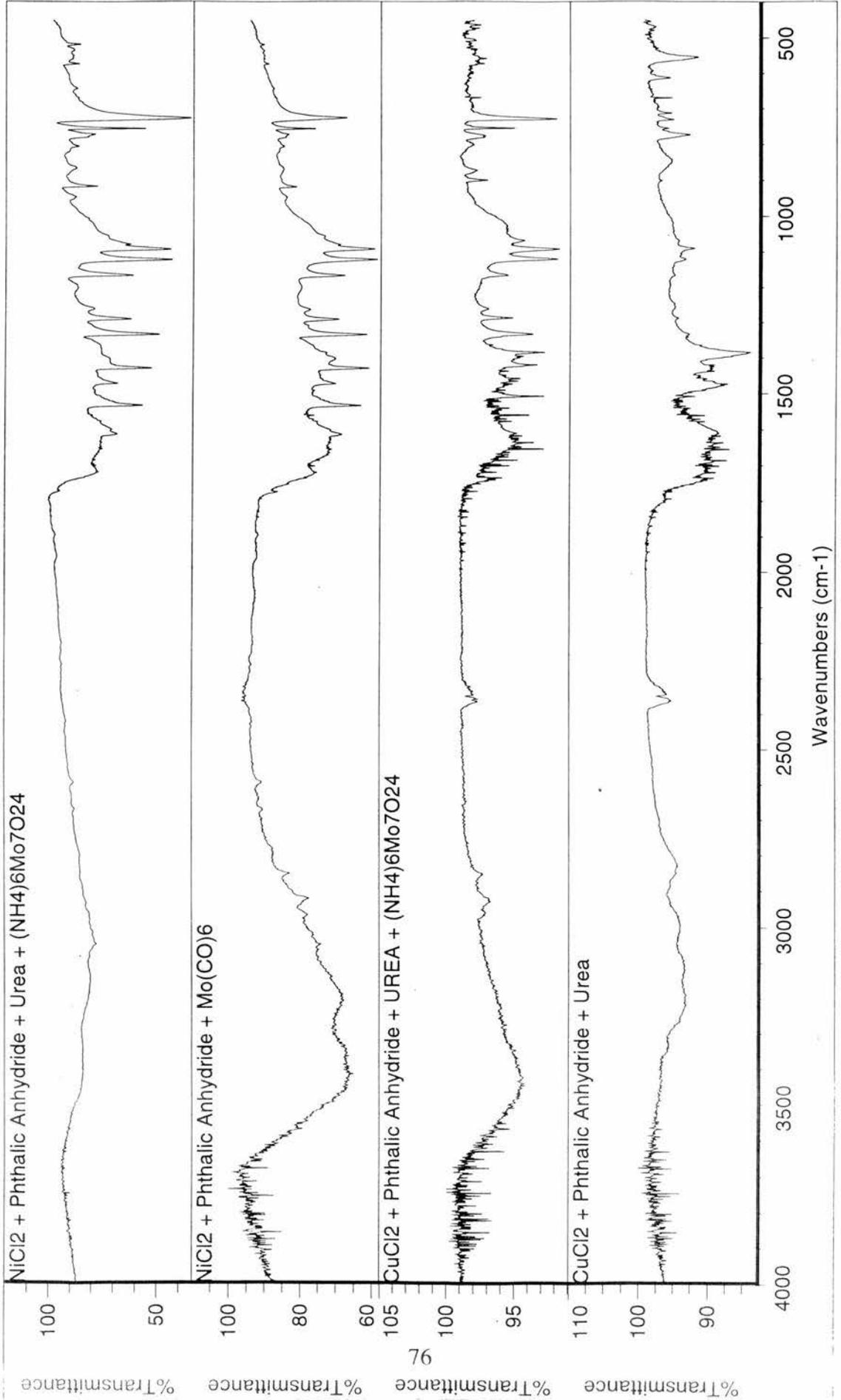
It may be possible that the molybdate catalyses the reaction between urea and phthalic anhydride and then plays little or no role in the further production of CuPc.

Once the reaction is complete the molybdenum is irretrievable from the reaction mixture leading to impurities. To determine if the main role of the catalyst is to catalyse the reaction between phthalic anhydride and urea, reactions were carried out using copper (II) chloride and nickel chloride. The metal chlorides were chosen because they react to give purer MPc and therefore a more detailed and clearer understanding of their role can be obtained. Also if no chlorinated CuPc is produced then this may be evidence for the molybdenum helping the decomposition of the metal complex. The results are listed in table 2.10 from the reactions carried out with a molybdenum source present and also in the absence of a catalyst.

Table 2.10 :- Catalytic Results from the Wyler Process

Copper Complex	Organic Precursor	Catalyst	MPc Produced
CuCl ₂	PA + Urea	None	No
CuCl ₂	PA + Urea	(NH ₄) ₆ Mo ₇ O ₂₄	Yes
CuCl ₂	PA + Urea	Mo(CO) ₆	???
NiCl ₂	PA + Urea	None	No
NiCl ₂	PA + Urea	(NH ₄) ₆ Mo ₇ O ₂₄	Yes
NiCl ₂	PA + Urea	Mo(CO) ₆	Yes

As in all the other cases the product is mainly characterised by FTIR and these clearly show, figure 2.15, that the CuPc or NiPc has been formed when ammonium molybdate

Figure 2.15 :- FTIR Spectra of the Catalytic MPc Syntheses

is used as a catalyst which is as expected from the literature¹⁷. When no catalyst is used then no MPc is produced. It can therefore be stated that the main role of the catalyst is in the reaction of phthalic anhydride and urea to produce an isoindole derivative which then reacts with the metal complex.

It is noted that when the hexacarbonyl is used care must be taken when heating as it decomposes at 150 °C. In the Wyler process the urea and the catalyst are heated and then the metal chloride and the phthalic anhydride are added, in this case the hexacarbonyl appears not to catalyse the reaction. For the nickel chloride if all the reactants are added together and then heated the hexacarbonyl catalyses the reaction producing NiPc. In the case when copper chloride is used it is not understood why there is a difference in the reaction.

It would appear that the catalyst may have a role to play even once the isoindole derivative has formed. If it reacts with the copper then this may create a pathway for a cleaner decomposition of the copper complex and thus allow the copper to react more cleanly with the isoindole unit.

2.3.0 CONCLUSIONS

There were a number of problems that were encountered throughout this chapter of work. It was found that CuPc could be synthesised by a gas phase reaction, however the yield was very low and the purity of the sample was not good. The impurity may be caused by a poor decomposition of the copper complex but it is most likely that the impurity arises from the organic precursor.

In all the gas phase reactions, part I and II, unreacted starting material had condensed in the cold trap having passed through the hot zone without reaction or decomposition. It is believed that this is caused by a combination of the dynamic vacuum rapidly pulling, and the high flow rate of carrier gas pushing, thus forcing the reactants rapidly through the furnace allowing no time for a reaction to occur. This short residence time of the precursors is also made worse by the different sublimation rates, and temperatures,

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between the copper complexes and the organic precursors. However this can be combatted by adjusting the heating tape temperatures so that sublimation rates of 4:1 occur.

The biggest problem is the reaction to produce CuPc goes against entropy, the reaction of five molecules to produce one, for the reaction to occur it would favour reaction conditions of higher pressure than that used to sublime the precursors. The pressure used in the reactions means that the precursor vapour is in very low concentrations and for all five molecules to be in the correct orientation to react together in an atmosphere of low concentration is very unlikely. The apparatus set up that is used may be too large for the quantities of reactants used. If a smaller set up was used then a reaction may occur more readily. The problem then lies in the residence time of the precursors in the hot zone. If the reaction zone is reduced in size then the residence time will be greatly reduced.

The solid state reactions carried out proved, as was expected, that the copper complexes chosen do react with both DCB and DIII to produce CuPc. Again an impurity is present, this is believed to be due to an isoindole derivative.

The spray synthesis of CuPc suggested that the precursors were not suitable for this type of reaction. Finding a suitable solvent that both precursors are soluble in is very difficult. When copper complex [Cu(COD)(hfac)], F, was used transportation into the furnace occurred, however when the DCB was added to the solution no or very little transportation occurred, therefore it looks like for a spray synthesis to occur then two separate solutions will be required or it may be possible the copper complex in solution and sublimation of the solid organic precursor.

From the catalytic reactions it would appear that the main role of the molybdenum catalyst is to catalyse the reaction between phthalic anhydride and urea producing an isoindole derivative, similar to DIII. It may however help with a cleaner decomposition of the metal complex. When the catalyst is reacted with the metal chlorides there is no evidence of a chlorinated MPc as would be expected in the absence of a catalyst. When NiCl₂ reacted with either of the molybdenum sources with phthalic anhydride and urea a reaction occurs

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producing NiPc. This further confuses the understanding of the possible role of the catalyst.

2.4.0 EXPERIMENTAL

2.4.1 GENERAL PROCEDURES

All operations, unless stated, were performed under a dry deoxygenated nitrogen atmosphere purified by passing through a series of columns consisting of Cr^{2+} on silica. Manipulations were carried out using standard Schlenk line and catheter tubing techniques. Petroleum ether, diethyl ether, THF were dried and distilled over sodium diphenylketyl, dichloromethane was distilled over calcium hydride and toluene was distilled over sodium and ethanol dried over magnesium ethoxide, activated with iodine. All liquid reagents and solvents were deoxygenated by flushing with dry nitrogen prior to use. Cuprous chloride was purchased from Avocado and purified using a literature method⁷⁹. Sodium 1,1,1,5,5,5-hexafluoropentane-2,4-dionate ($\text{Na}(\text{hfac})$) was synthesised using a literature method⁸⁰. All other chemicals used were purchased from a known supplier and were used without further purification.

Infrared data were recorded on either a Perkin Elmer 1710 FTIR or on a Nicolet 460 Protégé spectrometer, NMR data were recorded on a Bruker AM 300 spectrometer in 5 mm glass tubes. Absorbance spectra were recorded using a Perkin Elmer Lambda 14P UV/Vis spectrophotometer (900-300 nm), using 1 cm x 4 cm quartz cells. CHN data were obtained at the University of St. Andrews on a Carlo Ebra Model 1106. All data were compared with the literature, where possible.

2.4.2 SYNTHESSES OF THE COPPER COMPLEXES

Synthesis of $[\text{Cu}(\eta^2\text{-2-butyne})(\text{hfac})] [\text{A}]^{68}$

Cuprous oxide (6 g, 0.042 mol), (copper (II) oxide may also be used), was stirred in dichloromethane (125 cm^3) and 2-butyne (3.25 g, 4.71 cm^3 , 0.06 mol) was added.

1,1,1,5,5,5-Hexafluoropentane-2,4-dione (Hhfac) (12.5 g, 8.50 cm³, 0.06 mol) was added dropwise to the stirring solution. After addition of the Hhfac the mixture was left to stir for a further 30 min, the precipitate was then filtered and washed with dichloromethane. The dichloromethane was then evaporated in vacuo, leaving a dark green solid.

Synthesis of [Cu(hfac)₂] [B]⁶⁹

Copper (II) acetate monohydrate (2.0 g) was dissolved in hexafluoropentane-2,4-dione (10 cm³) by boiling for 5-10 min. The excess Hhfac was removed in vacuo and the residue was recrystallised from dichloromethane. The resulting green solid was dried in vacuo. IR data, (KBr disc), 1763 (w), 17422(m), 1647 (m), 1616 (m), 1564 (m), 1538 (m), 1436 (m), 1471 (m), 1255 (s), 1236 (s), 1200 (s), 1149 (s), 1107 (m), 1049 (m), 1008 (w), 807 (m), 747 (w), 681 (m), 596 (m), 530 (w) cm⁻¹.

Synthesis of [Cu(7-t-BuO-NBD)(hfac)] [C]⁷⁰

Copper (I) chloride (3.01 g, 30.4 mmol) was dissolved in diethyl ether (50 cm³) in a 250 cm³ Schlenk flask to which 7-t-BuO-NBD (7-tertiarybutoxy norbornadiene) (5.00 g, 30.4 mmol) was added. Na(hfac) (7.05 g, 30.5 mmol) was dissolved in diethyl ether (50 cm³) and the solution transferred to the reaction flask with stirring. The mixture was stirred for a further 4 h at room temperature after which the volatile components were removed in vacuo. Hexane (80 cm³) was added to extract the product and then filtered. After removal of the hexane a yellow powder was obtained which was recrystallised from hexane giving a yield of 65 %. NMR data, C₆D₆, ¹H δ 6.27 (s 1H, CH on hfac), 6.04 (br, s, 2H, noncoordinated CH=CH), 5.02 (br, s, 2H coordinated CH=CH), 3.31 (br, s, 1H, bridgehead H), 2.93 ppm (br, s, 2H bridgehead Hs), 0.85 (s, 9H, CBut). ¹³C {H} 177.6 (q, J_{FC}= 34 Hz, CF₃CO), 139.1 (s, noncoordinated CH=CH), 118.6 (q,

$J_{\text{FC}} = 325$ Hz, CF_3), 101 (s, coordinated $\text{CH}=\text{CH}$), 92 (s, bridgehead C), 89.4 (s, CH on hfac), 76.1 (s, $(\text{CH}_3)_3\text{C}$), 55.3 (s, bridge Cs), 27.6 (s, $(\text{CH}_3)_3\text{C}$) ppm.

Synthesis of $[\text{Cu}(\text{Cl})(\text{PEt}_3)_2]$ [E]⁷¹

Triethylphosphine (5 cm^3 , 33.8 mmol) was added dropwise to a slurry of copper (I) chloride (1.63 g, 16.5 mmol) in diethyl ether (100 cm^3). After complete addition the solution became clear and was stirred for 1 h, after which the volatile components were removed in vacuo. Recrystallisation from pentane gave a white solid. IR, KBr disc, 2958 (s), 2930 (s), 2902 (s), 2873 (s), 2363 (m), 2344 (m), 1458 (m), 1416 (m), 1377 (m), 1260 (w), 1037 (m), 765 (s), 712 (m), 670 (w), 623 (w) cm^{-1} .

Synthesis of $[\text{Cu}(\text{COD})(\text{hfac})]$ [F]⁷²

A suspension of copper (I) oxide (1.43 g, 10.0 mmol) in THF (75 cm^3) was stirred and 1,5-cyclooctadiene (2.45 cm^3 , 20.0 mmol) was added. The 1,1,1,5,5,5-hexafluoropentane-2,4-dione (2.80 cm^3 , 20.0 mmol) in THF (50 cm^3) was added dropwise over 30 min. The reaction was stirred for 3 h and then filtered leaving a yellow solution. The solvent was then removed in vacuo leaving a yellow solid which was recrystallised from cyclohexane. IR data, (KBr disc), 1652 (s), 1557 (m), 1538 (m), 1486 (s), 1258 (s), 1221 (s), 1207 (s), 1143 (s), 1092 (m), 808 (m), 796 (m), 746 (m), 725 (m), 672 (s), 585 (m), 527 (w) cm^{-1} .

2.4.3 GAS PHASE SYNTHESIS OF COPPER PHTHALOCYANINE

PART I

General Gas Phase Synthesis Procedure

The ortho benzo derivative (DCB OR DIII, 4 mmol) was placed in one arm, source 1, of the glass Y piece of the apparatus, shown in figure 2.6. The copper complex (1 mmol) was placed in the other arm, source 2. The apparatus set up was then evacuated and heat applied. The sources were heated, to 120-180 °C, using silicone rubber-encapsulated heating tape controlled by a thermolyne 45500 temperature controller. The quartz reaction tube was heated by a carbolite MTF 12/38/η00 tube furnace to temperatures of 250-600 °C. The carrier gas, N₂ or air, was allowed to flow through the system at approximately 4 dm³ min⁻¹, passing over the subliming precursors and carrying the vapour into the furnace. A dynamic vacuum was applied throughout the reaction to facilitate the sublimation of the reactants. After 3-6 h, the reaction set up was allowed to cool to room temperature, the vacuum pump switched off and the flow of carrier gas removed opening the system to the atmosphere. The reaction tube was removed from the set up and washed with dichloromethane, ethanol, acetone and diethyl ether, any solid left in the furnace was then washed with concentrated sulphuric acid, and then water was added to the acid to precipitate any copper phthalocyanine. Any solid recovered from the solvent washing was dried in vacuo. Any solid recovered from the acid pasting was dried in an oven at 120 °C.

2.4.4 SOLID STATE SYNTHESIS OF COPPER PHTHALOCYANINE

General Solid State Synthesis Procedure

The copper complex (1 mmol) and the benzo derivative (4 mmol) were ground together and placed in a 100 cm³ Schlenk flask. The flask was evacuated and the carrier gas, air or

CHAPTER 2

nitrogen, passed over the sample. The materials were heated to around 200 °C and left until the sample had turned completely dark blue (2-4 h). After the sample was cooled to room temperature the product was washed with dichloromethane, ethanol, acetone and diethyl ether until the washings become clear. The average yield obtained was around 70 %, this is lower than expected possibly due to the volatility of the starting materials. NiPc samples were also synthesised using this method. FTIR and UV-Vis data were recorded in order to determine the purity of the samples.

2.4.5 REACTION OF 1,2-DICYANOBENZENE AND 1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONE

DCB (4 mmol) was added to Hhfac (1 mmol) and the flask evacuated, then the carrier gas, air or nitrogen, was passed over the mixture. The flask was heated to 180-200 °C and left for 2-4 h. The resultant product was then dried in vacuo and analysed. The same procedure was used for the reaction of DIII and Hhfac.

2.4.6 HEATING OF DCB OR DIII

DCB, or DIII, (1 mmol), was ground and placed in a Shlenck flask. The flask was then evacuated and then air bled in. The flask was then heated to 180-200 °C and left for 1-2 h. The product was then washed with dichloromethan, ethanol, acetone and diethyl ether.

2.4.7 AEROSOL ASSISTED SYNTHESIS OF COPPER PHTHALOCYANINE

General Spray Synthesis Procedure

The reaction set up, shown in figure 2.13, was designed and used for the spray technique in the attempt to produce CuPc via the gas phase.

CHAPTER 2

All the solvents were used as purchased, no degassing or drying of the solvent was required.

The copper complex was dissolved in the solvent (0.05 M) and combined with an equal volume of a solution of the organic precursor in the same solvent (0.2 M). The solution was placed in a gas tight syringe which was then placed in a, Vickers Medical Treonic IP5, digital syringe pump, with an injection rate set at between 99.9 and 1 cm³ h⁻¹ (speeds given for a 50 cm³ syringe, a 10 cm³ syringe was used therefore actual speeds are approximately 20-0.2 cm³ h⁻¹). The tube was heated, the reaction temperature, by a carbolite MTF 12/38/η00, was kept a 400 °C and the glass tube into which the sample was injected was heated to between 120-160 °C by silicone rubber-encapsulated heating tape with a thermolyne 45500 temperature controller. Once all the liquid had been injected the apparatus was allowed to cool to room temperature. Any precipitate that formed was removed and washed in the following sequence of solvents dichloromethane, ethanol, acetone, diethyl ether and then dried in vacuo.

2.4.8 GAS PHASE SYNTHESIS OF COPPER PHTHALOCYANINE

PART II

General Gas Phase Synthesis Procedure Using the New Apparatus

The apparatus was modified from that in set up 1 and is shown in figure 2.14.

The ortho benzo derivative (DCB OR DIII, 4 mmol) was placed in one end and the copper complex (1 mmol) placed at the other end. The apparatus was then evacuated and heat applied. The sources were heated to 120-180 °C using silicone rubber-encapsulated heating tape controlled by a thermolyne 45500 temperature controller. The quartz reaction tube was heated by a carbolite MTF 12/38/η00 tube furnace to temperatures of 400-600 °C. The carrier gas, N₂ or air, was allowed to flow through the system at approximately 4 dm³ min⁻¹, passing over the subliming precursors and carrying the vapour into the furnace. A dynamic vacuum was applied throughout the reaction to facilitate the

sublimation of the reactants. After 3-6 h the reaction set up was allowed to cool to room temperature, the vacuum pump switched off and the flow of carrier gas removed opening the system to the atmosphere. The reaction tube was removed from the set up and washed with dichloromethane, ethanol, acetone and diethyl ether, any solid left in the furnace was then washed with concentrated sulphuric acid, which is then added to water to precipitate any copper phthalocyanine. Any solid recovered from the solvent washing was dried in vacuo. Any solid recovered from the acid pasting was dried in an oven at 120 °C.

2.4.9 CATALYTIC SYNTHESIS OF METAL PHTHALOCYANINE

General Gas Phase Synthesis using set up II in the Presence of a Catalyst

The procedure was as described in 2.4.8 above, except the molybdenum catalysts molybdenum hexacarbonyl, (0.02 g), or ammonium molybdate, (0.02 g), were added. The hexacarbonyl was ground with the precursor, due to its volatility, and then the reaction carried out as before. The molybdate was placed in a quartz boat within the furnace.

General Solid State Synthesis Procedure

These reactions were carried out in an attempt to find out the role of the molybdenum catalyst and also if the oxidation state of the Mo plays a part.

The copper complex (1 mmol) and the benzo derivative (4 mmol) were ground together with a small amount of the catalyst, (0.02 g), and placed in a 100 cm³ Schlenk flask. The reaction procedure was then the same as for a general solid state synthesis.

Reaction of Phthalic Anhydride, Urea and Metal Chloride

Urea (1.3 g) and phthalic anhydride (1 g) were melted at 150 °C. Metal, (copper or nickel), chloride (0.2 g) was then added to the melt and the reaction mixture heated to 200 °C. After a colour change (2-4 h) the mixture was cooled and then washed with DCM, EtOH, Me₂CO, EtO₂.

Reaction of Phthalic Anhydride, Urea and Metal Chloride in the Presence of a Catalyst

Urea (1.3 g), phthalic anhydride (1 g) and a small amount of the molybdenum source were melted at 150 °C. Metal, (copper or nickel), chloride (0.2 g) was then added to the melt and the reaction mixture heated to 200 °C. After a colour change (2-4 h) the mixture was cooled and then washed with DCM, EtOH, Me₂CO, EtO₂.

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CHAPTER 3

QUANTUM CONFINEMENT OF COPPER PHTHALOCYANINE

CHAPTER 3

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3.1.0 INTRODUCTION

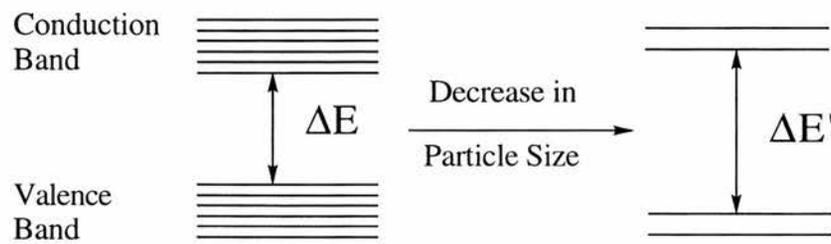
Currently there is a considerable amount of research interest in nanometre sized particles because they exhibit novel materials properties¹⁻²⁶. Nanometre sized semiconductor clusters in the size region of 1-10 nm have electronic, optical and chemical properties that differ vastly from the bulk material as a consequence of their finite small size. The properties of these materials are altered with changing particle size therefore by controlling the size of the particles it is possible to tune the properties of the material. Such particles are referred to as Q-particles or quantum dots and their structure property relationships have yielded new materials. Areas of application that can benefit from the small size and organisation of nanoscale objects include quantum electronics, nonlinear optics, photonics, chemoselective sensing, and information storage and processing and catalysis⁶.

3.1.1 QUANTUM CONFINEMENT

The study of quantum confinement, looks at how the optical and/or the electronic properties of nanometre sized semiconductors are affected by the alteration of the particle size. The observed semiconducting properties in many inorganic solids are not properties of individual molecules or atoms but result from their arrangement in an ordered manner, and their interactions. Semiconductor Q-particles represent a state of matter between bulk solids and molecular species and they have intermediate properties. Their properties arise from a combination of two phenomena. Firstly due to their small size the number of atoms at the surface becomes comparable to the number of atoms that make up the bulk lattice. Therefore the chemical and physical properties that are controlled by the bulk lattice become increasingly dominated by the surface structure; surface defects. The second phenomenon occurs only in nanometre sized semiconductors and metals. The de Broglie wavelength for electrons (and holes) becomes comparable to the size of the crystallite. The charge carriers become like a "particle in a box" where the size of the box

is the size of the crystallite¹². This causes a splitting of the valence and conduction bands into discrete energy levels with the spacing between these levels and the band gap increasing with decreasing particle size. Figure 3.1 shows a schematic of the energy splitting with decreasing particle size.

Figure 3.1 :- Band Gap Splitting



The band gap of these materials can be directly established from the absorbance spectra using the Einstein-Bohr equation, equation 3.1. The band gap energy is inversely proportional to the wavelength of light absorbed i.e. the longer the wavelength the smaller the band gap.

Equation 3.1 :- The Einstein-Bohr Equation

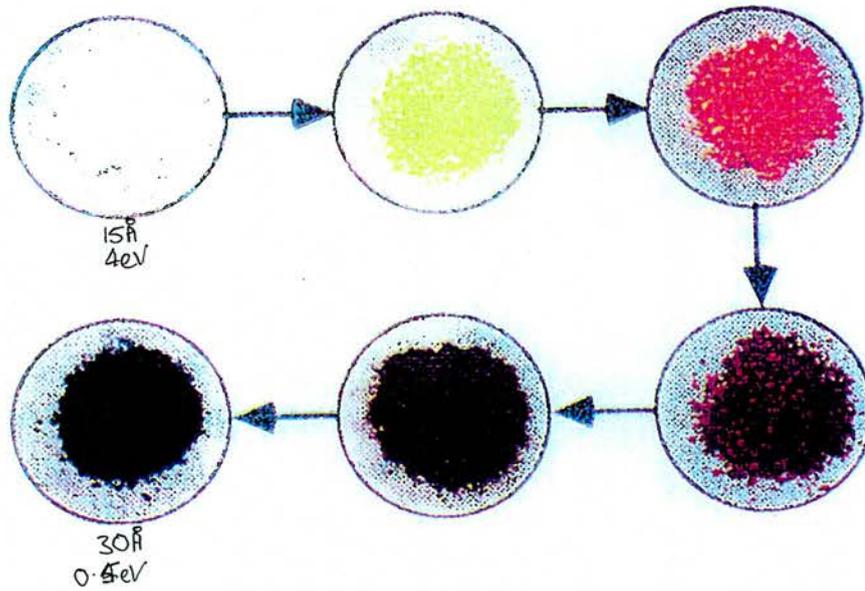
$$\Delta E = \frac{hc}{e\lambda}$$

Where ΔE is the band gap energy, h is Planck's constant, c is the speed of light, e is the charge of an electron, and λ is the wavelength of light absorbed.

Visually, size quantisation effects can be seen from a change in colour of the sample. This is due to an increase, a blue shift, in the absorbance energy which occurs as a result of a decrease in particle size. Such effects are diagnostic of quantum confinement. A good example of a visible colour change as the particle size is decreased is shown for cadmium phosphide particles in figure 3.2. The bulk solid is a black powder with a band gap of 0.5 eV and as the particle size is decreased the colour changes to brown, red,

orange, yellow and white and the band gap has increased from 1.5 eV to 4 eV as the particle size has halved from 30 Å to 15 Å¹¹.

Figure 3.2 :- Visual Effects of Quantum Confinement in Cadmium Phosphide



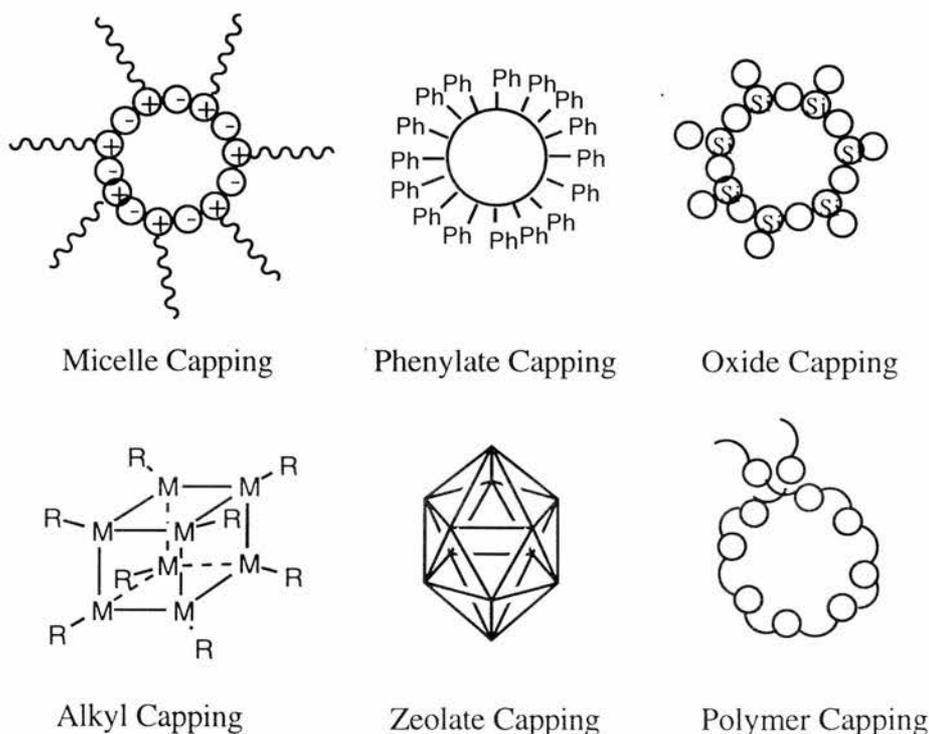
In the ideal case of a perfect semiconductor cluster crystal, deleterious effects would be reduced to a minimum, thereby producing a high concentration of uniformly sized nanoparticles. To produce such Q-particles which can be used in devices, two important criteria must be fulfilled. The first is the preparation of a high concentration of uniformly sized and shaped particles. These have an influence on the wavelength of light absorbed and by altering the particle size the absorption energy can be tuned. The size has to be uniform as a random size distribution will alter the overall colour and properties of the material. Reproducibility of colour will be almost impossible with random sized particles, making synthesis of a possible device extremely difficult.

The second criterion is the control of the surface atoms. As the particle size is reduced the ratio of surface atoms to those in the bulk is increased and these surface states can be highly reactive leading to the formation of agglomerates or may become involved in the

annihilation of the electron or hole formed in the initial photoexcitation leading to quenching or alteration of the wavelength of emission. These must, therefore, be eradicated. This can be achieved chemically by binding the particles to a suitable material of higher band gap, thus capping the Q-particle. There are many synthetic methods reported which target surface control and monodispersity and these include syntheses in colloidal suspensions, solutions of single-molecule precursors, sol-gels, zeolites, LB-films, micelles and polymer films. Figure 3.3 shows a graphic representation of some of the types of capping that are commonly used in controlling the size and monodispersity of nanoparticles²⁷.

Host-guest inclusion chemistry provides an attractive method for achieving the goal of monodispersity for these nanoscale semiconductor cluster materials. Here chemical protection and stabilisation, together with spatial restrictions imposed by the host, allow the synthetic nanochemist to nucleate, grow and arrest the "crystallisation" of nanometre semiconductor clusters in the desirable quantum size regime⁶.

Figure 3.3 :- Types of capping used for quantum confinement.

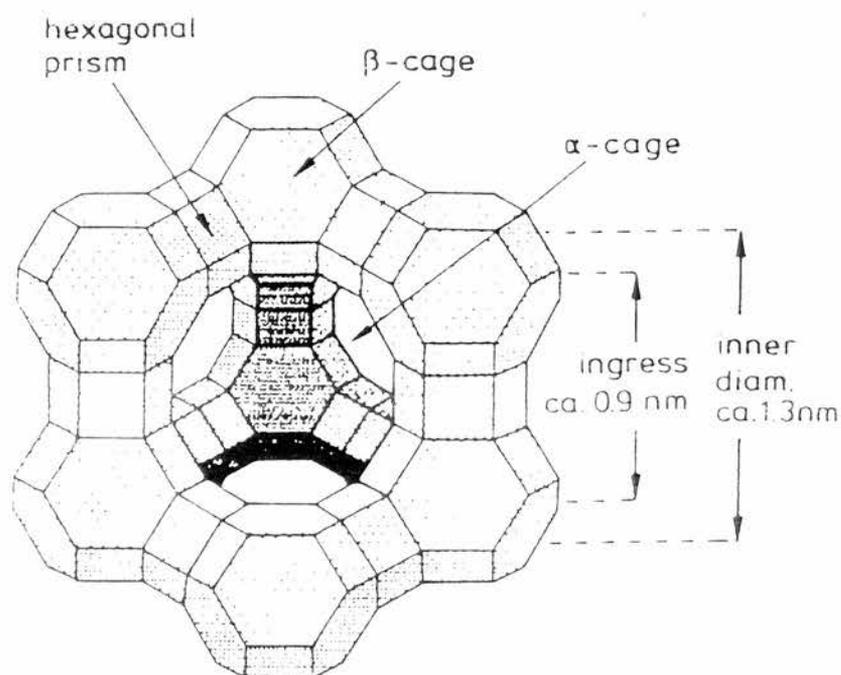


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Zeolite hosts allow the ordered inclusion of particles with dimensions in the range of 6-100 Å with a uniform, (monodispersed), size distribution. The term zeolite refers to a range of micro and mesoporous solids whose structures range from tunnels to cages of varying size and dimension. Such materials include zeolites and MCM-41 along with a vast number of other possibilities.

Zeolites X and Y are classed as faujasites and are isostructural differing in their silicon to aluminium ratios, with Y being slightly more acidic having less aluminium in the framework. The negative charge created by the presence of aluminium is balanced by a counter ion, normally sodium but other small cations such as protons, ammonium ions and potassium may be present. The sites at which the aluminium is present are acidic and despite zeolite-Y having less aluminium and therefore less acid sites each site is more strongly acidic than in zeolite-X. The framework, as shown in figure 3.4, is made up of sodalite cages connected to four other sodalite cages to form a supercage structure. The supercage structure is large enough to contain a sphere with a diameter of 13 Å, (1.3 nm). The three dimensional pore structure is large enough to fit a molecule with a diameter of 7.4 Å.

Figure 3.4 :- The Faujasite Framework



The general formula for zeolites X and Y is $\text{Na}_j(\text{AlO}_2)_j(\text{SiO}_2)_{192-j} \cdot z\text{H}_2\text{O}$, where $j = 48-76$ for zeolite Y and $77-96$ for zeolite X and $z \approx 260$ ²⁸. In the protonated form of zeolite-Y there is no sodium and much less aluminium present.

3.1.2 THE COLOUR OF COPPER PHTHALOCYANINE

The most desirable properties of Pcs for pigmentation are their high tinctorial strength and the brilliant colour they possess, along with their stability, which has made them excellent materials as colorants as described in chapter 2.

Such pigments generally have average particle sizes in the range of 0.1-10 μm , (100-10,000 nm). To achieve a size of less than 0.1 μm , mechanical devices are most often used and the most common devices include ball mills, sand/bead mills and roll mills. All these devices require moving parts to generate the mechanical forces required to break up the pigment particles. The large breadth of distribution of particle sizes resulting from mechanical processes and the length of time are great disadvantages. This results in the presence of particles in the μm range which leads to an inherent instability, or tendency to flocculate²⁹.

All Pcs have a characteristic absorption spectrum and they remain the same from solvent to solvent with slight shifts in energy dependent upon the nature of the solvent used³⁰. The low energy band, the Q-band, occurs between 600 nm and 700 nm, with the exact position being slightly dependant upon the metal atom. It is this band which gives rise to the brilliant blue/green colours of the Pcs. This band sometimes has a number of weaker bands associated with it, these are believed to be vibrational overtones³¹. The second band is of higher energy in the 300-400 nm region and is known as the SORET, or B, band. This band tends to be broader and the shoulder on the lower energy edge of the band may be due to $n-\pi$ type transitions from the peripheral azo links³². The bands observed from Pcs are predominantly associated with the $\pi-\pi^*$ transitions in the ring system.

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Eley demonstrated in 1948, as did Vartanyan, that Pcs had an ability to pass a small electric current which varied with temperature in a similar way to that of classical semiconductors³³. However, in molecular crystals of this type the binding energies of the delocalised π electrons are large in comparison to the intermolecular van der Waals binding energies, produced by the overlap of π electron clouds from neighbouring molecules. Consequently the splitting of the molecular energy levels to bands should be rather small, resulting in narrow band states^{34,35}. As a result the applicability of band theory is questionable. Calculations on Pcs suggest that in only one crystallographic direction are the criteria for band conduction satisfied.

If it is possible to alter the colour of the CuPc and allow it to keep its other desirable properties, good colour fastness, good thermal and excellent chemical stability, then the dye industry would have a dye with unbeatable properties with a range of colours.

Since CuPc does have a band structure in the solid state, we were interested in whether the colour of the CuPc's could be altered by controlling the size of the particles to be in the 1-10 nm region. Because the band structure is rather poorly disclosed, we might not expect the dramatic changes in colour observed with e.g. Cd₃P₂, (see above), but shifts in colour towards the red end of the spectrum might be possible if the Q-band could be shifted towards the UV and this may result in a colour change.

3.2.0 RESULTS AND DISCUSSION

Of the many techniques used to control particle size most are not suitable for the capping of CuPc. It is believed that zeolites should be effective for size control of CuPc and were therefore selected to determine if CuPc will undergo any quantum size effects. The preparation of zeolite encapsulated CuPc has been attempted before³⁶⁻⁴⁰, however, only one reference reports any colour change in the pigment³⁸. In this case the Pc has been used as a template and the zeolite synthesised around it. Upon soxhlet extraction of the product a slight colour change from blue to blue-green was observed. This gives us some hope that the colour of the CuPc may change when encapsulated within the zeolite.

A detailed study in the encapsulation of CuPc, with the use of zeolite-X and two forms of zeolite-Y, H, (zeolite-Y), and Na, (zeolite-Y-2), in an attempt to determine if the nature of the zeolite plays a role, has been carried out with unexpected results. Along with the most common method of producing zeolite-CuPc two new methods were devised to try and determine if the CuPc is internal or on the surface of the zeolite.

In encapsulation of materials in a zeolite the most common method of synthesis is the so called ship in a bottle method. During the reaction the counter ion in the zeolite, sodium or protons in the case of zeolite-Y, is 'metal exchanged', in this case with copper (II) ions, by addition of the zeolite to a copper acetate solution. The Cu-zeolite is then reacted with 1,2-dicyanobenzene, (DCB), to form zeolite-CuPc, hopefully within the supercages. Due to the acidity of the zeolite, especially in zeolite-Y, the copper ions are mobile within the framework and can migrate to the surface. It is therefore likely that on reaction with DCB, CuPc will form on the surface and possibly block the windows of the cages preventing any internal CuPc forming. Most of the surface CuPc can be removed by soxhlet extraction with ethanol, acetone, pyridine, and diethyl ether. However it is found that some surface CuPc still remains even after vigorous soxhlet extraction for a number of days. The samples prepared by this method of synthesis are referred to as zeolite-CuPc1.

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The second method, zeolite-CuPc2, of synthesis involves the sublimation of β -CuPc at 600 °C under vacuum and passing it, using nitrogen carrier gas, over the zeolite. The zeolite is placed between two plugs of glass wool at the end of the furnace. It was noted that after cooling the tube it was blue except for the zeolite-CuPc which was green, similar results were obtained on using α -CuPc. In this method of preparation it is expected that the CuPc will be deposited onto the surface of the zeolite and none should be found inside the cages due to size constraints. The CuPc is 13 Å in size and the pores leading into the cages are only 7.4 Å, therefore for any CuPc to enter into the cage it must be either highly distort from planarity on entering through the pore or decompose and then reform inside the cage. Both of these scenarios are highly unlikely to occur, so it can be safely assumed that any CuPc present will be on the surface. Even after vigorous soxhlet extraction, 3 days with acetone followed by 5 days with pyridine, the sample still remained green in colour and from analytical techniques used there still remains a very small amount of surface CuPc.

The third method, zeolite-CuPc3, of synthesis involves the solid state synthesis of CuPc in the presence of a zeolite. In this case there may be some surface CuPc but it is believed that some will form inside the cage of the zeolite. The copper complex, [Cu(7-tBuO-NBD)(hfac)] or [Cu(hfac)₂], DCB and the zeolite are ground together and the mixture heated to 180 °C for 2-4 hours. This reaction is similar to that of the solid state syntheses of CuPc described and carried out in chapter 2.

All three methods were used along with three different zeolites, zeolite-X, zeolite-Y, (protonated form), and zeolite-Y-2, (sodium form) to determine if CuPc is being formed on the surface or in the cages of the zeolite. The different zeolites were selected to see if the environment of the CuPc makes a significant difference to the resultant product, i.e. internal or surface CuPc or a change in colour. All three of the zeolites are isostructural but vary in the ratio of Al:Si which alters the acidity of the zeolite. The presence of sodium may play a role in the encapsulation of CuPc since it is known that small cations such as sodium can influence the behaviour of the internal complex due to its high charge

density⁴¹. If any effect is exhibited this can be investigated by using the protonated form of zeolite-Y.

Once the nine various zeolite-CuPc samples were prepared they were then soxhlet extracted, with methanol, acetone, pyridine, and diethyl ether to remove any surface CuPc and unreacted starting material. A slight change of shade in the material is observed after soxhlet extraction but no significant difference can be detected. In eight out of the nine syntheses carried out the resultant material was green, in the case of zeolite-Y-CuPc1 the resultant material was blue, see figure 3.5. The Initial assumption is that the difference in colour arises due to the presence of surface CuPc giving the blue colour and that in all the other samples the CuPc has been encapsulated. However, this can not be the case since the three zeolite-CuPc2 samples where the zeolite has been sublimed onto the surface and the resultant materials are green. These results mean that the change in colour of the CuPc is not a result of internal CuPc and that the colour change is not likely to be a result of the presence of sodium since all the zeolite-X-CuPc and zeolite-Y-2-CuPc samples are green and two of the zeolite-Y-CuPc samples are green. The colour change is therefore more likely to be from either a distortion from planarity, an interaction with the zeolite or an oxidation of the CuPc as it is reported that metal zeolite complexes show high reactivity towards oxygen⁴¹.

The difficulty with solids encapsulated in zeolites is being able to prove the solid is within the supercage and not attached to the surface, or be able to distinguish between surface and internal sample. To determine whether CuPc has formed within the cages a number of analytical techniques have been used including, elemental analysis, atomic absorption, FTIR, powder X-ray diffraction (PXRD), resonance Raman spectroscopy, thermogravimetric analysis (TGA), looking at the samples through a microscope, transmission electron microscopy (TEM), along with solution and solid state UV-visible spectroscopy.

In the formation of zeolite-CuPc1, the zeolite is stirred with a solution of copper acetate to exchange copper (II) ions into the zeolite structure. Normally the copper exchanges with the sodium and will do so in the cases of zeolite-X and zeolite-Y-2 but in the case of

Figure 3.5 :- The Colour of the Zeolite-CuPc Samples

Zeolite-X-CuPc1



Zeolite-X-CuPc2



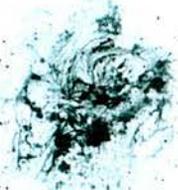
Zeolite-X-CuPc3



Zeolite-Y-CuPc1



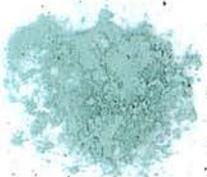
Zeolite-Y-CuPc2



Zeolite-Y-CuPc3



Zeolite-Y-2-CuPc1



Zeolite-Y-2-CuPc2



Zeolite-Y-2-CuPc3



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zeolite-Y there is no sodium to be ion exchanged. In this case it is hoped the copper will exchange with the protons. Atomic absorption analysis for copper were obtained on the three zeolite-Cu samples to determine the amount being exchanged and also the amount of copper present in all the other samples.

The atomic absorption data show that there is 3.13 wt % Cu in zeolite-X-Cu, 4.74 wt % Cu present in zeolite-Y-2-Cu, and 1.57 wt % Cu for zeolite-Y-Cu. This result shows that in all cases copper is exchanging and is present within the zeolite framework. It also shows that the copper ions exchange better with the sodium than with the protons.

The elemental analysis, table 3.1, of the zeolite-CuPc1 series show that it is mainly zeolite present accounting for the low values, however, the values are close to the expected C:N ratios, given in parenthesis and normalised for carbon, for CuPc but show that there is still a small amount of unreacted copper present except in the case of zeolite-Y-CuPc1. The free copper ions may not have been able to react with the DCB due to surface CuPc forming, due to the mobility of the copper ions, and blocking the pores. The amount of hydrogen present in the zeolite-X and zeolite-Y-2 samples is very high which is attributed to zeolitic water, in the case of zeolite-Y-CuPc1 there appears to significantly less zeolitic water.

Table 3.1 :- Percentage C:H:N:Cu for the zeolite-CuPc1 samples

Sample	% Carbon	% Hydrogen	% Nitrogen	% Copper
CuPc	66.72 (32)	2.80 (16)	19.45 (8)	11.03 (1)
Zeolite-X-CuPc1	5.10 (32)	2.04 (152)	1.75 (9.4)	2.99 (3.5)
Zeolite-Y-CuPc1	11.60 (32)	0.57 (19)	3.42 (8)	1.65 (0.86)
Zeolite-Y-2-CuPc1	11.21 (32)	1.74 (59)	3.91 (9.5)	3.70 (2)

The results show that there is significantly less CuPc present in the case of zeolite-Y due to the poor exchange of copper with the protons.

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In some cases there appears to be a small amount of starting material, or possibly solvent from soxhlet extraction, present in the sample. It is unlikely that metal free or any other Pc has formed as there is no further evidence of its existence.

It is unlikely that any colour change occurring is caused by a dilution effect of the CuPc by the zeolite. For this to be the case then zeolite-Y-CuPc1 would also have to be green since it has the least amount of CuPc present but this sample is blue. A colour change by dilution can be disproved by grinding a very small amount of CuPc with the zeolite and no colour change is observed, the material is still blue.

As expected for the zeolite-CuPc2 samples, where the CuPc has been sublimed onto the zeolite, there is significantly less CuPc present, see table 3.2, ratios given in parenthesis and normalised for carbon, as most of the CuPc should have been removed during the soxhlet extraction, however, not all of the CuPc has been removed a small amount still remains. All three of the samples are green in colour but have varying amounts of CuPc present with a trend of increasing wt % CuPc going from zeolite-X, to zeolite-Y-2, to zeolite-Y. In the case of zeolite-X-CuPc2 the amount of CuPc present is very low.

Table 3.2 :- Percentages of C:H:N:Cu for the zeolite-CuPc2 samples

Sample	% Carbon	% Hydrogen	% Nitrogen	% Copper
CuPc	66.72 (32)	2.80 (16)	19.45 (8)	11.03 (1)
Zeolite-X-CuPc2	1.00 (32)	1.87 (715)	0.23 (6)	0.14 (1)
Zeolite-Y-CuPc2	6.21 (32)	0.33 (20)	1.72 (7.6)	1.13 (1.1)
Zeolite-Y-2-CuPc2	3.81 (32)	1.91 (191)	1.16 (8.3)	0.56 (0.9)

Elemental analysis and atomic absorption data suggest that for the zeolite-CuPc3 samples there is still some unreacted copper complex present, despite being soxhlet extracted, see table 3.3, ratios given in parenthesis and normalised for carbon. Zeolite-X-CuPc3 shows considerably more starting copper complex, [Cu(7-t-BuO-NBD)(hfac)], present than for the other two zeolite samples.

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In the zeolite-CuPc1 and zeolite-CuPc3 samples no catalyst is used during their synthesis. Normally when CuPc is synthesised a catalyst is used. A lack of catalyst may therefore explain the presence of some unreacted starting material in these reactions.

Table 3.3 :- Percentages of C:H:N:Cu for the zeolite-CuPc3 samples

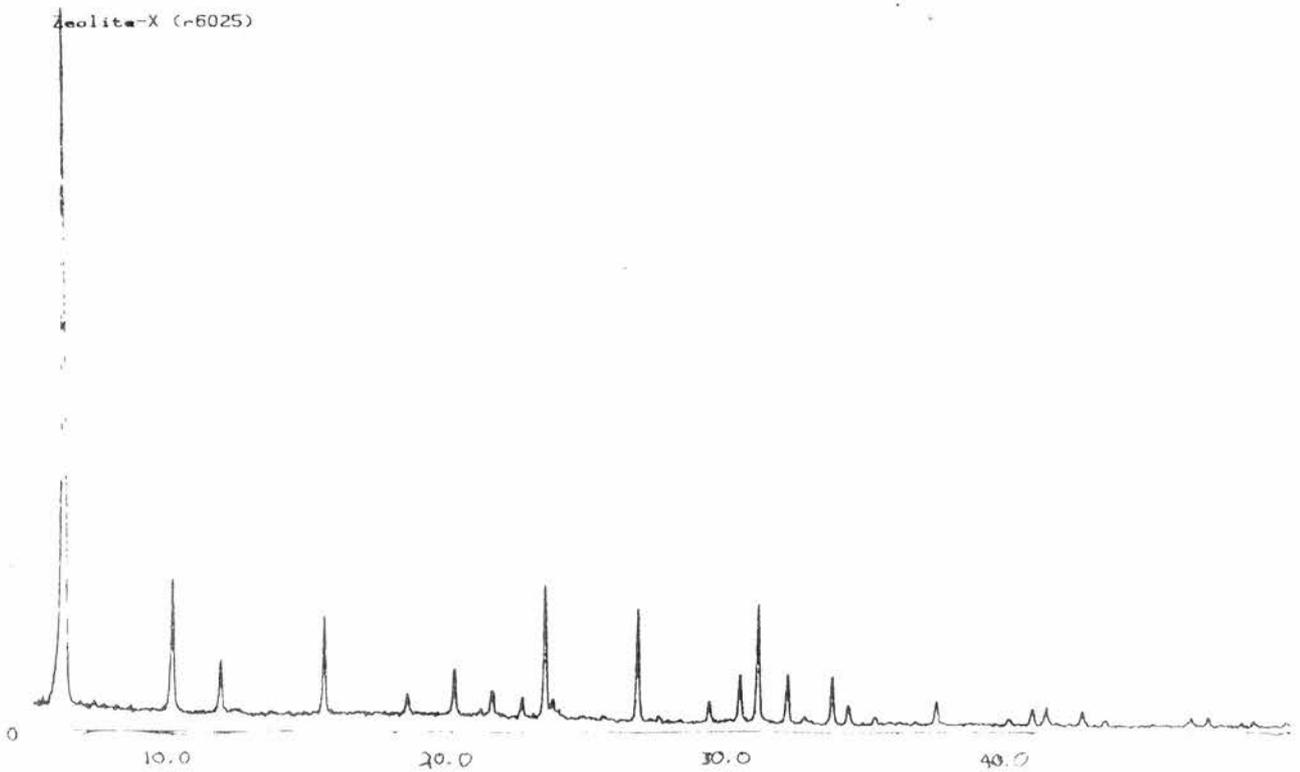
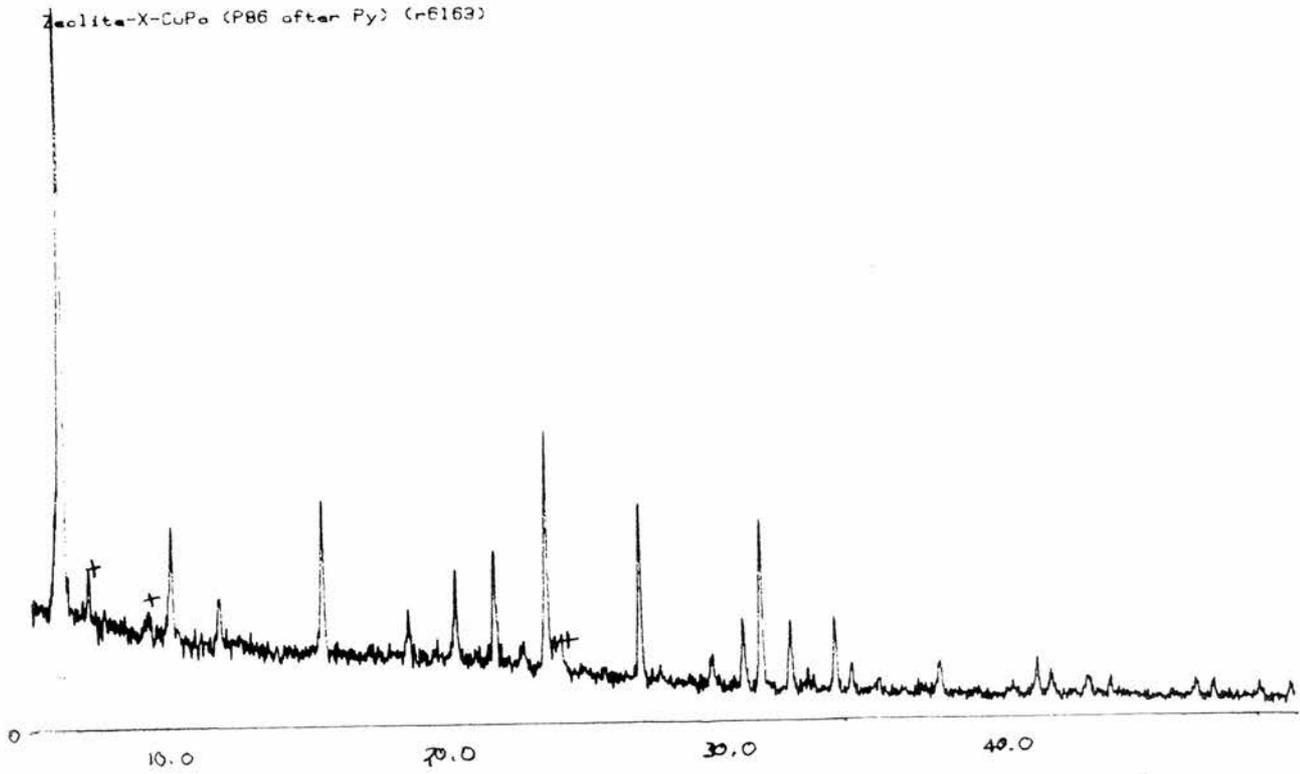
Sample	% Carbon	% Hydrogen	% Nitrogen	% Copper
CuPc	66.72 (32)	2.80 (16)	19.45 (8)	11.03 (1)
Zeolite-X-CuPc3	3.83 (32)	1.47 (146)	1.03 (7.4)	1.43 (2.3)
Zeolite-Y-CuPc3	14.87 (32)	1.09 (28)	3.27 (6)	3.93 (1.6)
Zeolite-Y-2-CuPc3	17.44 (32)	1.75 (33)	4.01 (6.4)	4.36 (1.5)

When the zeolite-CuPc samples, except for zeolite-Y-CuPc1, are crushed onto paper the paper is coloured green suggesting that the colour is genuine and arises from the chromophore and not due to a dilution effect or a refraction or reflection of light. In these cases the colour when crushed onto paper would be expected to alter.

FTIR has been used previously⁴⁰ to determine whether CuPc is present, however, when used for the samples prepared the spectra have very broad bands. It is believed that the zeolite is masking the CuPc vibrational frequencies or possibly restricting them and therefore FTIR is of no use in characterising the zeolite-CuPc samples.

Powder X-ray diffraction, (PXRD), patterns between 5 and 50 two theta were obtained and in all cases show the two most intense peaks of β -CuPc, figure 3.6 shows zeolite-X and zeolite-X-CuPc1, with the CuPc peaks marked. The fact that the bands belong to the β phase suggest that the CuPc is on the surface since any internal CuPc should show considerable line broadening or exhibit no bands at all. The fact that the β phase is present also suggests that small clumps of crystals are forming giving rise to the PXRD pattern. The intensity of the bands is very weak leading us to believe that the amount of surface CuPc is small. It is noted that the zeolite-CuPc2 samples show the weakest intensities in the PXRD, possibly because they have the least amount of sample or

Figure 3.6 :- Powder XRD Patterns Showing Surface CuPc



because the CuPc has formed a thin film around the zeolite and the scattering of the X-rays is less than for the other samples. Even after vigorous soxhlet extraction the peaks still remain suggesting that the solvents used for soxhlet extraction are not removing all the surface CuPc.

The presence of surface CuPc is also shown by TGA experiments. The samples were heated in a nitrogen environment at $10\text{ }^{\circ}\text{C min}^{-1}$ up to $700\text{ }^{\circ}\text{C}$. β -CuPc was also heated under the same regime and a weight loss was observed at around $550\text{ }^{\circ}\text{C}$ which is attributed to the sublimation of CuPc. For the zeolite samples it is thought that any surface CuPc should sublime at this temperature and any internal CuPc should remain inside the zeolite. It is noted that any CuPc near the surface may decompose and cause a slight weight loss at slightly higher temperatures.

The three zeolites X, Y and Y-2 were heated under the same regime to enable assignment of weight loss observations, see figure 3.7. The zeolites show a weight loss up to about $250\text{ }^{\circ}\text{C}$ before levelling off. This is attributed to the loss of water from the zeolite. Zeolite-Y shows a more pronounced weight loss up to $150\text{ }^{\circ}\text{C}$ and tails off before levelling near $250\text{ }^{\circ}\text{C}$. It is noted that there is no significant weight loss in the zeolites after $250\text{ }^{\circ}\text{C}$ enabling easy assignment of any weight loss above this temperature in the zeolite-CuPc samples.

Upon heating the zeolite-CuPc samples to $700\text{ }^{\circ}\text{C}$ the characteristic weight loss up to approximately $250\text{ }^{\circ}\text{C}$, for the zeolite, due to water loss and possibly solvent from the soxhlet extraction is observed.

The TGA of the three zeolite-CuPc1, figure 3.8, samples show that surface CuPc is present, as indicated by the PXRD pattern, with a characteristic weight loss for CuPc around $550\text{ }^{\circ}\text{C}$. Both zeolite-Y-CuPc1 and zeolite-Y-2-CuPc1 show weight loss between $250\text{ }^{\circ}\text{C}$ and $550\text{ }^{\circ}\text{C}$, this may be due to unreacted DCB or solvent being trapped, by surface CuPc, in the zeolite and slowly escaping at elevated temperatures. It is possible that an impurity has formed, it has been suggested that other unidentified nitrogen containing products can form³⁷, and they are decomposing or subliming giving rise to the weight loss. However, other analytical techniques used have not detected such a product.

Figure 3.7 :- TGA of Zeolites, X and Y

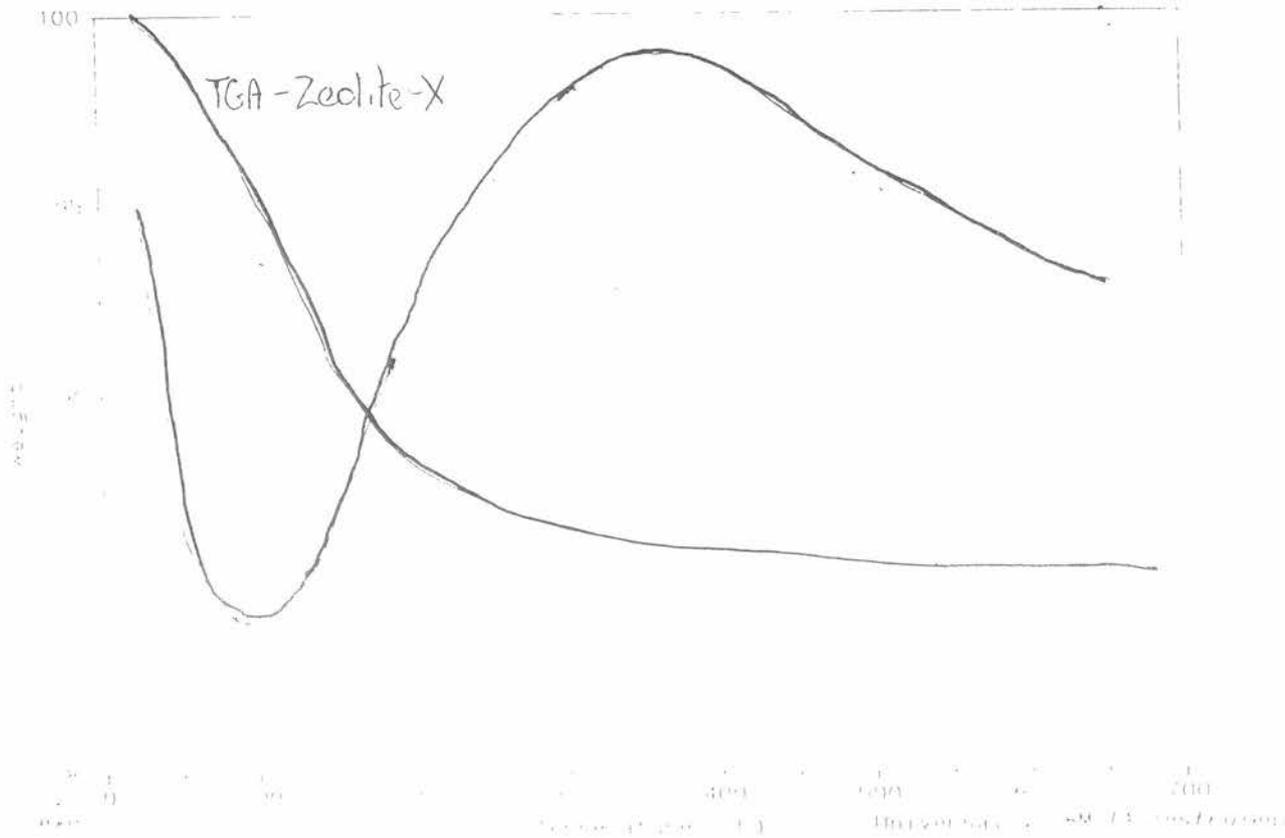
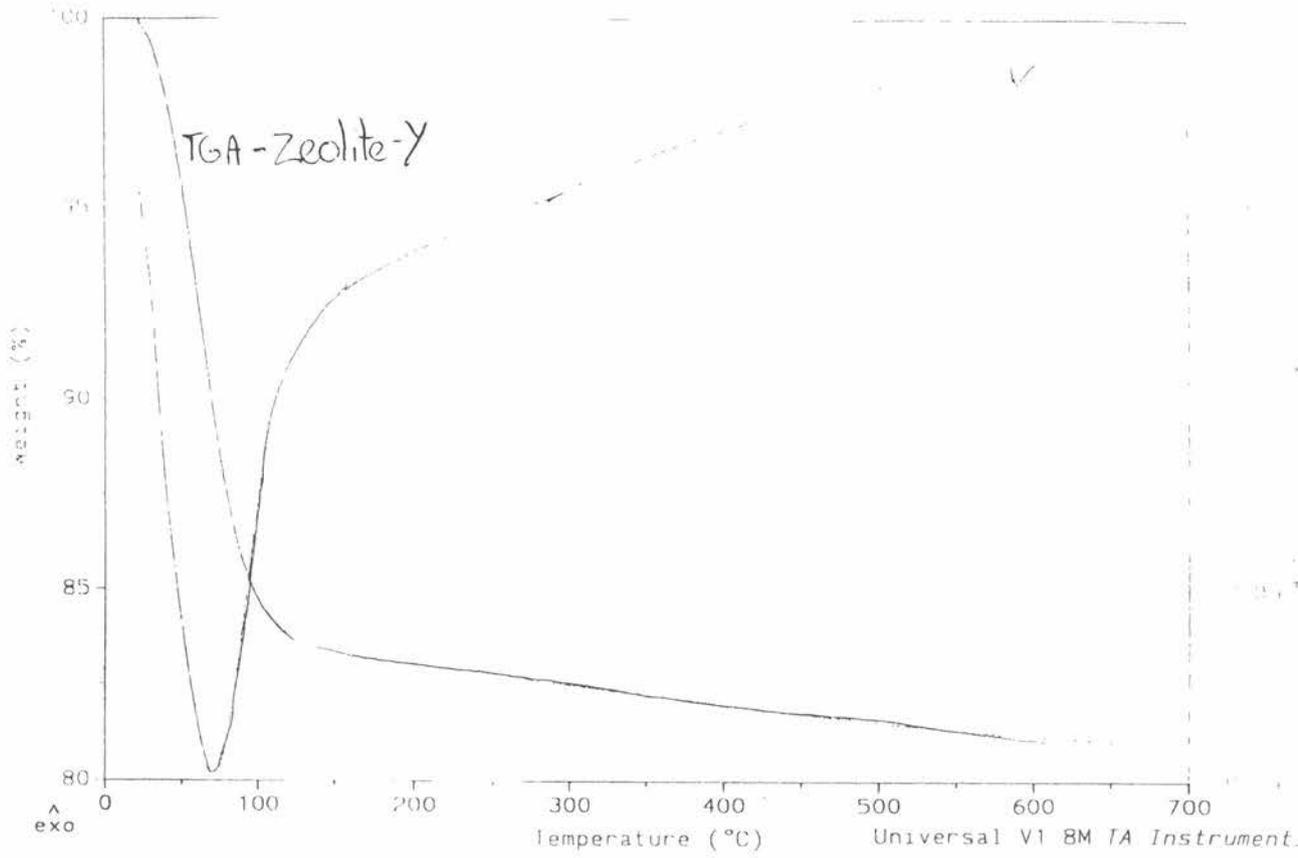
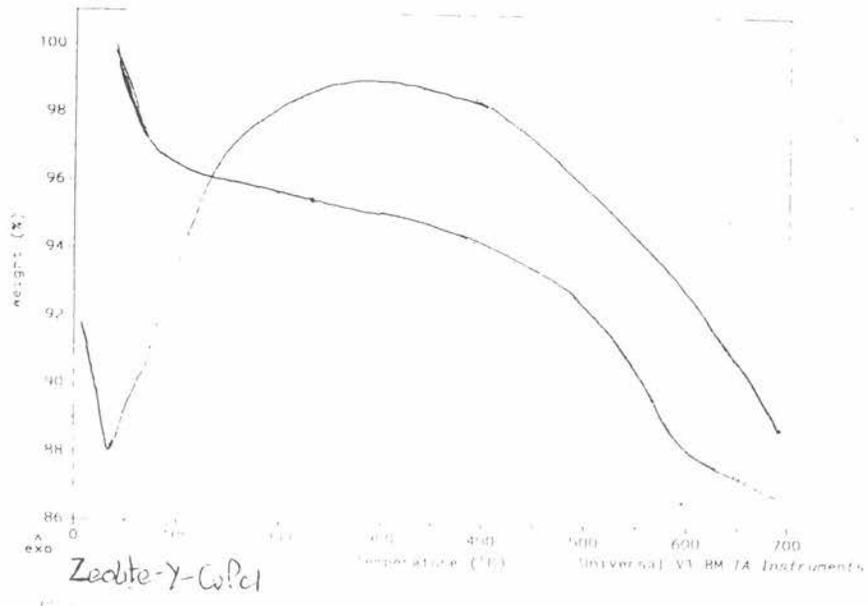
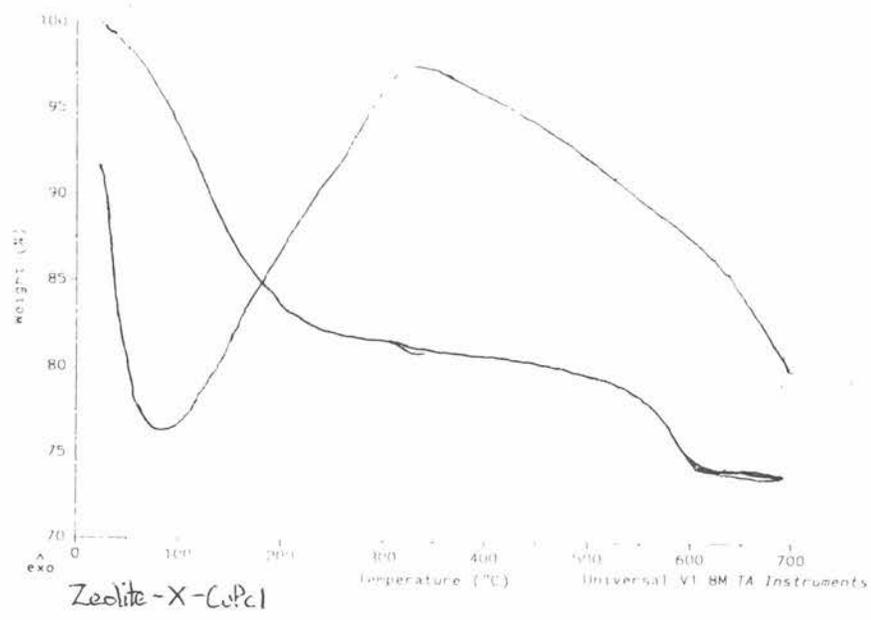


Figure 3.8 :- TGA of Zeolite-CuPc1 Samples



On removal of the zeolite-CuPc1 samples from the TGA a brown solid was obtained except for zeolite-Y-CuPc1 in this case a green solid was obtained. It is thought that the brown solid is formed by oxidation of the CuPc at elevated temperatures. The PXRD pattern of the green zeolite-Y-CuPc recovered from the TGA experiment shows that there is no surface CuPc present. This result suggests that the blue colour of the sample did, as initially thought, arise from a large amount of surface CuPc and the green colour is a result of removing the excess surface CuPc.

From the amount of CuPc lost in the TGA and the amount believed to be present from elemental analysis, see table 3.4, and atomic absorption there is still a small amount of CuPc left within the zeolite in all three zeolite-CuPc1 cases.

Table 3.4 :- Elemental Analysis Versus TGA Weight Loss

Sample	% of CuPc in Sample*	% Weight Lost in TGA [§]
Zeolite-X-CuPc1	8	5
Zeolite-Y-CuPc1	17	7
Zeolite-Y-2-CuPc1	17	13
Zeolite-X-CuPc2	2	1
Zeolite-Y-CuPc2	9	0
Zeolite-Y-2-CuPc2	6	0.5
Zeolite-X-CuPc3	6&	1.5
Zeolite-Y-CuPc3	21&	8.5
Zeolite-Y-2-CuPc3	25&	10

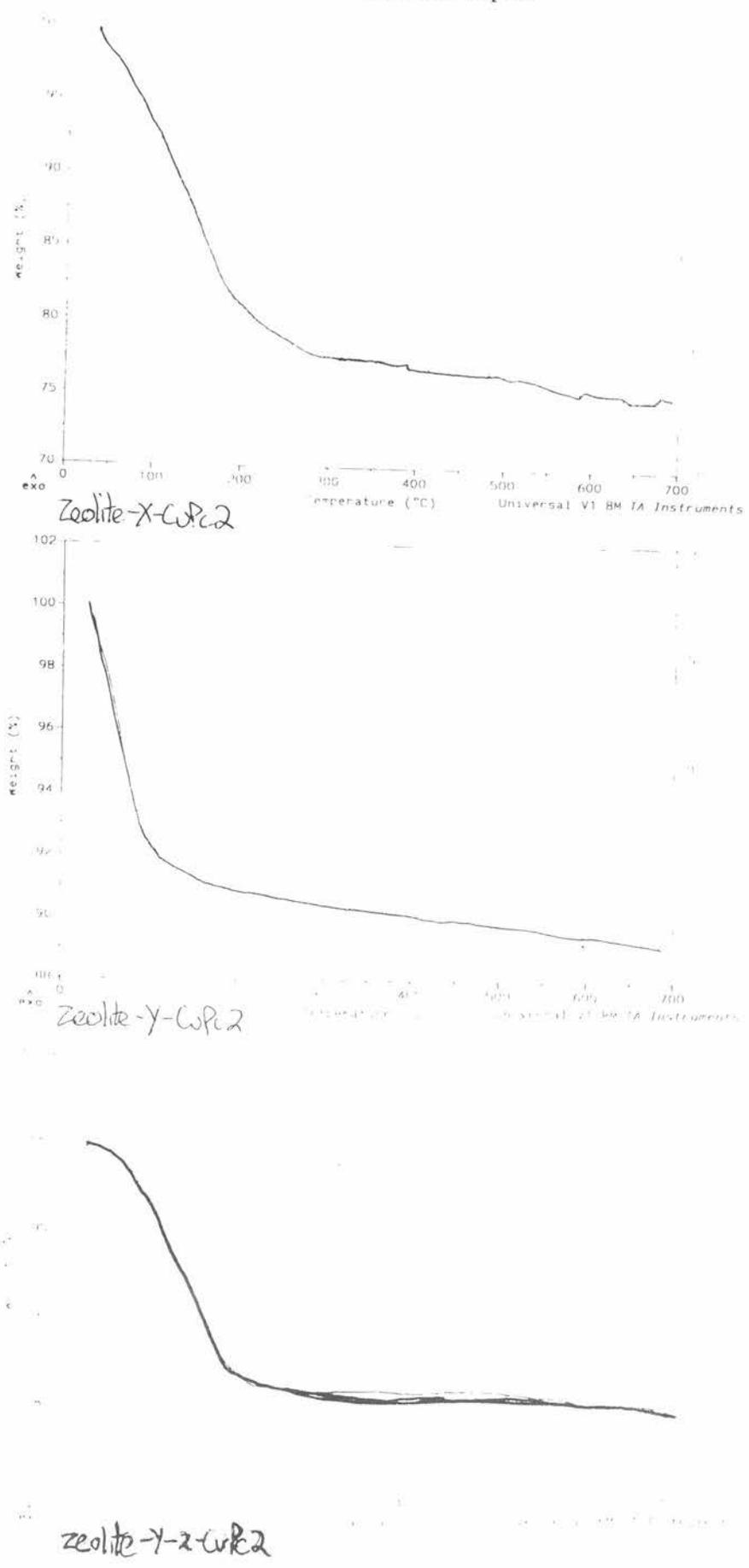
* Weight estimated from elemental analysis and atomic absorption.

§ Estimated weight loss from TGA due to CuPc.

& Values may be slightly higher than the actual amount of CuPc present.

The results obtained from the zeolite-CuPc2 samples, figure 3.9, was unexpected but fits in with the PXRD data obtained. In the three cases there is very little weight loss, (> 2 %), observed between 250 °C and 700 °C where the CuPc would be expected to

Figure 3.9 :- TGA of Zeolite-CuPc2 Samples



sublime. Even though there is only a small amount of CuPc believed to be present it was expected for there to be a higher weight loss than observed. This result would suggest that the CuPc is tightly bound to the surface of the zeolite forming a thin film coating the zeolite. However, on removal of the solids from the TGA the material had turned brown similar to that of the zeolite-CuPc1 samples suggesting that some decomposition of the CuPc is taking place.

The TGA data for the zeolite-CuPc3 samples, figure 3.10, is as expected with a slight weight loss observed near 550 °C for surface CuPc. It is noted that there is a sharper weight loss between 100 °C and 300 °C than expected which is due to the presence of unreacted starting material, [Cu(hfac)₂] or [Cu(7-t-BuONBD)(hfac)], and DCB, as shown by elemental analysis in table 3.4. It would appear that the presence of the unreacted material has little effect on the colour since the zeolite-CuPc3 samples are green as are most of the other zeolite-CuPc samples.

As with the previous samples removed from the TGA the materials turned brown in colour.

With the difficulty of characterising zeolite-CuPc a nickel derivative was synthesised using method number three so that solid state NMR could be used to prove that the MPc was forming. Zeolite-X-NiPc3 was synthesised using the method described earlier producing a dark blue/green coloured material. Despite the colour difference in the copper to nickel samples it is believed that the same reaction will have taken place. Solid state ¹³C NMR data were obtained for zeolite-X-NiPc3 and NiPc, synthesised in the solid state in the absence of zeolite-X, and show, figure 3.11, that NiPc is most likely to have been synthesised. The spectra show a broad band around 130 ppm from which a number of peaks can be detected and attributed to the carbons on the Pc ring. No further information can be gained due to the nature of the material.

Zeolite-X-CuPc1 and zeolite-X-CuPc2 were studied using a transmission electron microscope, (TEM), in the hope of being able to differentiate between internal and external CuPc. The two micrographs are shown in figure 3.12 and it can be clearly seen, by the arrow, that zeolite-X-CuPc1 sample has surface CuPc present. However, no

Figure 3.10 :- TGA of Zeolite-CuPc3 Samples

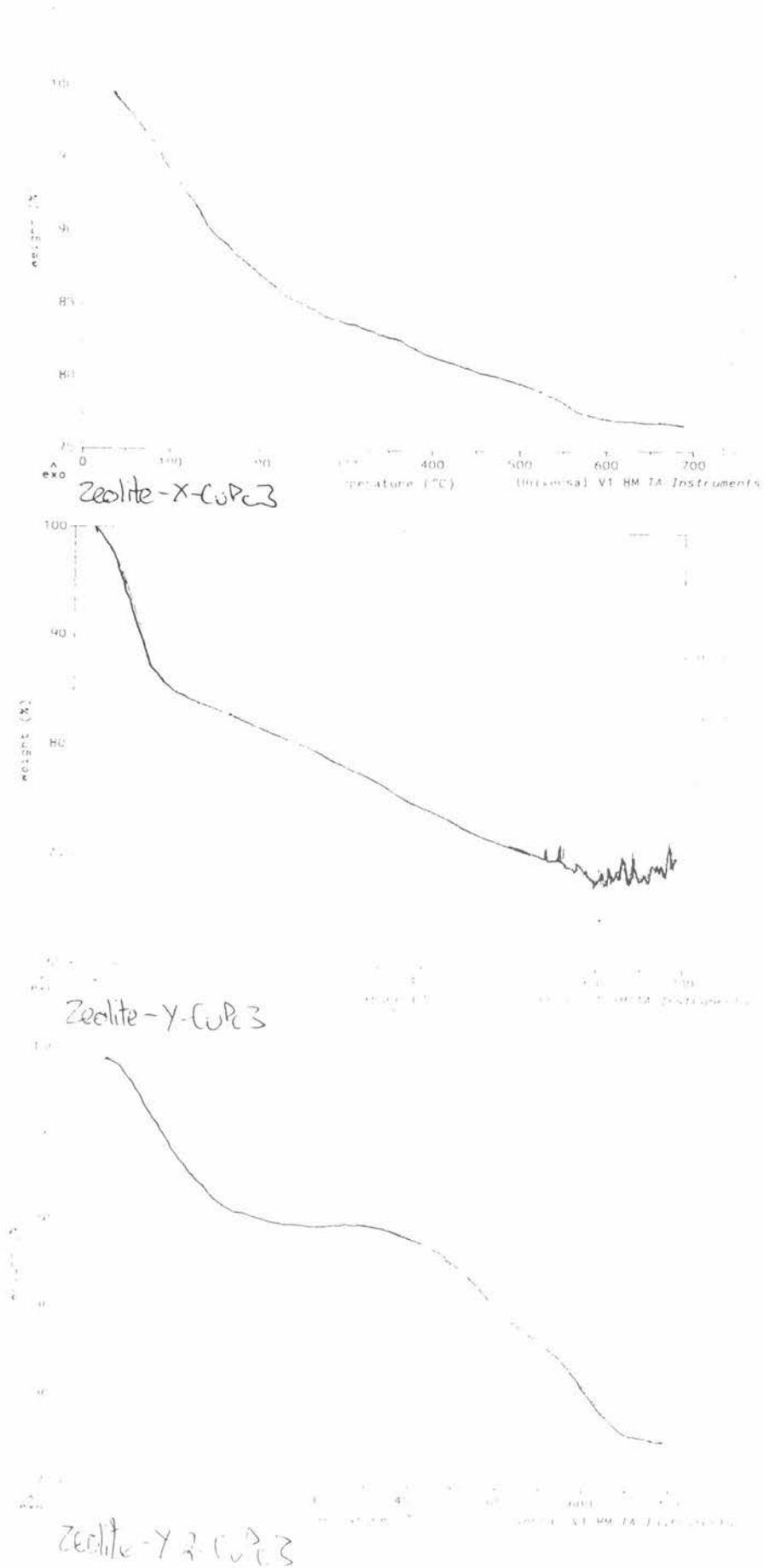
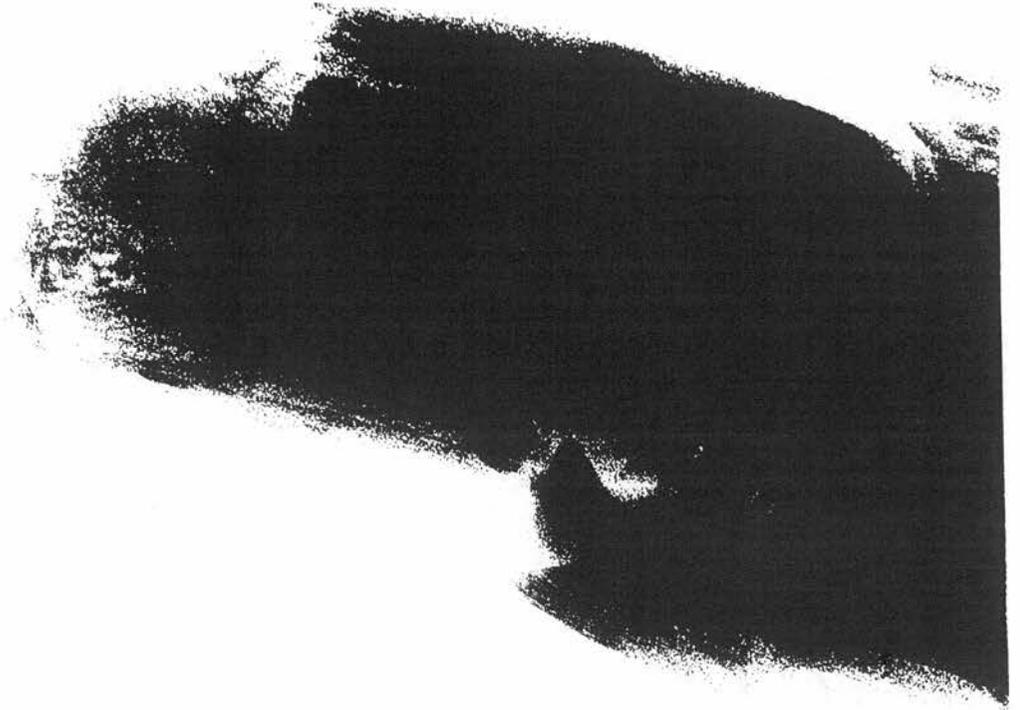
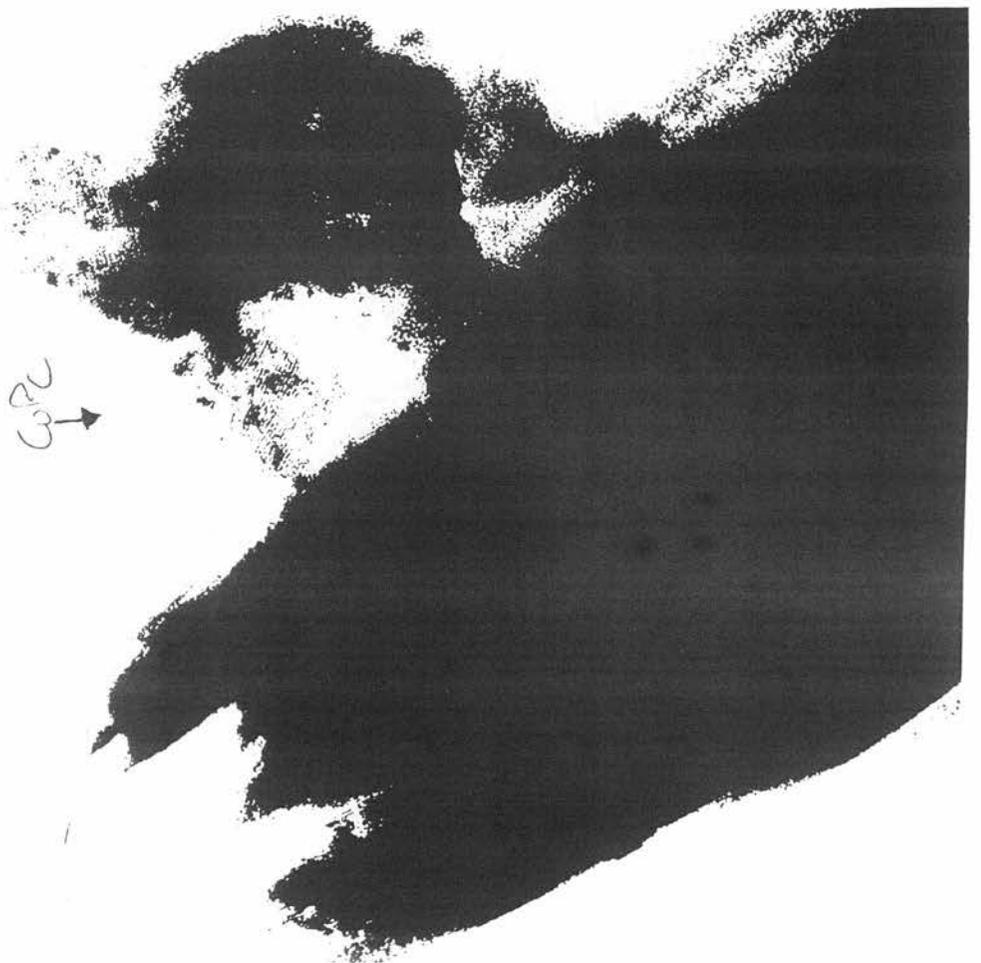


Figure 3.12 :- TEM of Zeolite-X-CuPc1, (A), and Zeolite-X-CuPc2 (B)

B TEM of zeolite-X-CuPc2.



A TEM of zeolite-X-CuPc1.



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surface CuPc could be detected on the zeolite-X-CuPc2. This is possibly due to high dilution of the sample but the result fits with the TGA and PXRD data which point to a lack of surface CuPc. These results are unexpected since the CuPc is being sublimed onto the surface of the zeolite. Unfortunately, due to the nature of the technique, no internal CuPc could be detected. It had been hoped that there may have been a trace of where any internal CuPc may have been but this was not the case.

From the results thus far it appears that the three zeolite-CuPc1 samples have some surface CuPc present, the three zeolite-CuPc3 samples also have surface CuPc present and also a small amount of unreacted starting material and the three samples that it was expected to have surface CuPc, zeolite-CuPc2, appear to have very little. All but one of the samples is green in appearance. Upon looking at the samples under a microscope it was hoped a clearer picture would be obtained on what the samples look like. In these cases only small areas of the sample can be studied at one time and any inhomogeneous material may not be detected using this technique.

Under a microscope zeolite-X-CuPc1 and zeolite-Y-CuPc1 had a similar appearance comprising of a mixture of blue crystals scattered on a white background with the odd green crystal. The crystals appear small but they could be clearly seen. It is not understood why the crystals look blue under the microscope yet the colour of the solid appears green and upon crushing the material a green colour is still observed. Very little coloured material could be detected for zeolite-Y-2-CuPc1 mainly white material was observed. It is possible that in the previous two cases surface CuPc was being looked at and in the case of zeolite-Y-2-CuPc1 the area under study contained very little or no surface CuPc.

Looking at zeolite-Y-CuPc2 under the microscope the material looked nearly all green with no large crystals noticeable and very little white material present. It is thought that in this case a thin film of CuPc has coated the zeolite giving the green colour.

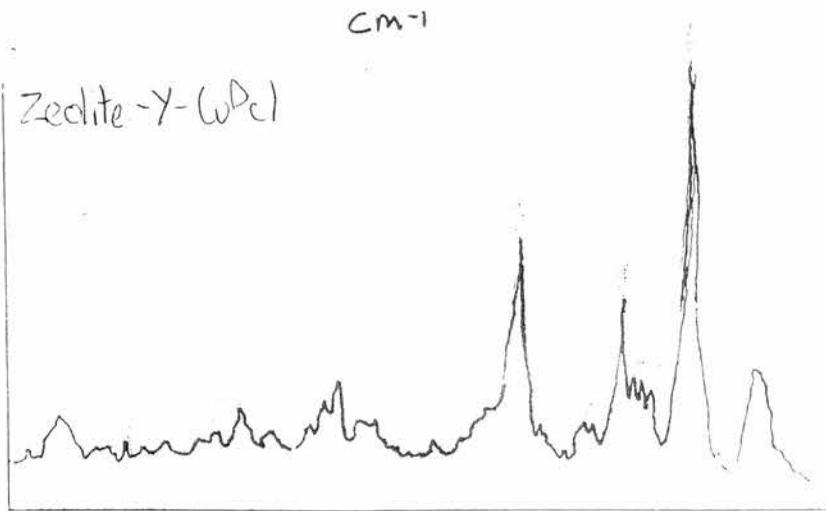
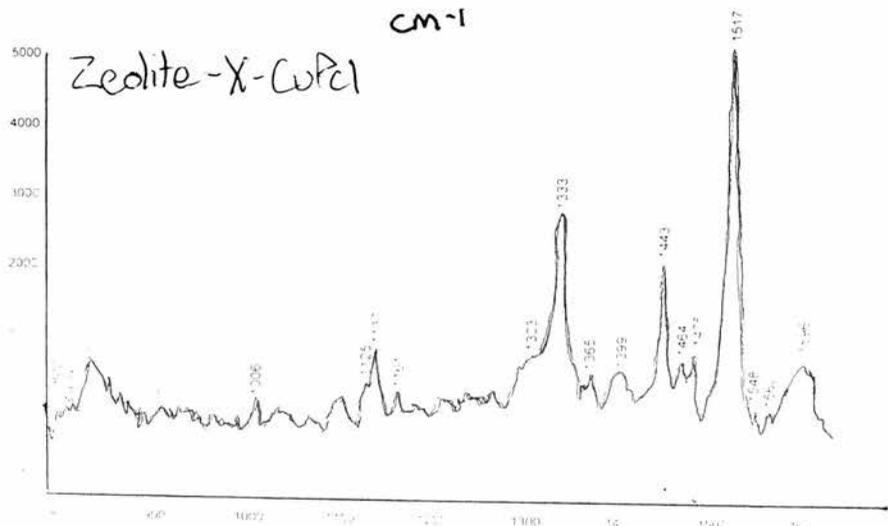
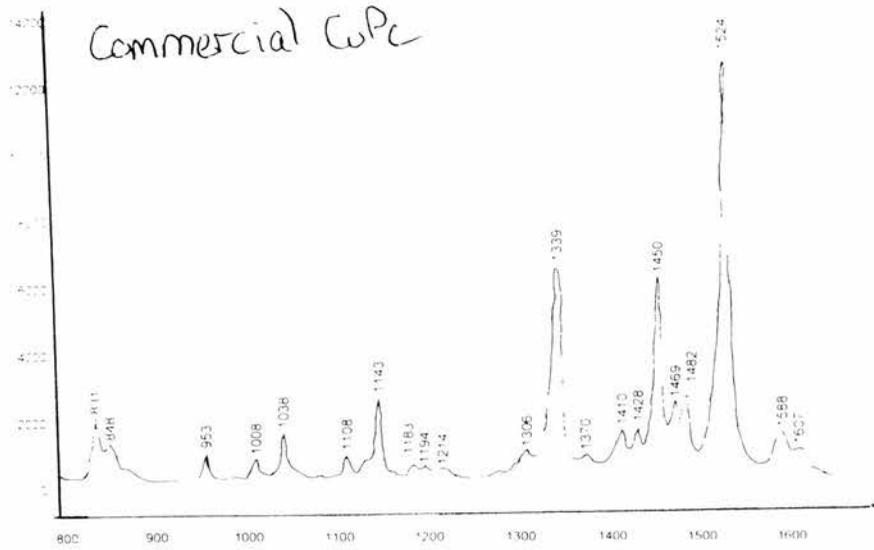
The zeolite-CuPc3 samples were all fairly similar to each other and similar to those of the zeolite-CuPc1 samples. The samples show blue crystals and green crystals are present on a white background.

These results show that the CuPc being formed tends to grow in little clumps and that the zeolite is not such a good host for the control of particle size. In the case of zeolite-Y-CuPc₂ it appears that upon subliming the CuPc it has deposited on the zeolite forming a thin film coating most of the zeolite. Previous reports on thin films have not reported any colour change from the normal brilliant blue of CuPc so it is not thought that the colour is green because of a dilution effect.

Resonance Raman spectra were obtained on the zeolite-CuPc samples to try and obtain further structural data on the CuPc. In Resonance Raman scattering occurs when an electronic absorption band is located near the exciting line of the laser used. In this case a wavelength of 514 nm was used to excite the CuPc molecule as a spectrum is produced when molecular motion produces a change in the polarisability in the molecule⁴². A good advantage of this technique is it allows spectra to be obtained of samples in low concentration, as is the case in the zeolite-CuPc samples. The results will be able to determine whether the CuPc present is structurally intact or otherwise. In a similar way to IR, Resonance Raman gives a fingerprint like spectrum, however, if any impurities are present these will not be detected by the Raman.

The samples produced a spectrum similar to that of pure CuPc, however, there was a problem with fluorescence with most of the samples and in some cases this tended to swamp any signals from the CuPc. The Raman results suggest that in almost all cases CuPc has been formed and that the ring system is not distorted but that there has been an electronic change. Figure 3.13 shows the resonance Raman spectra obtained for the zeolite-CuPc samples compared to pure CuPc. It is noted that the peak at 1588 cm⁻¹ is due to the zeolite matrix. Some of the peaks are slightly shifted from their positions in pure CuPc. This may be experimental error or it may be a real shift caused by a small change in the structure. It is unlikely that any major distortion to the ring has occurred thus ruling out protonation, interaction from the zeolite framework or distortion from planarity causing the resultant colour change.

Figure 3.13 :- Resonance Raman Spectra of the Zeolite-CuPc samples



More detailed Resonance Raman experiments were carried out for the samples zeolite-X-CuPc2 and zeolite-Y-2-CuPc2 enabling photographs of the material to be taken, figure 3.14 and figure 3.15 respectively. The zeolite-X-CuPc2, figure 3.14, shows inhomogeneity throughout the sample with blue crystals easily seen. The areas circled in the picture are where the resonance Raman spectra, figure 3.16, and 3.17, have been taken from. Figure 3.16, spectrum 440, clearly shows that there is no CuPc in this part of the sample but a high level of fluorescence is observed. Figure 3.17, spectrum 445, shows the expected Raman spectrum for CuPc.

Figure 3.15 shows that there are no blue crystals but from the photograph there is a blue tinge to the material, despite the material being green in colour. The resonance Raman spectrum 57, figure 3.18, shows no CuPc but fluorescence is again observed.

These results suggest that it is likely that the zeolite, or possibly an impurity, is causing the fluorescence and in the cases where no CuPc is picked up this may be due to a lack of CuPc throughout the sample. If the CuPc is forming a thin coating around the zeolite then this might not be picked up and it may be this that gives rise to the green colour.

Suspension UV-visible spectra were obtained in 1-chloronaphthalene. All the zeolite-CuPc samples exhibit the characteristic spectra for CuPc with a Q-band maximum between 677 nm and 679 nm thus proving that CuPc is present. It is possible that the spectra arise from surface CuPc and that any internal CuPc is being masked by the zeolite thus explaining the difference in colour of the samples and the spectra being similar to that of pure CuPc.

The resonance Raman spectra suggested that there may be electronic changes in the zeolite-CuPc samples from that of CuPc which is likely since the colour of the samples is green. Solution UV-visible spectroscopy did not pick up any changes but it is possible that solid state spectra may since the samples are green solids. CuPc is also believed to have an extended band structure which occurs in the solid and this is of interest in the encapsulation of the CuPc particles within the zeolite cages.

Figure 3.14 :- Photograph of Zeolite-X-CuPc2

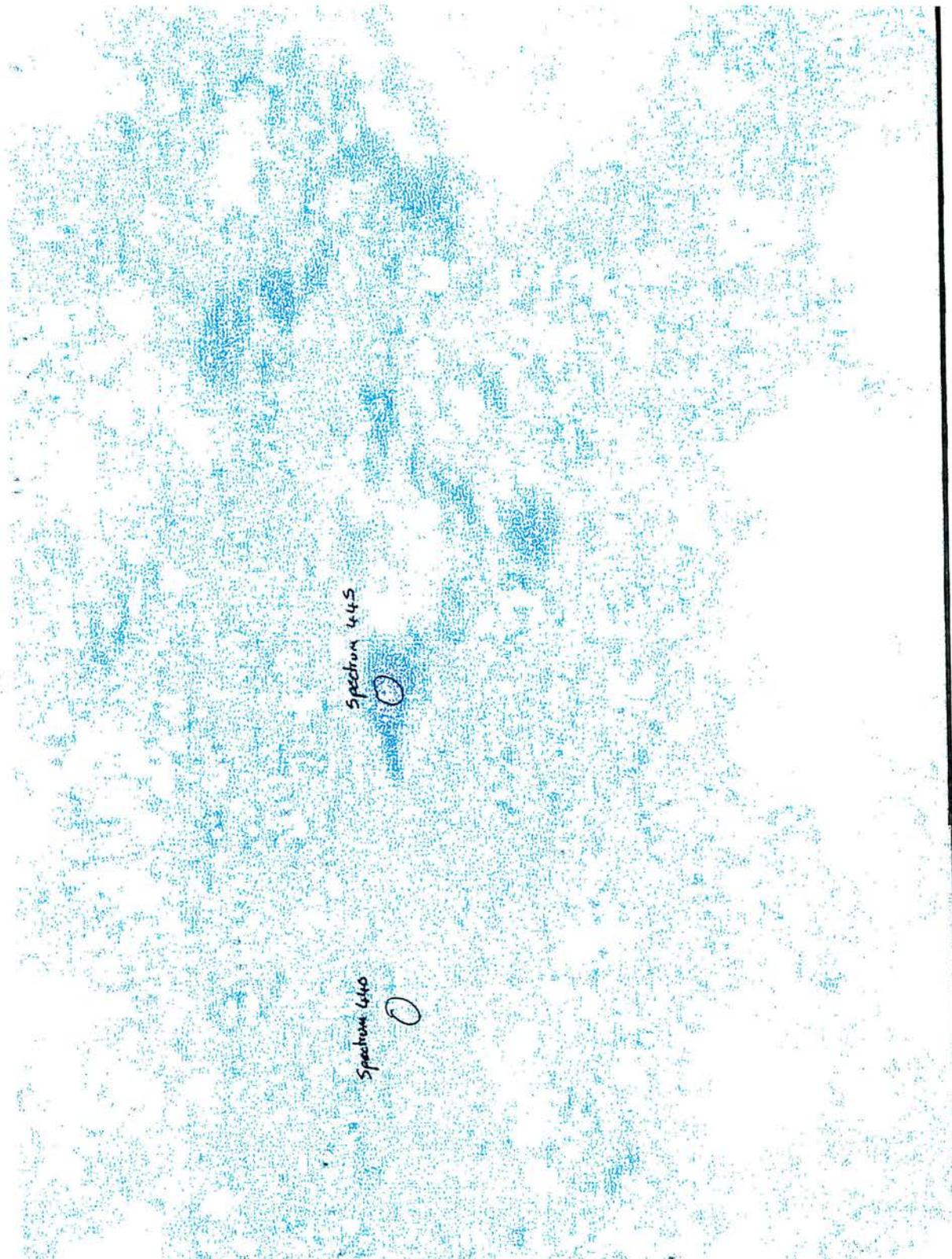


Figure 3.15 :- Photograph of Zeolite-Y-2-CuPc2

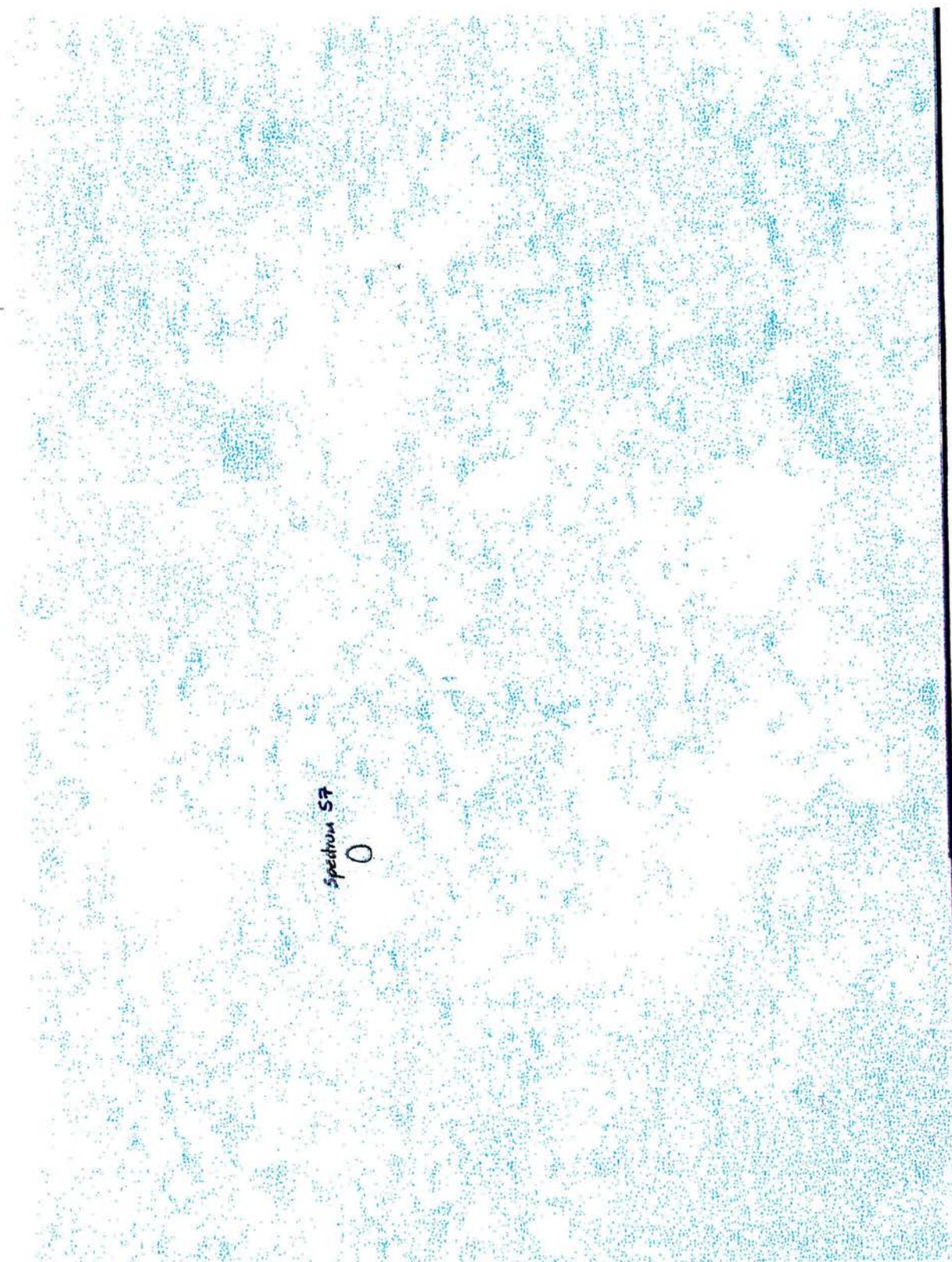


Figure 3.16 :- Resonance Raman Spectrum 440 from Zeolite-X-CuPc

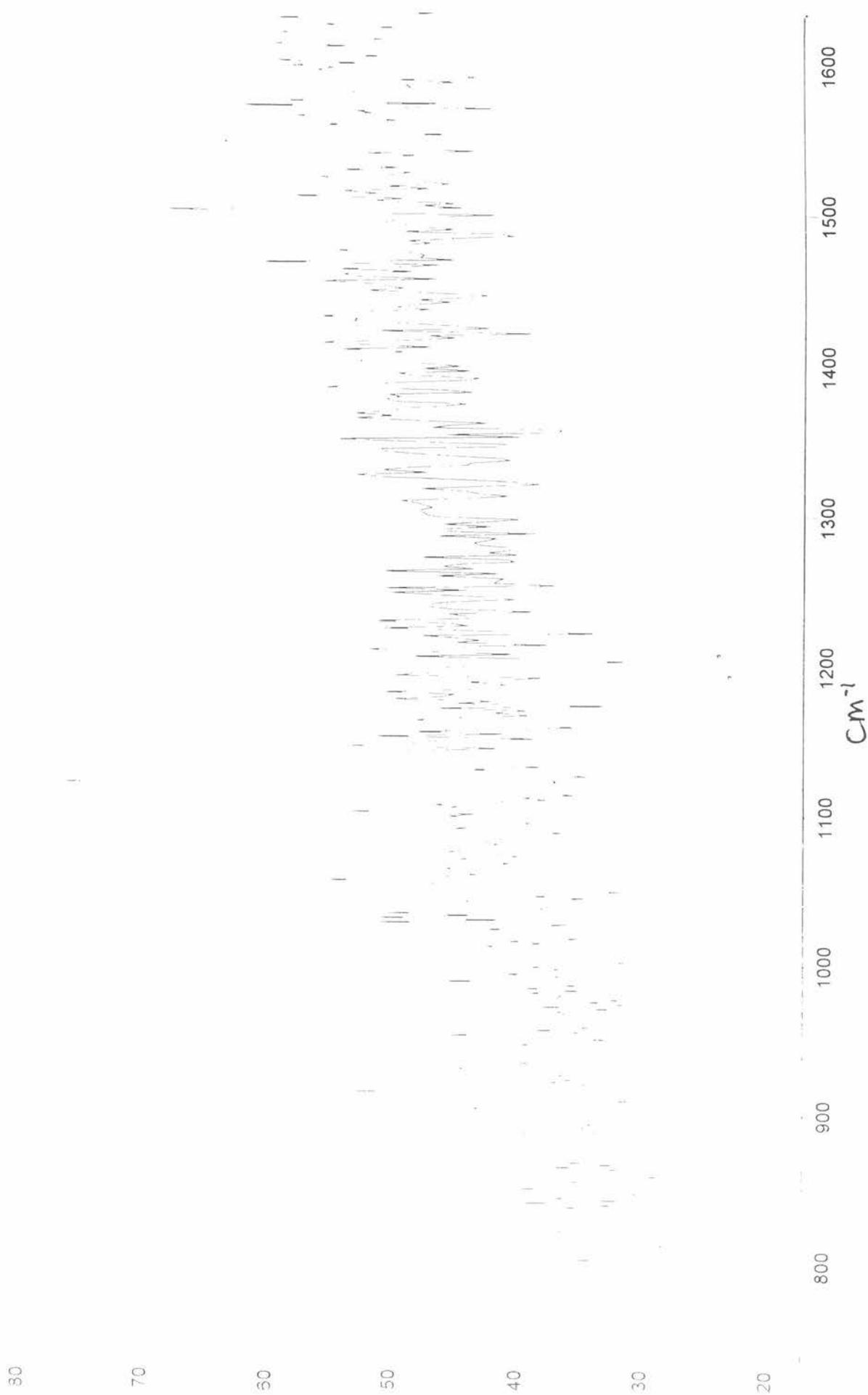


Figure 3.17 :- Resonance Raman Spectrum 445 from Zeolite-X-CuPc

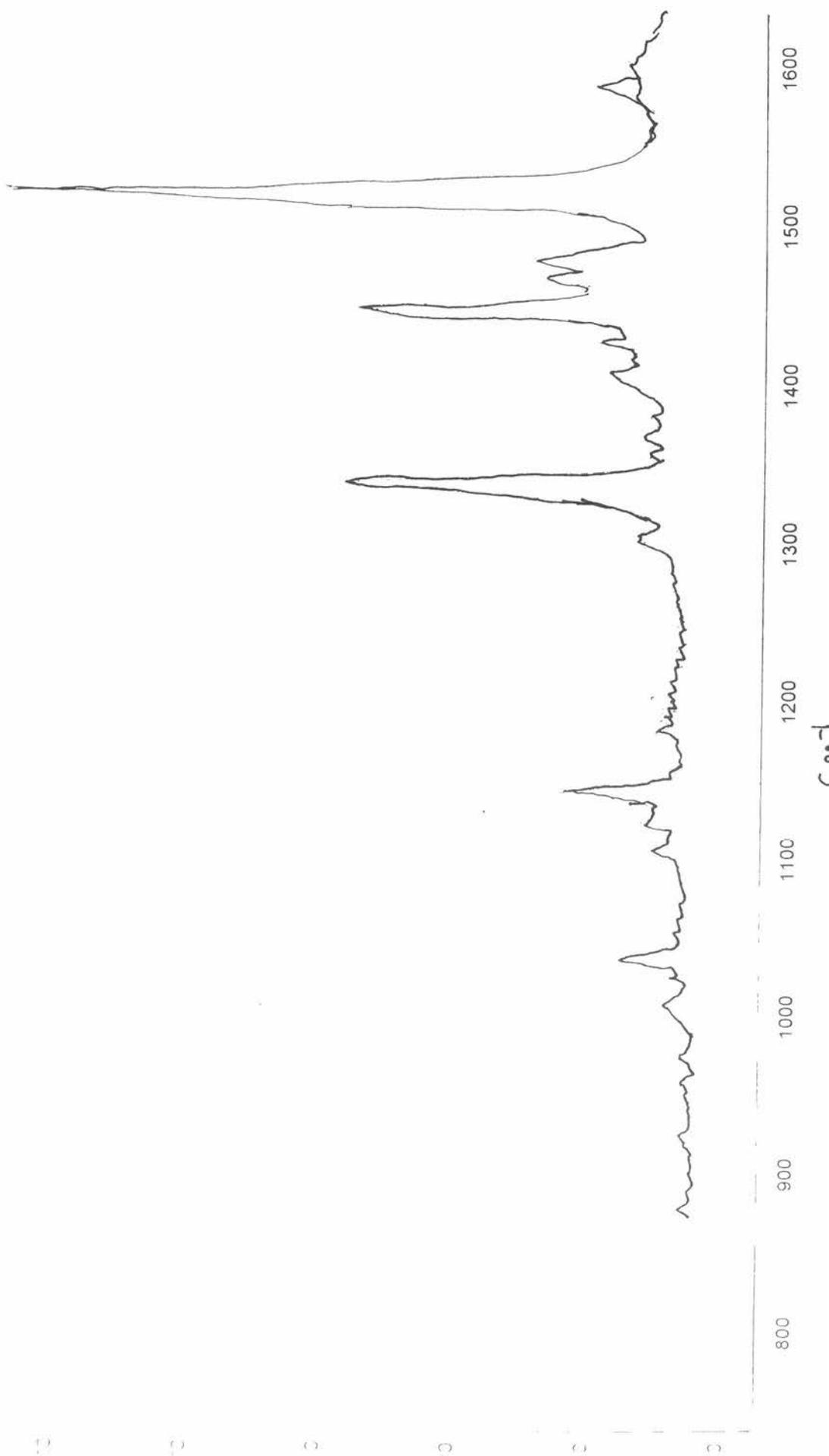
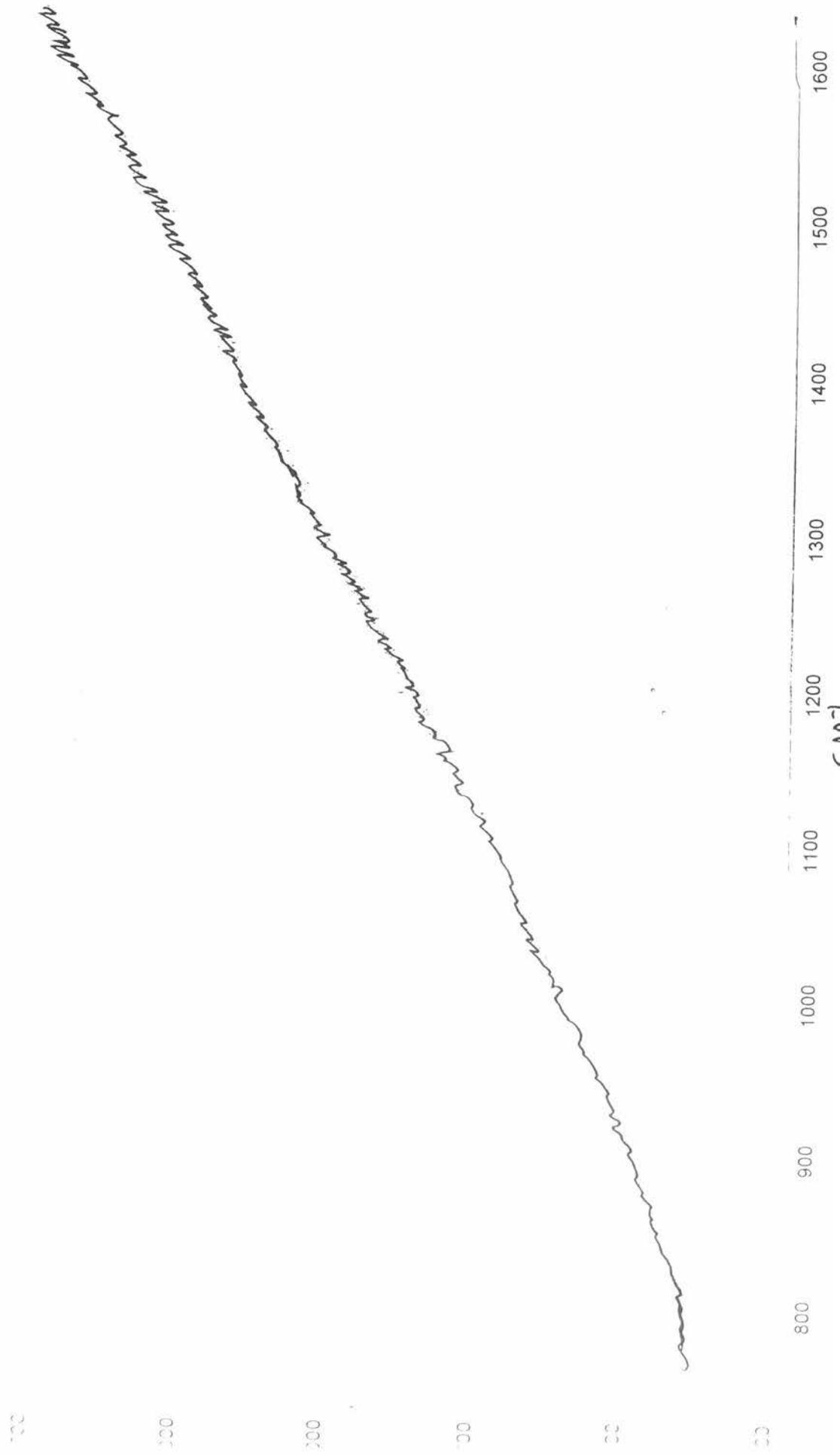


Figure 3.18 :- Resonance Raman Spectrum 57 from Zeolite-Y-2-CuPc



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The solid state spectra were obtained for the nine zeolite-CuPc samples and compared with those of α -CuPc and β -CuPc. The α and β modifications of CuPc differ in their particle size and crystal structure which may have an effect on the solid state UV-visible spectrum.

The solid state UV-visible spectra are obtained by grinding the sample, zeolite-CuPc or α or β -CuPc, and adding a small amount of nujol making a paste which is then spread evenly onto a piece of filter paper. The reference cell is filled with a piece of filter paper covered in nujol and in the case of the zeolite-CuPc samples the nujol is mixed with the relevant zeolite, X, Y or Y-2. The samples were run between 350 nm and 900 nm.

As with the solution spectrum there is a B band between 300 and 400 nm, however, there are two absorptions, or a double absorption, between 550 nm and 700 nm. These two absorptions are a result of the splitting of the Q-band energy possibly due to Jahn-Teller effects and relating to a loss of symmetry in the individual molecules. A splitting of the Q-band energy has been reported for aluminium sulphonated phthalocyanine⁴³, in this case the splitting is due to a loss of D_{4h} symmetry due to coordination of water molecules to the aluminium and the nitrogens of the Pc ring. Therefore it is likely that the cause of the double absorption is from a loss in symmetry caused by interactions between molecules of CuPc in the crystal structure.

It is generally believed that the Q-band transition arises from $a_{1u} \rightarrow e_g$ transition^{31,32,44} and the e_g is doubly degenerate thus giving rise to the possibility of two Q bands existing. The energy splitting between the two bands gives an indication of the deviation from D_{4h} symmetry⁴⁵, the smaller the difference the less the splitting and the Q band will become nearer a single absorption.

The two bands present between 550 nm and 750 nm for CuPc are blue shifted in energy for the α modification but the splitting between the bands remains the same around 112 nm to 114 nm. The blue shift in energy of the bands, see table 3.5, from the β phase to the α phase can be a result of the different crystal structures however it is possible that it is a result of a size effect. Since the α phase is reported⁴⁶ to have a smaller average particle size than the β phase therefore a small blue shift in energy may be expected for

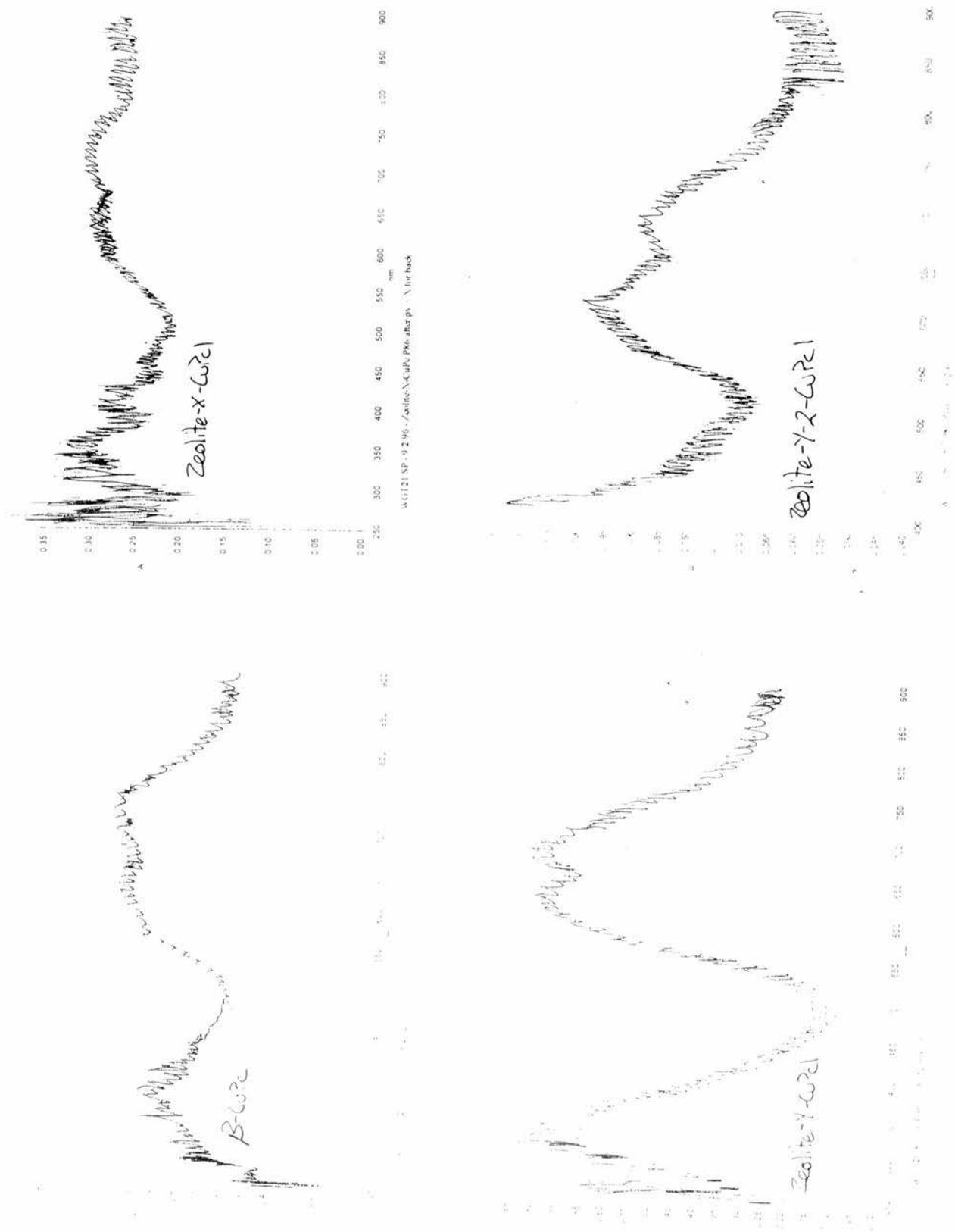
the α phase similar to quantum confinement effects. The visual difference in colour is hardly noticeable to the naked eye but they are recognised as being slightly different shades and they are used as separate pigments in industry. The β phase is slightly more green and the α slightly more red from pure blue and this is shown by the position of the Q-band maxima. In the case of the splitting of the Q-band the value of the splitting between the bands can differ depending upon the deviation from D_{4h} symmetry⁴³. The splitting gap for both α and the β phase is the same suggesting an equal loss of symmetry is occurring for both phases and that the copper is coordinated in a similar manner for both phases. In both the α and β phase of CuPc the copper ions are coordinated axially to the azo nitrogens of the next ring above and below, see chapter 2, creating a similar distortion from D_{4h} symmetry.

Table 3.5 lists the band absorptions and the splitting between them for all the zeolite-CuPc samples and compared with α and β -CuPc and figure 3.19 shows some of the spectra.

Table 3.5 :- The Bands, Splitting Gap and the Colour of the Zeolite-CuPc Samples

Sample	Blue Band (nm)	Red band (nm)	Splitting (nm)	Visual Colour
α -CuPc	627	741	114	Dark Blue
β -CuPc	636	748	112	Dark Blue
Zeolite-X-CuPc1	657	736	79	Green
Zeolite-Y-CuPc1	636	695	59	Blue
Zeolite-Y-2-CuPc1	621	699	78	Bottle Green
Zeolite-X-CuPc2	-----	730	-----	Green
Zeolite-Y-CuPc2	-----	747	-----	Bottle Green
Zeolite-Y-2-CuPc2	-----	742	-----	Bottle Green
Zeolite-X-CuPc3	655	748	93	Green
Zeolite-Y-CuPc3	629	705	76	Bottle Green
Zeolite-Y-2-CuPc3	629	724	95	Bottle Green

Figure 3.19 :- Solid State UV-visible Spectra of Zeolite-CuPc



The most striking result is that the zeolite-CuPc2 samples, in which CuPc has been sublimed onto the surface of the zeolite, produce UV-visible spectra with only one Q-band maximum. The other two methods of synthesis, zeolite-CuPc1 from ion exchanged zeolite and zeolite-CuPc3 from the solid state reaction, both produced spectra similar to that of α or β -CuPc showing a double absorption between 550 nm and 700 nm although the splitting is less than for α or β -CuPc.

At first glance, it would appear that the bands in the zeolite-CuPc1 and zeolite-CuPc3 spectra have been blue shifted, as would be expected from the colour change in the samples, however, this is only the case for the red band. In the case of the zeolite-CuPc2 samples the Q-band has been blue shifted in comparison to the red band and red shifted in comparison to the blue band. This suggests that the Q-bands have come together and thus the splitting gap is zero as would be expected in the case of D_{4h} symmetry. For this to happen the CuPc present must be aligned in a stack through the copper atoms or they must form a thin film of one or two CuPc molecules thick coating the zeolite surface thus explaining the TGA, PXRD data and also the TEM of zeolite-X-CuPc2.

From the splitting gaps it appears that the presence of sodium plays a role. Both zeolite-X and zeolite-Y-2 have similar splitting gaps whereas for zeolite-Y the gap is 20 nm less for both zeolite-CuPc1 and CuPc3. It is believed that since sodium is a bigger cation than a proton it causes the gap to increase. In the case of the zeolite-CuPc3 samples it is thought that the presence of copper starting material results in a further deviation from ideal symmetry causing a further increase in the splitting gap.

For both the zeolite-CuPc1 and zeolite-CuPc3 samples the energy between the bands has decreased significantly. The decrease in the splitting is likely to be caused by the formation of a more molecular species of CuPc. If D_{4h} symmetry is exhibited then there should be no splitting of the Q-band and a single absorption observed as is the case for CuPc in solution. In the bulk each CuPc has a number of other molecules surrounding it and therefore each molecule can not exhibit D_{4h} symmetry. When a more molecular species is formed there is less interaction from other CuPc molecules and therefore the

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symmetry shown becomes more closely related to D_{4h} and the deviation is a result of counter ions or unreacted starting material present.

The formation of metal free Pc or sodium Pc have been ruled out since when DCB is reacted with the sodium zeolite no reaction takes place. A white solid is obtained and the DCB can be washed out. No evidence from the solution UV-visible suggests that any other Pc is present in the mixture. It is thought that in the presence of copper the DCB will preferentially react with it to form CuPc which is the more stable of the Pcs.

It has been suggested that small cations such as sodium can influence the behaviour of the guest within the zeolite due to their charge density⁴¹ this may explain the difference in shades of green between the samples but it doesn't explain why the samples are green. The presence of sodium is believed to explain the difference in the splitting gap. Zeolite-Y-2-CuPc1 and zeolite-X-CuPc1 have the same splitting gap at approximately 80 nm and the zeolite-Y-CuPc1 has a gap of approximately 60 nm. This difference is attributed to the presence of sodium in the cages with the CuPc causing a larger distortion in the symmetry.

In the solid state UV-visible spectra of the zeolite-CuPc2 samples only a single absorption is observed with the band being blue shifted from β -CuPc. The single absorption suggests that there is no or little loss of D_{4h} symmetry. From elemental analysis and atomic absorption for copper the zeolite-CuPc2 samples have significantly less CuPc present than for the other methods of synthesis. This can arise from either less CuPc being sublimed onto the zeolite than is synthesised by the other two methods and or a combination of washing the surface CuPc off by soxhlet extraction. It is thought that in these cases the CuPc forms a thin coating of one or two molecules thick around the zeolite, as indicated by visual examination under a microscope, and therefore little or no loss of symmetry occurs giving a UV spectrum with only a single absorption between 500 nm and 700 nm. If there is only a thin film two or three molecules thick the PXRD pattern would have very broad or no peaks observed for the CuPc, as is the case.

When CuPc was used as a template for the formation of zeolite-X a blue material is reported and upon soxhlet extraction of this material for a number of days using pyridine

a slight colour change is observed with the material becoming blue/green in colour³⁸. Therefore α -CuPc and β -CuPc were used in a template synthesis of zeolite-X in this case the CuPc should fit perfectly within a cage as the zeolite forms around it. Both the samples produced are blue in colour but are of different shades with the α -CuPc-Zeolite-X being the more pale of the two. From the atomic absorption data there is very little copper present and it is unlikely that in these cases CuPc is present. The experiments were repeated several times with the same results suggesting that the conditions used are too harsh.

Another method used in controlling particle size is that of refluxing the material in 4-ethylpyridine in a nitrogen environment²¹. A solution of α -CuPc in 4-ethylpyridine (10 mM) was refluxed (170 °C), under nitrogen. The α phase was chosen over the β phase of CuPc because, on attempting the reaction with the β phase, very little happened and very little of the solid dissolved in the solvent. The α phase has smaller particles and appeared to dissolve better although it is more likely that it has formed a suspension. Solution UV-visible spectra were taken before reflux and then every hour of reflux for 6 hours. All the spectra have a band between 669 nm and 676 nm which is believed to be due to the CuPc and there are two other bands to the higher energy side of this band which are attributed to the overtone bands. There is also a broad band between 732 nm and 740 nm which is believed to be from an interaction between the 4-ethylpyridine and the CuPc, the intensity of these bands changes with the amount of time the CuPc has been refluxed. Table 3.6 shows the absorption energies for the bands, it is not known what causes the low energy, red, band, the intensities of the bands are mentioned in parenthesis.

Before reflux as would be expected the CuPc band is strong and the broad band at 740 nm has low intensity. As the solution is refluxed the intensity of the CuPc band decreases and the intensity of the broad band at 740 nm increases. Figure 3.20 shows the UV-visible spectra after 0, 3 and 6 hours of reflux.

Table 3.6 :- α -CuPc Refluxed in 4-Ethylpyridine

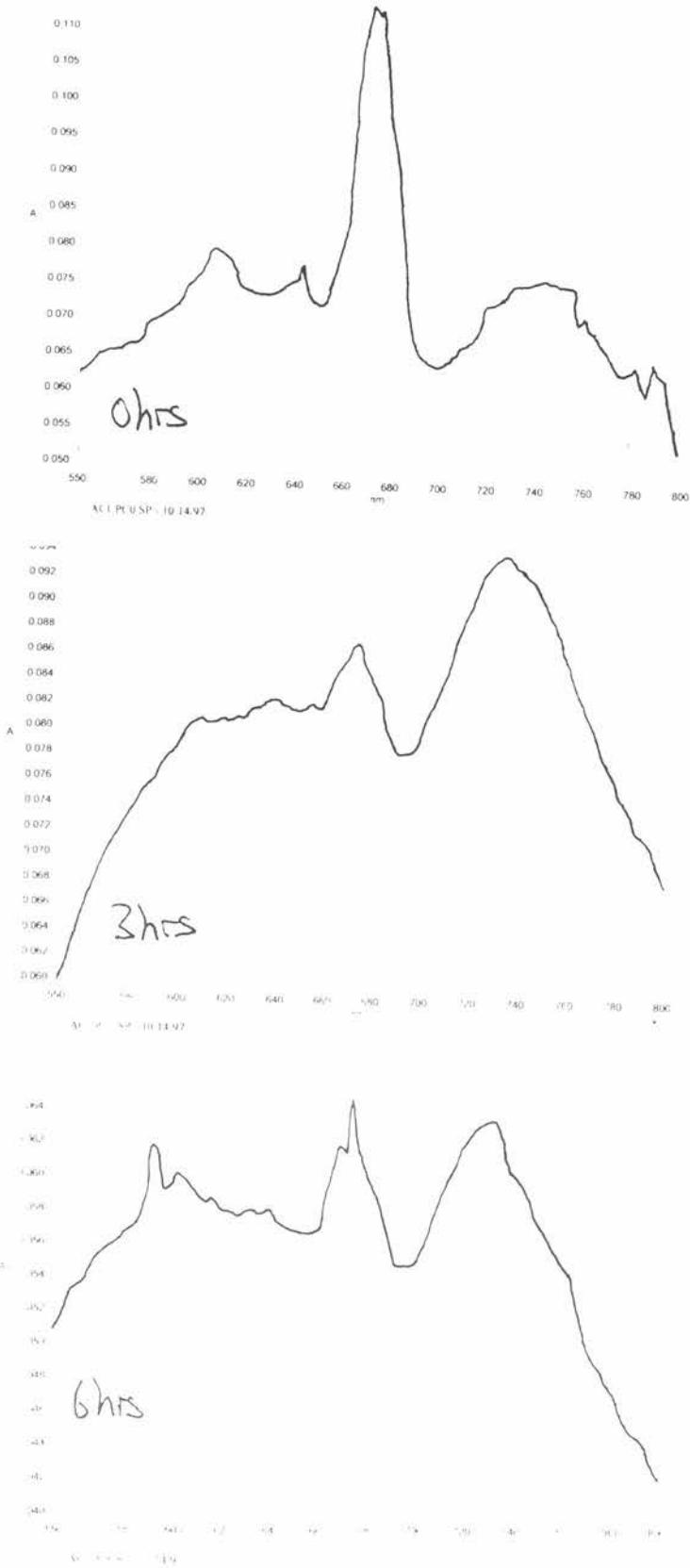
Time (h)	CuPc (nm)	Red Band (nm)
0	669 (Strong)	740 (Low)
1	675 (V.Low)	736 (Strong)
2	675 (V.Low)	734 (Strong)
3	672 (Low)	732 (Strong)
4	676 (Medium)	735 (Med-Strong)
5	675 (Medium)	732 (Medium)
6	674 (Medium)	732 (Medium)

From the intensity it is believed that the red band is due to a CuPc ethylpyridine type complex or interaction. After the first hour of reflux it appears that the 4-ethylpyridine band has reached a maximum in intensity in comparison to the CuPc band. After 4 hours of reflux the intensity of the CuPc starts to increase again and the broad band at 740 nm decreases in intensity suggesting that the CuPc is no longer interacting or complexing with the 4-ethylpyridine and it may be precipitating out of solution.

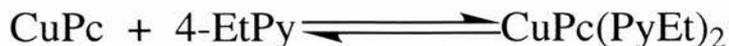
It is noted that on leaving the solution standing for about 30 min after taking the UV-visible spectrum a blue solid precipitates out therefore the complex formed by the ethylpyridine is not stable. Since the colour of the complex does not significantly alter it would appear that no quantum effects are being exhibited by CuPc, perhaps because the particle size remains relatively high, (>10 nm).

It is believed that the nitrogen atom in the pyridine complexes with the copper atom in the CuPc forming an octahedral type complex. This complex forms quickly upon refluxing the solution and can withstand a number of hours reflux before dissociating and precipitating. It appears that CuPc is likely to be more soluble in boiling 4-ethylpyridine and forms the complex shown in scheme 3.1. On cooling the solution CuPc starts to precipitate and pulls the equilibrium to the left.

Figure 3.20 :- UV-Visible Spectra of α -CuPc-4-Ethylpyrindine



Scheme 3.1 :- Formation of CuPc-4-Ethylpyridine Complex



The red shift in energy of the CuPc band is believed to be due to the nature of the octahedral complex formed. The blue shift in the lower energy band may also be due to the formation of the complex.

3.3.0 CONCLUSIONS

Attempts at encapsulation of CuPc within a zeolite showed that it is extremely difficult to prove that the material is within the cages and not on the surface. From all the data obtained on the three different methods of zeolite-CuPc synthesis and using the three different zeolites it can be conclusively proved that CuPc has been formed. The majority of the CuPc is formed on the surface, from powder XRD and TGA results but it is believed that a small amount is formed internally for methods zeolite-CuPc1, ion exchanged synthesis, and zeolite-CuPc3, solid state synthesis. The solution UV-visible spectra for all the samples show that CuPc is present, however, it can not be determined if it is internal or surface, in the light of other results it is likely to be surface CuPc.

The solid state UV-visible spectra of the samples show that there is a splitting of the Q-band except for zeolite-CuPc2 samples. This splitting is believed to be caused by a loss of symmetry, in which the presence of the sodium cation also plays a role. It is believed that the sodium occupies the cage and interacts in some way with the CuPc causing a larger split in the bands. It is also thought that copper starting complex used in method three causes the splitting to be further increased.

Protonation does not give the resulting green colour since Raman spectroscopy shows that the CuPc is intact and has not been attacked. The change in colour is not due to another Pc as no other evidence can be found for its existence. Copper is present in all the zeolites and CuPc is most likely to form over either sodium or metal free Pc.

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It can be concluded that the zeolite does interact with CuPc since the resultant material is green. It is possible that the CuPc is forming a thin coat around the surface of the zeolite, hence the presence of surface CuPc, and in the case of zeolite-CuPc₂ this coat is extremely thin. It is also possible that in the other cases internal CuPc is being formed.

From the interaction between CuPc and 4-ethylpyridine it is believed that it is unlikely that nanoparticles of CuPc can be formed in this way. The most likely way in which the colour of CuPc can be changed is electronically by adding substituents onto the outer benzene rings, this however will only result in a slight colour change to greens as is seen with sulphonated and chlorinated CuPc⁴⁵.

3.4.0 EXPERIMENTAL

3.4.1 GENERAL PROCEDURES

All chemicals used were purchased from either Avocado, Aldrich, BDH, Fluka, Strem or Lancaster and were used without further purification.

Powder X-ray diffraction (PXRD) was carried out on a STOE STADI/P diffractometer (Cu K α radiation of wavelength 1.54056 Å), data were collected (in transmission mode) with a sample mounted in vaseline on a rotating disc. Absorbance spectra were recorded using a Perkin Elmer Lambda 14P UV/Vis spectrophotometer (900-250 nm), with 1 cm x 4 cm plastic cells with the sample in a nujol mull spread onto filter paper. Elemental analysis and atomic absorption data were obtained at the University of St. Andrews. Transmission Electron Microscopy (TEM) data were obtained from Angstrom Consultants Ltd. Thermogravimetric analysis (TGA) were carried out on a Thermal Analyst 3100, SDT 2960 simultaneous DTA-TGA, with a flow rate of 100 cm³ min⁻¹. Solid state NMR data were recorded on a Bruker MSL 500 spectrometer. Resonance Raman data were obtained from the University of Strathclyde. All data were compared with data in the literature, where possible.

3.4.2 SYNTHESIS OF ZEOLITE-CuPc1

Encapsulated CuPc in zeolite X, Y or Y-2⁴⁰

Zeolite-X and Y are aluminosilicates made up from Si-O-Al tetrahedra, both having the same structure with cage sizes of 12-13 Å and pore sizes of 7.4 Å. Zeolite-Y is the more acidic having a higher Si:Al ratio, 2.4:1 while zeolite-X has a ratio of 1.2:1.

Preparation of the Metal Exchanged Zeolite

A mixture of zeolite X, Y or Y-2 (6 g) with a solution of copper acetate ($0.025 \text{ mol dm}^{-3}$) in deionised water was stirred for 48 h at room temperature. The slurry was then centrifuged and the solid washed with deionised water and then dried at $250 \text{ }^{\circ}\text{C}$ overnight. Zeolite-Ni was synthesised using nickel acetate and the same procedure.

Preparation of the Encapsulated Phthalocyanine

The dried exchanged zeolite (1 g) was mixed with 1,2-dicyanobenzene (1 g) (6:1 excess) and placed in an autoclave which was evacuated for 2 h. The system was then sealed and heated to $200 \text{ }^{\circ}\text{C}$ for 24 h. The product was then purified by soxhlet extraction using the following sequence: methanol, diethyl ether, acetone, methanol, acetone, pyridine, diethyl ether. The resulting powder was then vacuum dried at $180 \text{ }^{\circ}\text{C}$ overnight. Synthesis of zeolite-NiPc-1 was carried out following the same method.

3.4.3 SYNTHESIS OF ZEOLITE-CuPc2

The zeolite, (X, Y or Y-2), (1 g) was placed in a quartz tube between two plugs of glass wool, the β -CuPc (1 g) was sublimed at $600 \text{ }^{\circ}\text{C}$ and nitrogen passed over to carry the CuPc over the zeolite with a small amount of the CuPc passing through. After approximately 1 h the furnace was cooled and the zeolite-X-CuPc was soxhlet extracted with acetone, methanol, pyridine and diethyl ether. The mixture was then vacuum dried at $180 \text{ }^{\circ}\text{C}$ overnight.

3.4.4 SYNTHESIS OF ZEOLITE-CuPc3

Copper complex C, $[\text{Cu}(7\text{-tBuO-NBD})(\text{hfac})]$ or $[\text{Cu}(\text{hfac})_2]$, (1 mmol), DCB (4 mmol) and zeolite X, Y or Y-2 (1 g) were ground together and heated to $200 \text{ }^{\circ}\text{C}$ for 4 h. The

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mixture was then cooled and soxhlet extracted with acetone, methanol, pyridine and diethyl ether before being vacuum dried at 180 °C for 24 h. Synthesis of zeolite-NiPc-3 was carried out in the same way but using [Ni(acac)₂].

3.4.5 SYNTHESIS OF CuPc-ZEOLITE-X³⁸

α or β -CuPc (0.04 g) was stirred with silica (2 g) and a solution of sodium hydroxide (1.6 g in 4 cm³ water), added. Aluminium isopropoxide (4.5 g) was added to a solution of sodium hydroxide (1.6 g in 6 cm³ water). The two solutions were mixed, water (18 cm³) was added, and the reaction mixture placed in a polypropylene bottle. It was stirred at room temperature for 24 hrs and then heated to 90 °C for 7 h. The solid was then washed with copious amounts of water and dried at 90 °C for 8 h.

3.4.6 REACTION OF CuPc WITH 4-ETHYLPYRIDINE²¹

A solution of (α or β) CuPc in 4-ethylpyridine (10 mM) was refluxed (170 °C), under nitrogen. Samples were taken every hour and UV-Vis spectra measured. On cooling the samples, CuPc precipitated.

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CHAPTER 4

SYNTHESIS OF CERIUM SULPHIDE

CHAPTER 4

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4.1.0 INTRODUCTION

At present there are only a few yellow, orange and red pigments available that have high performance in their chemical, thermal and UV stability. These pigments tend to be based on heavy metals such as cadmium, lead and chromium and are currently the most widely used in industry. Despite their excellent performance characteristics, their toxicity presents a number of environmental and health problems¹. Several stringent international regulations now limit or forbid their use in a range of applications². Thus, due to new international policy changes to prevent long term health damage, there has been a renewed interest to develop new classes of inorganic pigments of practical use to the plastics industry for the replacement of the convenient cadmium sulphoselenides³. To this end the rare earth sulphides offer attractive possibilities for use as new pigments.

Cerium sulphides and other lanthanum sulphides were originally investigated in the 1940s in the search for new refractory materials as crucibles for the casting of plutonium and uranium. Ce_2S_3 and CeS are considered to be useful refractory materials due to their high melting point and are thermodynamically stable at elevated temperatures⁴.

The, $\gamma-Ln_2S_3$, rare earth (sesqui)sulphides offer several attractive characteristics, in particular, they fulfil most of the preparation, colour, and stability requirements for a pigment. In the rare earth sulphide series, the cerium derivative is particularly interesting because of its orange/red colour. The cerium sulphide can be sodium doped making it possible to tune its colour from maroon to orange^{1,5} offering a wide range of colours which can be used as pigments. This is shown by Rhone-Poulenc who recently launched *Neolor* pigments for colouring plastics and coatings which are based on sodium doped cerium sulphide⁶. The *Neolor* range provides an alternative to the existing inorganic pigments based on heavy metals which are health threatening at very low concentrations and can accumulate in organisms causing chronic injury.

In some reports⁴ it has been claimed that Ce_2S_3 has high thermal stability, however, in other reports⁶ the main disadvantage of Ce_2S_3 as a pigment is described as its moderate

thermal and chemical stability. Rhone-Poulenc tackled any stability problems by using a protective thin film of polymer only a few nanometres thick.

Ce₂S₃ has a number of potential and actual technological⁷ uses, ranging from infrared lenses^{8,9}, (transmission range ca. 1-14 μm), catalysts¹⁰, colour phosphors¹¹, lasers¹², semiconductor dopants to ionic conductors¹³ and recently its use as a pigment⁶ can be added to this list.

4.1.1 STRUCTURE OF LANTHANUM SULPHIDES

It is believed that in the Ln₂S₃ series there are five possible different crystal structures that can exist. There is some confusion about the assignment of these structures with some references using Greek letters¹⁴ and others using English letters¹⁵, table 4.1 shows the structure types along with their assigned letters.

Table 4.1 :- Structures Types of Lanthanide Sulphides

English Letter	Greek Letter	Structure Type	Coordination No.
A	α	Orthorhombic	7 + 8
B	β	??	?
C	γ	Cubic	8
D	δ	Monoclinic	6 + 7
E	ε	Corundum	6

It is thought that only three structure types exist for the formula Ln₂S₃, with the larger lanthanides, La through to Dy, having the α type structure and the δ type structure is prevalent from Dy through to Tm. The third structure type, ε, is thought only to exist for Yb and Lu¹⁶. The most common structure type that occurs for the Ln₂S₃ is the γ type which is formed at elevated temperatures but this is thought to be sulphur deficient as is with the β type. Since rare earth sesquisulphides were generally prepared in open

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systems and in such cases the stoichiometry of the product sulphide is not well controlled¹⁵, this explains why the β and γ structures may be sulphur deficient.

The α structure has two nonequivalent cerium atoms. One is seven coordinate and the other is six coordinate. The δ type has six nonequivalent cerium atoms three of which are six coordinate and the other three are seven coordinate.

Ce_2S_3 is thought to exist in three polymorphic forms α , (A), β , (B), and γ , (C)⁴. In fact it is thought that β - Ce_2S_3 is an oxysulphide^{4,5} with a formula of $Ce_{10}S_{14}O$ and that the γ type fits a formula closer to Ce_3S_4 . Therefore the α type is probably the true structure of stoichiometric Ce_2S_3 , although at elevated temperatures it is converted to the γ type.

It is the γ form of Ce_2S_3 that has generated most interest as a pigment since it can be doped with sodium with little or no structure change and this produces a range of colours. In the parent structure of pure γ - Ce_2S_3 the cations form a body centred cubic lattice with twelve cationic sites per unit cell. The structure of γ - Ce_2S_3 is formally derived from Ce_3S_4 by removing one out of nine Ce atoms from the lattice. The vacancies are randomly distributed and thus one can expect a statistical occurrence of different environments around each vacancy. Upon doping of γ - Ce_2S_3 with sodium, all the vacancies are filled thus stabilising the structure¹. The presence and arrangement of the vacancies have a strong effect on the band gap altering it by as much as 1 eV. The sodium homogenises the valence and conduction bands in the sense that the variations in the band gap which depend on the distribution of the vacancies are less pronounced. As a result the amount of sodium present can affect the colour of the material thus leading to a range of colours from maroon to orange for γ - Ce_2S_3 .

4.1.2 PROPERTIES OF CERIUM SULPHIDE

Cerium is the most reactive member of the lanthanide series and has two stable oxidation states, +3 and +4. Complexes of cerium tend to be ionic in nature as it is an electropositive metal and readily oxidises to either of its stable oxidation states. Cerium

(III) complexes tend to be air sensitive and are easily oxidised whereas cerium (IV) complexes tend to be more air stable.

Unlike many cerium complexes cerium sulphide is air stable although there are contradicting reports upon its stability at elevated temperatures. Ce_2S_3 is considered to be useful as an advanced refractory material due to its high melting point and it is thermodynamically stable at elevated temperatures⁴. However, it has been reported that cerium sulphide has only moderate thermal and chemical stability⁶. The later statement is likely to be true in air since cerium sulphide loses sulphur at high temperatures and the β structure type is also believed to be an oxysulphide. In a non oxidising atmosphere it is more likely that cerium sulphide would be thermally stable, however, the possibility of losing sulphur still exists.

Cerium sulphide in the native form is yellow but due to the structure of the γ form it can accommodate alkali or alkaline earth metals by doping. This allows a controlled modification of the colour shade and intensity through the adjustments of the stoichiometry. The same phenomenon is observed for all members of the $\gamma-Ln_2S_3$ family³. It is also noted that there is a change of colour of the $\gamma-Ln_2S_3$ compounds as the 4 f shell is progressively filled across the lanthanide series from an orange tinge to a more yellow colour.

4.1.3 METHODS OF SYNTHESIS OF CERIUM SULPHIDE

The conventional route to lanthanum sulphides is usually by a high temperature reaction ($>900\text{ }^\circ\text{C}$) between a cerium source, (cerium metal, cerium oxide or the conversion of cerium salts such as, oxalate, carbonate, or nitrate, to the oxide), with a sulphur containing compound producing a powder comprising of particles and aggregates of a variety of shapes and sizes^{3,4,17-19}.

The structure type obtained depends upon the reaction conditions. The α phase is stable at low temperatures and is irreversibly converted to the β type of various compositions at elevated temperatures ($1150\text{ }^\circ\text{C}$). The γ type is the most common form of the lanthanide

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sulphides and it is thought to have the defect Th_3S_4 structure which occurs over a range of composition. This form is formed at elevated temperatures which make the stoichiometry of the reactants hard to control due to the volatility of sulphur.

Due to the high temperatures used and the difficulty in controlling the stoichiometry there is considerable scope for new processes in which the synthesis can be carried out under mild conditions.

Attempts to prepare lanthanum sulphide by treatment of lanthanum isopropoxide with H_2S led to materials containing metal, sulphur and hydrocarbon and despite all attempts to exclude air and moisture from the reaction the product always contained oxygen (up to 20 %) ¹⁹. Unfortunately aqueous methods cannot be used for the preparation of lanthanum sulphide as these metals are oxophilic and therefore oxygen will be present in the final product.

It has been reported that lanthanum sulphide (La_2S_3) can be synthesised by a reaction of $[\text{La}(\text{N}(\text{SiMe}_3)_2)_3]$ in an organic solvent with H_2S at temperatures between 20 °C and 100 °C. This gives an amorphous yellow powder which is then heated to 510 °C in a stream of H_2S to produce the yellow crystalline solid, La_2S_3 ¹⁹. The room temperature reaction of $\text{La}\{\text{N}(\text{Me}_3\text{Si})_2\}_3$ and gaseous H_2S in toluene or benzene produced a pale yellow gel like material which is non-stoichiometric lanthanum sulphide. If exposed to air the sample oxidised or adsorption of water occurred. Impurities could be removed by heating the product at 400-500 °C for 2-3 h in a stream of H_2S . Heat treatment caused the product to crystallise.

4.1.4 A LOW TEMPERATURE ROUTE TO CERIUM SULPHIDE

Despite the low temperature initially used by Allen et.al. ¹⁹ the final reaction to produce La_2S_3 requires a fairly high temperature of 500 °C, it would therefore be ideal if this last step could be eliminated and lead to a truly low temperature route to producing a Ln_2S_3 . The possibility can be considered of general reactions of an organic soluble lanthanide complex with H_2S to give the lanthanide sulphide by metathesis, scheme 4.1.

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Scheme 4.1 :- Reaction of a Lanthanide Complex and Hydrogen Sulphide



X is the anion of a weaker acid than H₂S

L is an optional solubilising ligand

Ln is a lanthanide element

In the late seventies organolanthanoids became known on a broad front and since then there are a vast number that can be synthesised with relative ease. However nearly all the organocerium compounds are both air and moisture sensitive making them more difficult to handle²⁰ and less suitable for the synthesis of cerium sulphide.

Due to the interest in the production of thin films by MOCVD some air stable cerium β -diketonates have been synthesised^{21,22}, Ce(fdh)₄, Ce(fdh)₃Phen and Na[Ce(fdh)₄]. It may be possible that these complexes will react with H₂S in a similar manner to the La{N(Me₃Si)₂}₃ to produce cerium sulphide.

Organolanthanoids containing sulphur exist in dithiocarbamates. Many studies have been carried out on transition and non transition metal dithiocarbamates, but only a few reports have appeared on the corresponding lanthanide derivatives²³⁻²⁵. This is mainly because of their strict preparation conditions and instability to moisture. The solutions hydrolyse readily to produce basic salts and oxygen must also be excluded from the reaction mixture. The cerium dithiocarbamates can be synthesised by reaction of the anhydrous chloride or bromide with a stoichiometric amount of the sodium or ammonium dithiocarbamate.

Many monosubstituted dithiocarbamates have been found to be air stable and can be synthesised in an air atmosphere using hydrated lanthanide salts²⁵. They report that the cerium salt can be synthesised in this manner, however, no other paper involving the synthesis of cerium dithiocarbamates reports any air stability of such complexes. In the case of Su et.al.²⁵ they produce an ammonium salt of the cerium complex, [NBu₄:Ce(S₂CNHPh)₄]. When synthesised in the absence of tetrabutylammonium iodide an unstable complex is formed. It is thought that the presence of four anions around the cerium sterically protects it making it more air stable. It is reported that the

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lanthanide salts are air stable as solids. However, the cerium derivative decomposes more rapidly and after a few days has completely decomposed.

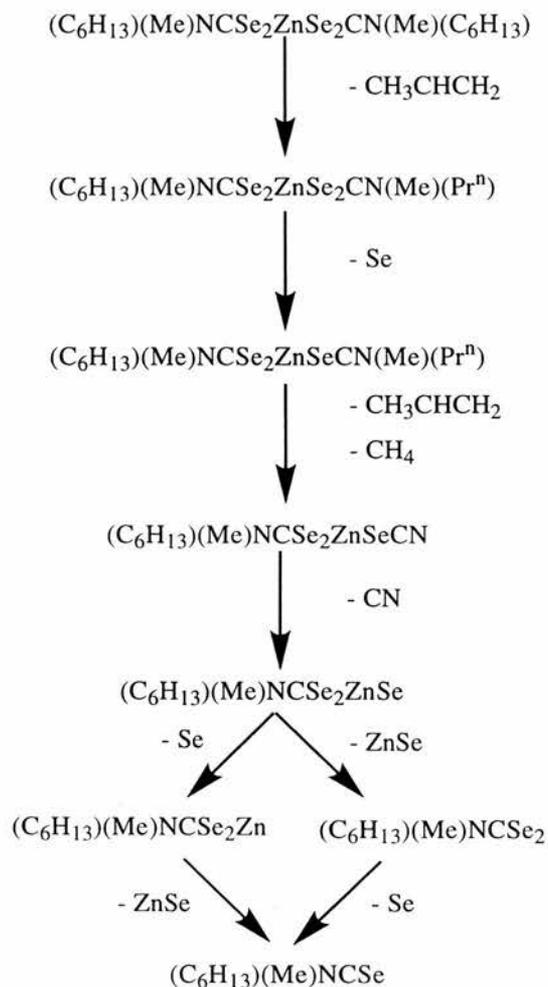
The use of cerium dithiocarbamates for the production of cerium sulphide may be very useful as dithiocarbamates are currently used as single source precursors for the production of ZnS and CdS²⁶⁻³¹ and also for the production of CaS³². In most cases the sulphide is formed by thermal decomposition of the metal dithiocarbamate at moderate temperatures depending upon the groups on the dithiocarbamate. Dialkyl dithiocarbamates tend to have a higher decomposition temperature and in the case of production of CaS gave carbonised samples except for diisopropyl dithiocarbamate. In the case of the monosubstituted dithiocarbamates purer samples of CaS were obtained, however, at extremely slow heating rates of 1 °C min⁻¹. In production of ZnSe and CdSe the dialkyl substituted methyl hexyl diselenocarbamate produced the best results producing films that had less contamination from carbon and elemental selenium than from using the simple diethyl diselenocarbamate.

A plausible decomposition mechanism has been proposed for the complex, bis[methyl(*n*-hexyl)diselenodicarbamato]-Zinc,³⁰ and is illustrated in scheme 4.2.

During the decomposition of diethyl diselenocarbamate an ethene fragment is lost first followed by the loss of selenium, it appears that these fragments react together to form diethyl diselenide. This reaction is apparently hindered by the alteration of the dialkyl substituents, to methyl and hexyl, on the carbamate and therefore reduces the amount of carbonised contamination. It is also believed that the diethyl diselenide decomposes at higher temperatures to give clusters of selenium leading to contamination of the MSe films. In the case of the methyl hexyl diselenocarbamate very little or no contamination is detected from either carbon or elemental selenium suggesting that the byproducts do not deposit onto the MSe film because of their increased volatility. Therefore by selecting suitably volatile cerium dithiocarbamates, thus preventing or at least reducing the chance of forming the sulphur analogue of diethyl diselenide, (diethyl disulphide), then contamination from carbon and sulphur should be reduced to a minimum.

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Scheme 4.2 :- Decomposition of a $[\text{Me}(\text{n-C}_6\text{H}_{13})\text{NCSe}_2]_2\text{Zn}$



It may therefore be possible to produce Ce_2S_3 from the thermal decomposition of a cerium dithiocarbamate. Along with the thermal decomposition of the cerium dithiocarbamate, the addition of sulphur or a reaction with H_2S may help tackle any stoichiometry difficulties encountered.

4.2.0 RESULTS AND DISCUSSION

In the attempt to find a low temperature route to Ce_2S_3 reactions between cerium complexes and H_2S , similar to those in the literature,¹⁹ were studied. A number of organocerium complexes were selected, $Ce(fdh)_3Phen$, $Ce(hfac)_3$, $Ce(thd)_3Phen$, $Ce(iPrCp)_3$, and $[Ce\{N(SiMe_3)_2\}_3]$ were synthesised or purchased from a known supplier. The cerium β -diketonates, $Ce(fdh)_3Phen$, $Ce(hfac)_3$, $Ce(thd)_3Phen$, were used due to their stability in air and their use in Metal-Organic Chemical Vapour Deposition (MOCVD). (fhd is 6,6,6-trifluoro-2,2-dimethyl-3,5-hexanedionato; hfac is 1,1,1,6,6,6-hexafluoropentanedionato; thd is 2,2,6,6-tetramethyl-3,5-heptanedionato; phen is 1,10-phenanthroline). The other complexes are extremely air sensitive but are more likely to be reactive towards H_2S and contain no oxygen.

The cerium complexes were dissolved in degassed toluene and then H_2S gas bubbled through as indicated in the literature procedure¹⁹.

Table 4.2 lists the complexes and the results obtained from their reaction with H_2S . In each case, a precipitate formed almost immediately on contact of H_2S the precipitates were collected and examined by infra-red spectroscopy.

When $Ce(hfac)_3$ was suspended in toluene no reaction occurred on addition of H_2S , the brown material that was left on removal of the solvent was found to be unreacted starting material. The starting material was not very soluble in toluene and therefore is not a suitable starting material for this type of reaction. A similar result was obtained when $Ce(fdh)_3Phen$ was used as the starting complex.

The reaction between $Ce(thd)_3Phen$ and H_2S produced a yellow precipitate almost immediately. Over the time of the reaction the colour darkened. On removal of the solvent, either by vacuum or catheter filtration, the solid darkened even further, producing a light brown coloured material. The FTIR of the solid showed a number of bands similar to that of the starting material. It is thought that a partial reaction with the H_2S has taken place and it is this product that has precipitated out of solution thus

preventing any further reaction. The possibility exists that a sulphur molecule is bridging between two cerium atoms forming a polymeric type material is forming.

Table 4.2 :- Reaction of Cerium Complexes with Hydrogen Sulphide

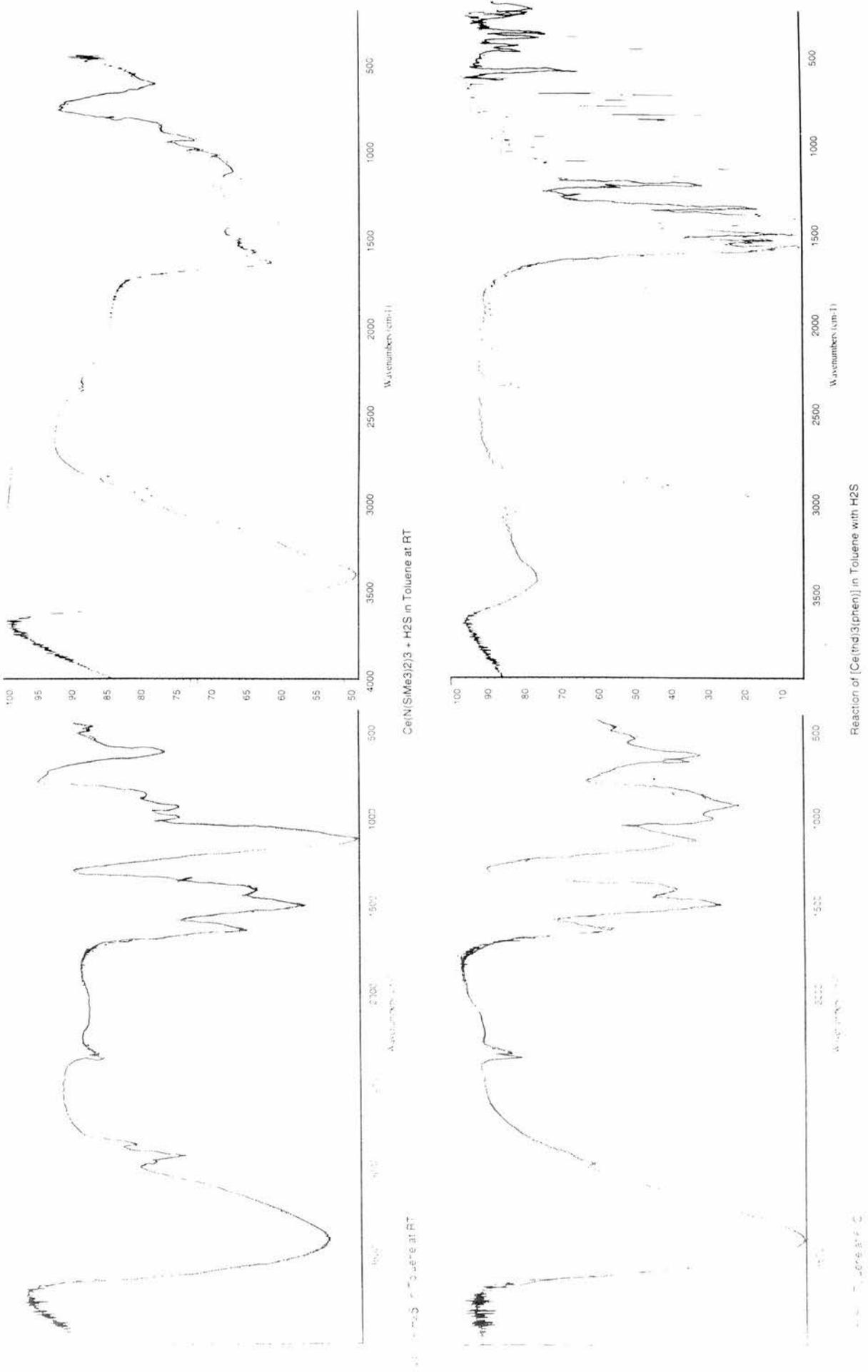
Cerium Complex	Temperature / °C	Product
Ce(hfac) ₃	25	Brown Solid
Ce(fdh) ₃ Phen	25	Brown Solid
Ce(thd) ₃ Phen	25	Yellow (Brown)
Ce(thd) ₃ Phen	60	Brown
Ce(thd) ₃ Phen	80	Brown
Ce(ⁱ PrCp) ₃	25	Yellow (brown)
Ce(ⁱ PrCp) ₃	60	Brown
Ce(ⁱ PrCp) ₃	80	Brown
Ce{N(SiMe ₃) ₂ } ₃	25	Brown
Ce{N(SiMe ₃) ₂ } ₃	25*	Deep Brown

* A brown precipitate is formed which was then heated to 500 °C in a flow of H₂S

The reaction was repeated at elevated temperatures, 60 °C and 80 °C but at these temperatures a light brown solid precipitated with no hint of a yellow precipitate forming first. The FTIR of the solids, a sample of which are shown in figure 4.1, suggest that only a partial reaction is taking place between the cerium complex and H₂S since there is a considerable amount of organic material present. Powder XRD patterns, a sample are shown in figure 4.2 and compared to Ce₂S₃, of the light brown products showed that in all the reactions no or an undetectable amount of crystalline Ce₂S₃ had formed.

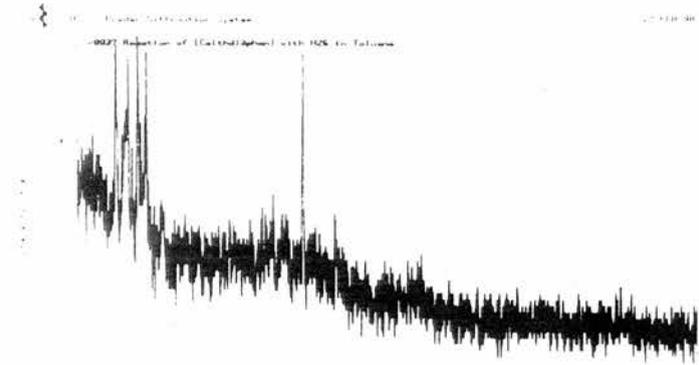
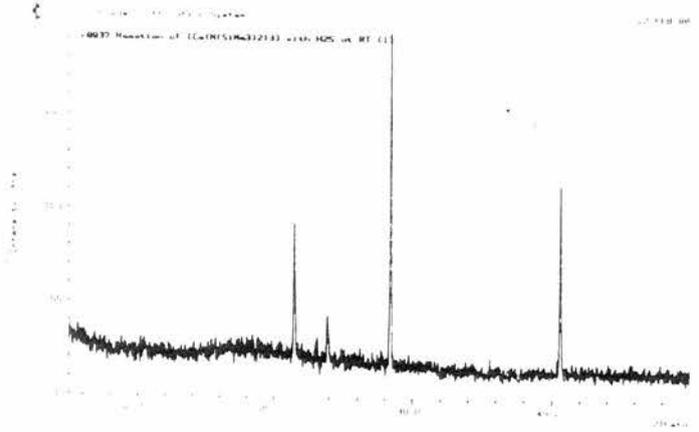
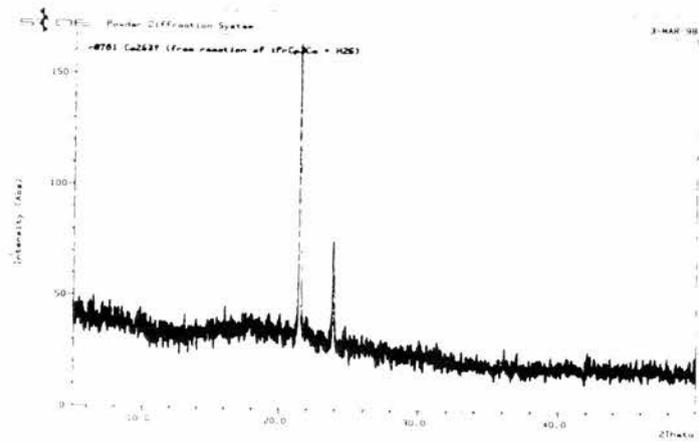
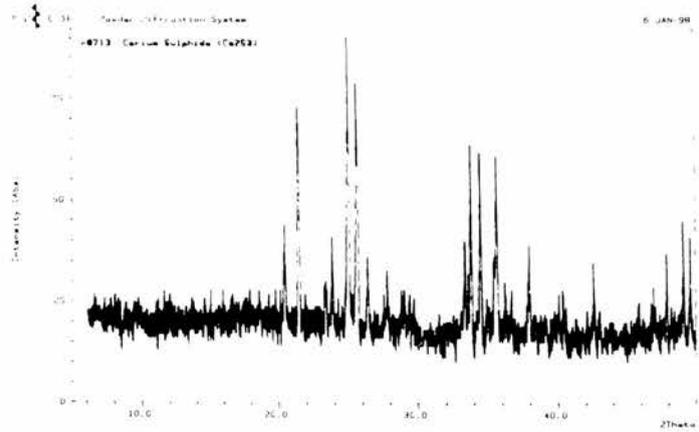
It is possible that partial substitution of the anions around cerium by S²⁻ occurs, but that these sulphides are insoluble materials that are unreactive towards H₂S, even when the temperature is increased. It is thought that the presence of oxygen in the β-diketonate complexes may make the formation of Ce₂S₃ unlikely at low temperatures. Cerium is a

Figure 4.1 :- FTIR Spectra of Reacting Cerium Salts with H₂S



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Figure 4.2 :- Powder X-Ray Diffraction Patterns of Products Obtained



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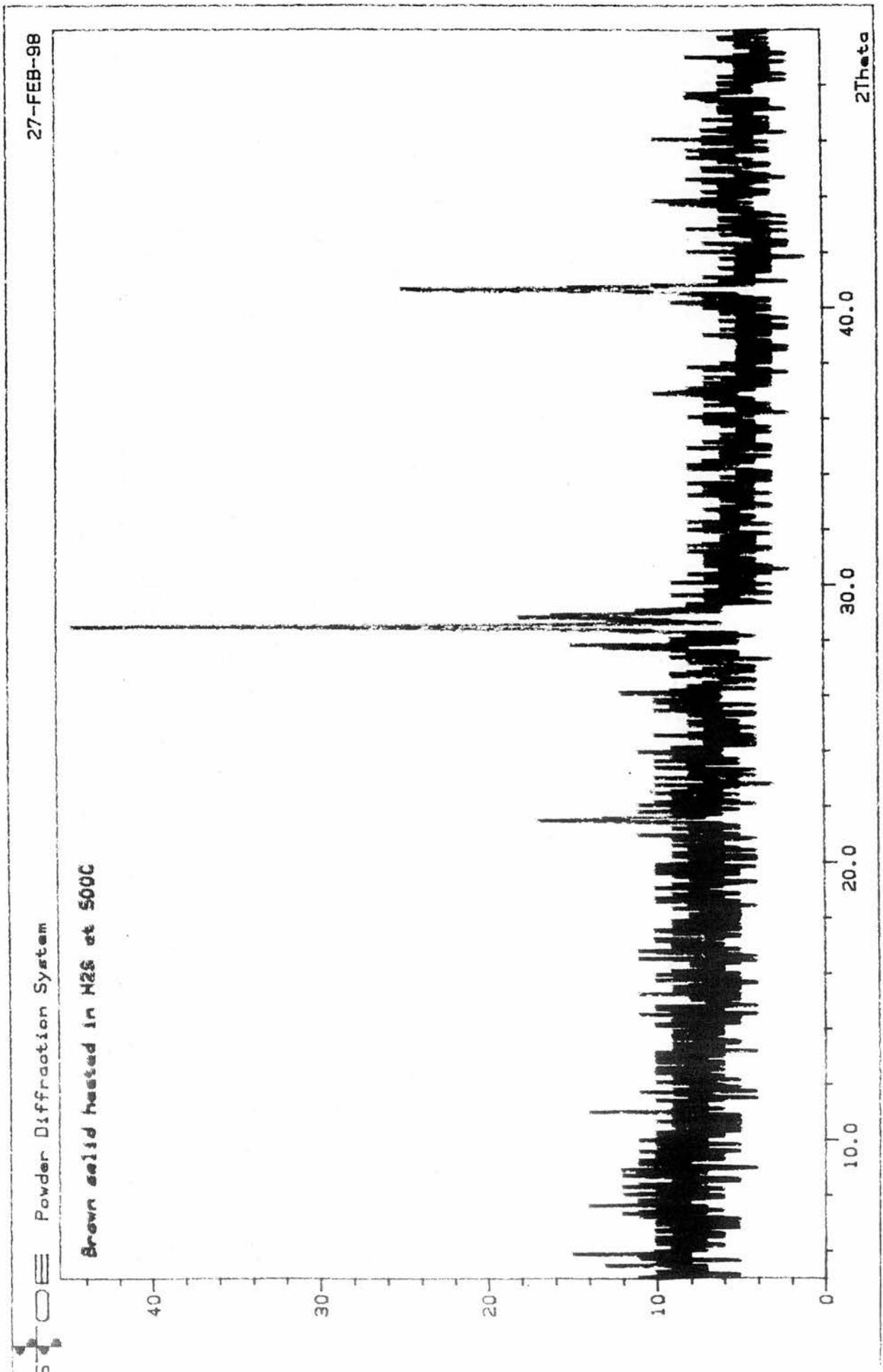
hard oxophilic metal and prefers oxygen to sulphur therefore it will require a significant amount of energy to replace the oxygen with sulphur. A reaction between cerium isopropoxide and H_2S produced a material that contained metal, sulphur, hydrocarbon, and oxygen¹⁹. A similar process may be occurring in the reactions carried out between the β -diketonate complexes and H_2S . It is unlikely that a solution reaction between a cerium β -diketonate and H_2S will produce Ce_2S_3 . Since the cerium β -diketonates were found to be unsuitable starting materials the reaction between $\text{Ce}(\text{iPrCp})_3$ and H_2S was then studied. As with the previous reactions a precipitate formed almost immediately on bubbling H_2S through a toluene solution of $\text{Ce}(\text{iPrCp})_3$. In this case the precipitate was yellow. However, on removal of the solvent by vacuum or by catheter filtration the solid immediately went light brown in colour. It is most likely that a partial reaction had taken place and that the solid formed is unstable and oxidises. Even when a small amount of solvent covers the solid it remains yellow but on removal of the last portion of solvent the colour darkens. Despite all attempts to eliminate this problem the solid always went brown upon removal of the solvent.

As with the $\text{Ce}(\text{thd})_3\text{Phen}$ the reaction was repeated at higher temperatures, 60 °C and 80 °C but only produced, as previously, a brown precipitate, suggesting that the yellow solid has little thermal stability. Again it is possible that the S^{2-} is substituting with the iPrCp ligands but on exposure to air or moisture oxidises immediately.

The FTIR spectra of the material show that there is organic material present in the sample but in this case it is unlikely to be the starting material due to its air sensitivity.

The reaction between $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and H_2S , the analogous reaction to that which had been successfully used for La_2S_3 ¹⁹ again produced a brown precipitate. $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]$ is extremely air sensitive even more so than the lanthanum derivative and it is believed that it has oxidised before being able to react with the H_2S . On repeating the reaction the same results were obtained. It was thought that heating the brown solid in a similar manner to that in the reference may produce Ce_2S_3 . The solid was heated to 500 °C in a stream of H_2S and the resultant powder retrieved from the furnace was a deeper brown almost black in colour. The powder XRD pattern, figure 4.3, shows the

Figure 4.3 :- Powder X-Ray Diffraction Pattern of the Black Solid



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possibility of some crystalline material present but there is no Ce_2S_3 present, the FTIR data shows that there is little organic material present. It has been observed for yttrium sulphides that a light brown grey surface coating forms³³, it is possible that this is the case for the brown cerium solid formed. However, on grinding of the material in a glove box it would appear that the material is brown and that it was not a surface coating.

It would appear that even if Ce_2S_3 can be synthesised by a solution method a second step of heating in a flow of H_2S will be required to remove any impurities and to produce a crystalline material. From the literature the yellow gel that formed was nonstoichiometric lanthanum sulphide and therefore another reaction is required to increase the sulphur content to obtain stoichiometric Ln_2S_3 . It is plausible that a cerium complex containing sulphur may decompose to give the desired product either in the presence of or without another sulphur containing compound thus combating stoichiometry problems.

Metal dithiocarbamate complexes are known for almost all elements³⁴ and have been used in the production of ZnS , CdS ²⁶⁻³¹ and also CaS ³². It may therefore be possible that cerium dithiocarbamates can be used in a similar manner to produce Ce_2S_3 . However, there are only a few reports of cerium dithiocarbamates in the literature²³⁻²⁵ most likely due to their stringent methods of preparation because of the air sensitive nature of cerium (III).

A recent report on cerium dithiocarbamates²⁵ presented a simple method of production of $\text{Ce}(\text{S}_2\text{CNHPh})_4:\text{NBu}^n_4$ from hydrated cerium chloride and ammonium phenyl dithiocarbamate in air. It was hoped that this method could be adapted to produce $\text{Ce}(\text{S}_2\text{CNRR}')_3$ salts where R and R' are various alkyl or aryl substituents along with the ammonium or even sodium salts of the tetra dithiocarbamate cerium. The tris dithiocarbamates were preferred over the ammonium or sodium salts as it was thought these would give cleaner decompositions.

From the literature there are an enormous number of dithiocarbamates that have been synthesised³⁴ and table 4.3 lists the R and R' groups selected for synthesis of $\text{Ce}(\text{S}_2\text{CNRR}')_3$ and $\text{M}[\text{Ce}(\text{S}_2\text{CNRR}')_4]$, where M is either Na, NH_4 or $\text{NH}_2\text{RR}'$. A number of other R and R' substituents were attempted but were disregarded either

because of a difficulty in synthesis of the cerium complex or because the cerium salts were extremely air sensitive, making them very difficult to handle. Initially the tris dithiocarbamate complexes were synthesised followed by the ammonium or sodium salts of the tetra dithiocarbamate cerium analogues.

Table 4.3:- Substituents on the Dithiocarbamate

R	Et	H	H	Pr ⁱ	Me
R'	Et	Ph	Bu ^t	Pr ⁱ	Hex

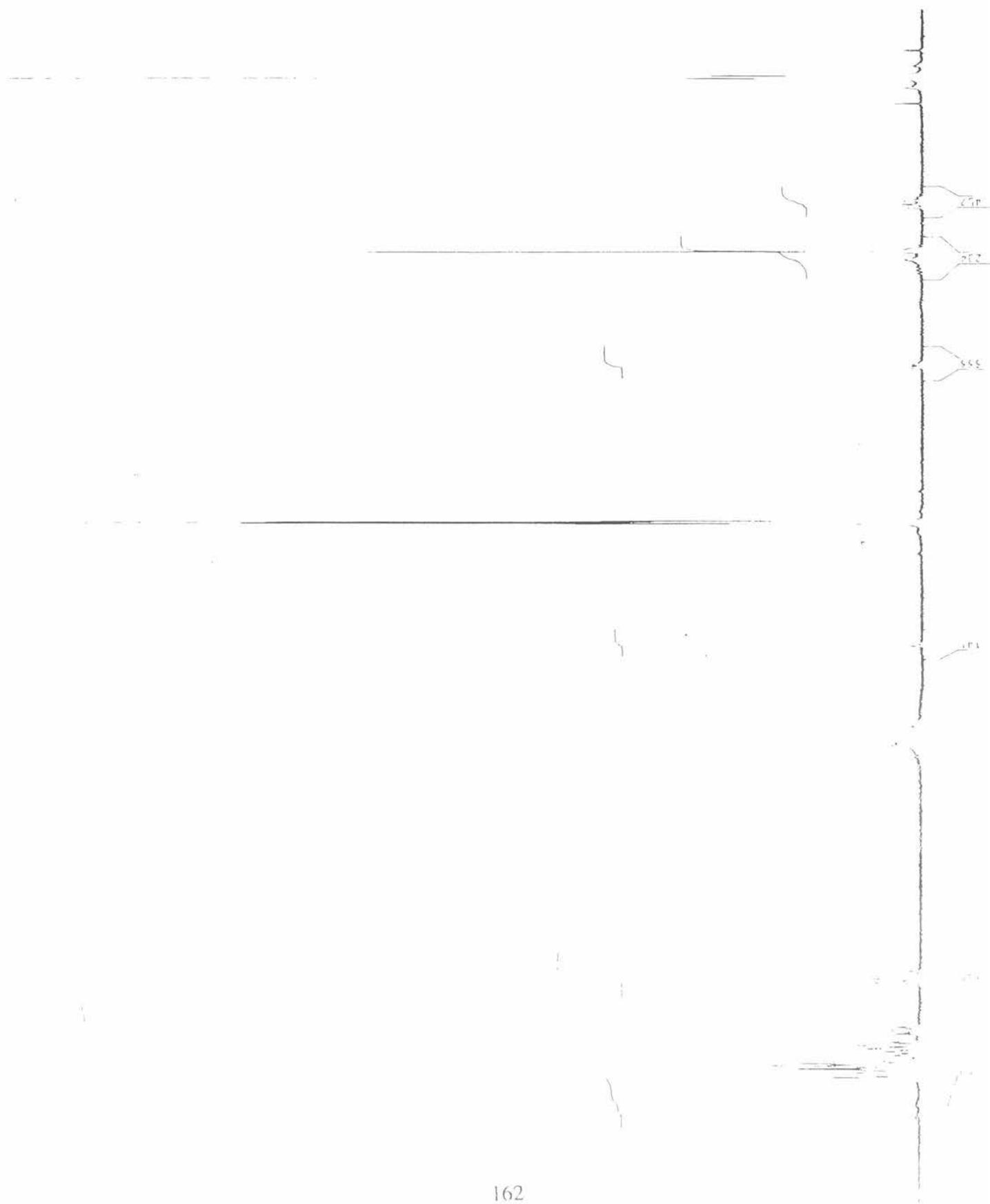
Before the cerium salts can be synthesised the ammonium or sodium salts of the dithiocarbamates have to be synthesised. This involves the reaction of carbon disulphide with the relevant amine and either sodium hydroxide or concentrated ammonia solution^{25,35}. The mixtures are stirred rapidly for up to 10 h. In the case of the sodium salts the solvent, ethanol, is evaporated using a dynamic vacuum to leave a yellow white precipitate which is then washed with small portions of ethanol and then dried over phosphorous pentoxide under reduced pressure. In the case of the ammonium salts a yellow white precipitate forms after approximately 15 min which is then filtered and washed with small portions of ethanol before being dried in the same manner as the sodium salts.

The NMR data obtained, figure 4.4 shows the NMR spectrum of NH₄S₂CNHPH, in deuterated methanol, of the ammonium salts showed two sets of peaks for the NRR' group when only one is expected, see scheme 4.3.

Scheme 4.3 :- Reaction of CS₂, NHRR' and NH₃



Figure 4.4 :- NMR Spectrum of $\text{NH}_4\text{S}_2\text{CNHPh}$



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Initially the extra set of signals was thought to arise from free amine which had not been fully removed, however, elemental analysis, (table 4.4, expected values are shown in parenthesis), of the samples fit the expected formula, $\text{NH}_4\text{S}_2\text{CNRR}'$, and no excess amine is thought to be present.

Table 4.4 :- C, H, N Analytical Data for $\text{NH}_4\text{S}_2\text{CNRR}'$

Sample	% C	% H	% N
$\text{NH}_4\text{S}_2\text{CNHPh}$	45.13 (44.90)	5.38 (5.38)	14.90 (15.04)
$\text{NH}_4\text{S}_2\text{CNPr}^i_2$	43.24 (43.26)	9.57 (9.33)	14.16 (14.41)
$\text{NH}_4\text{S}_2\text{CNPr}_2$	44.20 (43.26)	9.66 (9.33)	14.38 (14.41)

However, it is possible, especially if the second amine has a similar basicity to that of ammonia, or if the solubility of the product is lower than that of $\text{NH}_4\text{S}_2\text{CNRR}'$, that an alternative reaction, scheme 4.4, might occur to give the secondary ammonium salt of the dithiocarbamic acid.

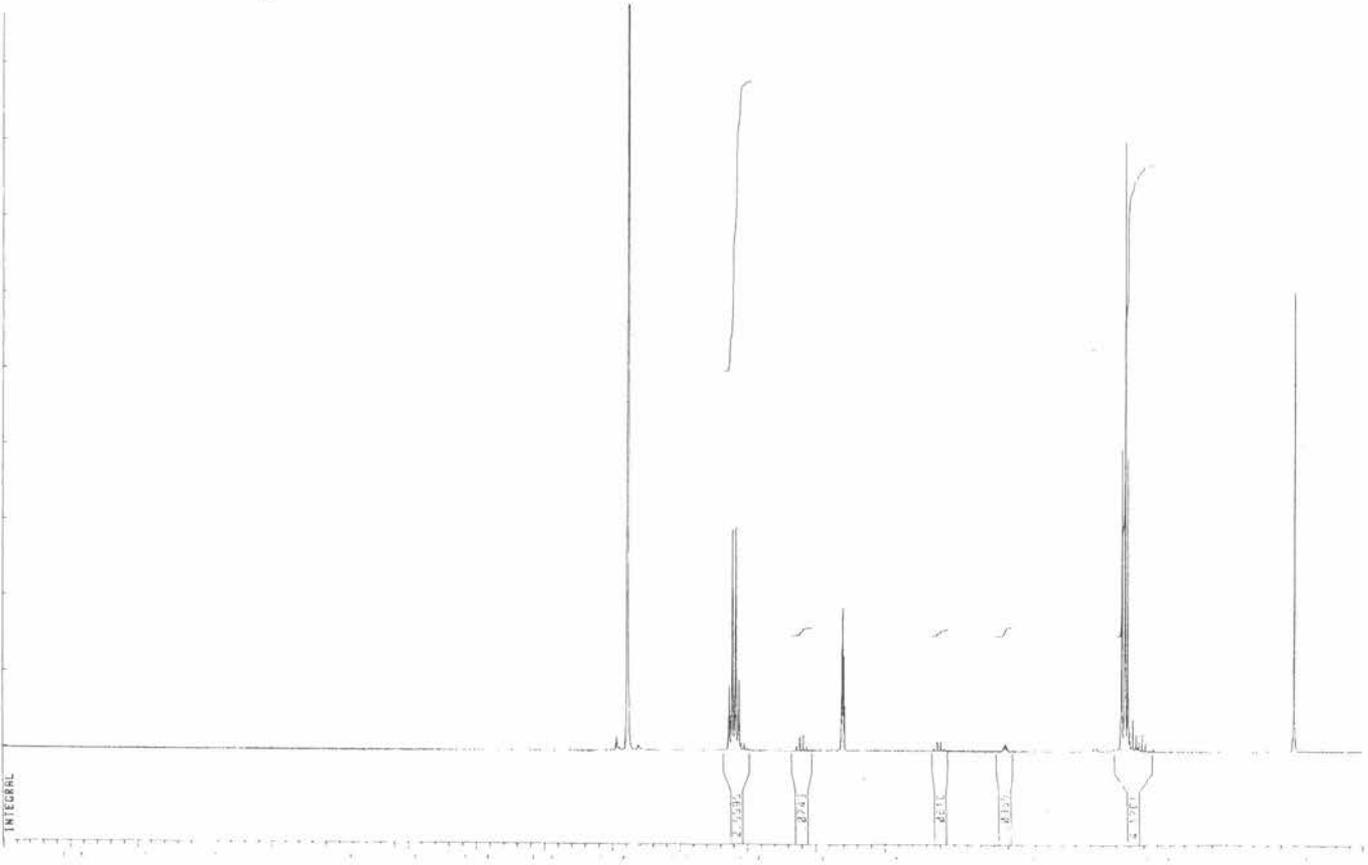
Scheme 4.4 :- Alternative Reaction of CS_2 , NHRR' and NH_3



It is therefore most likely that there is a mixture of products being formed thus accounting for the second set of peaks in the ^1H NMR to the species $\text{NH}_2\text{RR}'\text{S}_2\text{CNH}_2$. It is also plausible that both the dithiocarbamic acid salts are in equilibrium with one another in solution, scheme 4.5. Further evidence for this exchange is provided by the NMR spectra, figure 4.5, when sodium diethyl dithiocarbamate and excess diethyl amine are mixed together. Two sets of peaks are obtained, one for each of the different amine groups. On acidifying the medium, only one set of peaks is observed, in the ^1H NMR spectra thus showing that exchange reaction becomes fast on the NMR timescale.

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Figure 4.5 :- NMR Spectra of Exchange Reaction in $\text{NaS}_2\text{CNET}_2$



Scheme 4.5 :- Equilibrium Between $\text{NH}_4\text{S}_2\text{CNRR}'$ and $\text{NH}_2\text{RR}'\text{S}_2\text{CNH}_2$



When only one amine, $\text{NH}_2\text{RR}'$, is used the only dithiocarbamate species that can form is $\text{NH}_2\text{RR}'\text{S}_2\text{CNRR}'$, scheme 4.6. The NMR data, figure 4.6, for $\text{H}_3\text{NPhS}_2\text{CNHPh}$ shows this to be the case.

Scheme 4.6 :- Reaction of CS_2 and 2 NHRR'

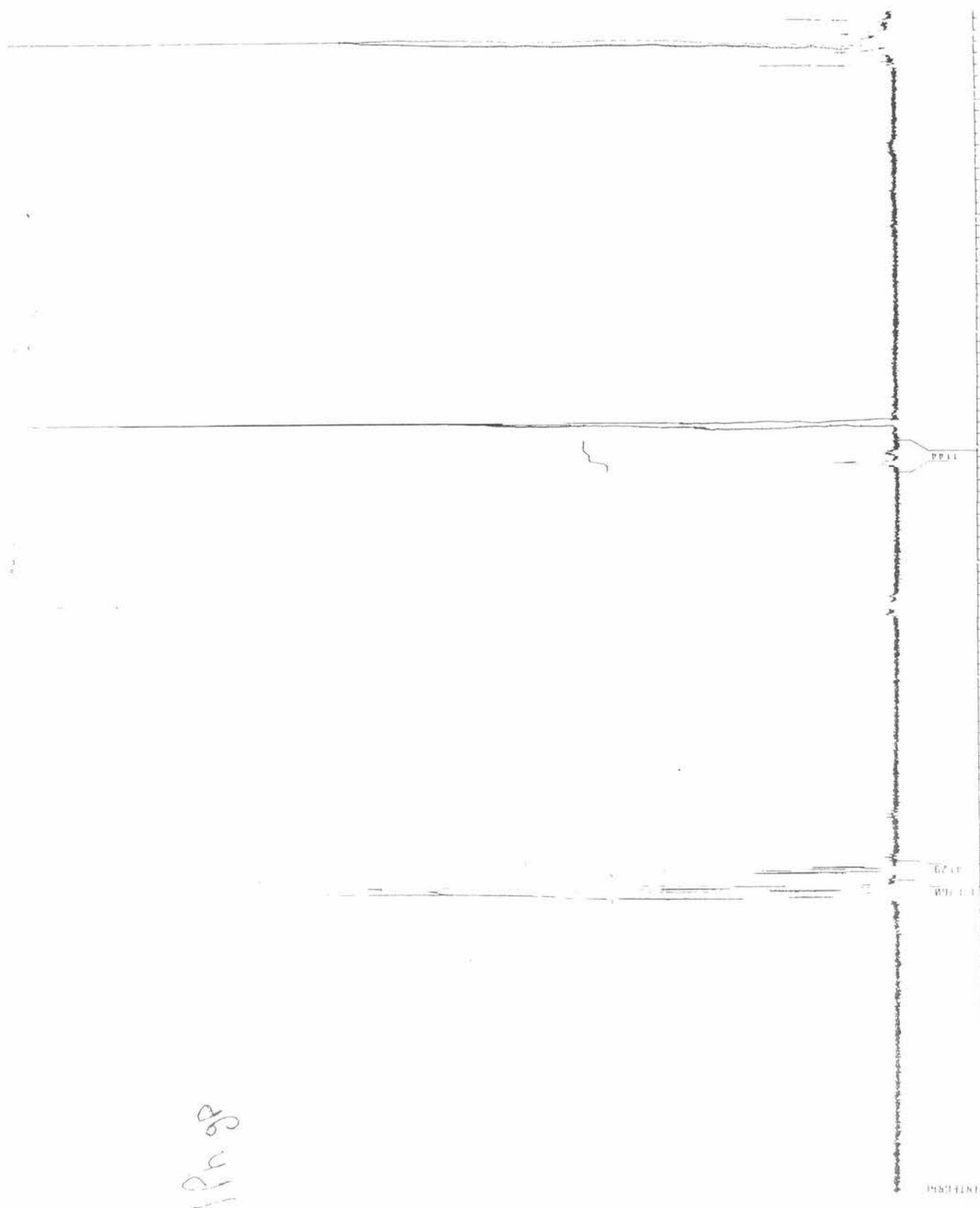


The synthesis of $\text{NaS}_2\text{CNMeHex}$ was a straight forward reaction between CS_2 , NHMeHex and NaOH in methanol with the solvent being removed to leave a yellow white solid which was dried and stored over phosphorous pentoxide³⁵.

The synthesis of the cerium salt, $\text{Ce}(\text{S}_2\text{CNEt}_2)_3$, by reacting $\text{NaS}_2\text{CNEt}_2$, (1 mmol), and a stoichiometric amount of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, (3 mmol), in methanol was attempted using the literature method by Su et.al.²⁵. On addition of the two solutions the mixture immediately went black, this is thought to be caused by the presence of oxygen in the methanol. On repeating the reaction using degassed solvent a yellow solid forms which rapidly turns black. When a closed system is used a yellow solid is formed and upon opening the solution to the air it remains yellow for a matter of minutes before the solution turns black. When the closed system is used and the solvent removed the surface of the yellow solid turns brown and then slowly goes black over a short period of time. It is thought that the lack of sterically large groups makes the dithiocarbamate unstable in the absence of solvent.

Other cerium dithiocarbamate syntheses were attempted but in each case when using the literature method the solution became black in colour as soon as the ammonium dithiocarbamate and the cerium halide were mixed together. When degassed solvent and a

Figure 4.6 :- NMR Spectrum of H_3NPhS_2CNHPh



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closed system are used a reaction proceeds to produce what is believed to be the desired product. A yellow precipitate appears within a matter of minutes and providing that there is solvent covering the solid then the solution can be exposed to air and the solid remains intact. However, if the solution is exposed to air, the system closed and then the solvent removed the yellow solid forms a brown/black coating very rapidly with the uncoated solid remaining yellow but slowly turning black. We conclude here that the yellow solids are not water sensitive but are extremely air sensitive and to obtain the cerium dithiocarbamate in a pure form oxygen must be excluded from the reaction at all times and especially before the removal of the solvent. However, it is thought that the exclusion of water in the synthesis would be beneficial for the decomposition of the cerium dithiocarbamate.

The older literature methods^{23,24} presented a method of synthesis that excluded air and water for the production of cerium dithiocarbamates. The cerium chloride, bromide and ethanol, acetonitrile, and ether, were all dried using literature procedures^{23,36,37}, the solvents were also degassed and the dithiocarbamates were dried over phosphorous pentoxide prior to use. The anhydrous cerium halide, (1 mmol), was dissolved in ethanol (5 cm³) and to this solution was added a solution of the dithiocarbamate salt, (3 mmol), in ethanol, (5 cm³). The mixture was then stirred for 5-10 min and the solvent removed under vacuum before extracting the product into cold acetonitrile and then filtered using catheter techniques. The product was then precipitated by adding ether to the solution and then the solvent removed by catheter techniques before drying the solid under vacuum.

It was found that the cerium dithiocarbamates were difficult to synthesise with minute amounts of oxygen present causing the solution to turn black rapidly. The disubstituted dithiocarbamates appeared more stable and were easier to synthesise than those containing only one organic group. This suggests that steric effects may be important in stabilising the cerium complexes. The steric bulk helps stabilise the metal centre which would prefer to have a higher coordination number. This has also been observed for other low coordination number cerium complexes³⁸. In the case of the monosubstituted

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dithiocarbamates a coordinating solvent or oxygen can penetrate through to the metal centre easier than when the bulk of two alkyl groups are present.

Due to their air sensitive nature and paramagnetic behaviour Ce^{3+} complexes are difficult to characterise. The FTIR of these complexes were obtained and it is believed that $Ce(S_2CNRR')_3$ is likely to be present see table 4.5. Evidence for their formation is shown by a double band for the C-S stretch between $1200-1050\text{ cm}^{-1}$. The C-N stretch can also be found near 1500 cm^{-1} , this is as expected for a bidentate dithiocarbamate³⁹. The M-S stretch which was not detected because it lies between 400 cm^{-1} and 300 cm^{-1} but the spectra were obtained on the neat sample and scanned between 4000 cm^{-1} and 450 cm^{-1} .

Table 4.5 :- FTIR Data of the $Ce(S_2CNRR')_3$ Series

$[Ce(S_2CNHPh)_3]$	$[Ce(S_2CNHBu^t)_3]^*$	$[Ce(S_2CNPr^i_2)_3]$	$[Ce(S_2CNMeHex)_3]^*$
2980	2975	2980	2960
2920	2905	2910	2910
1520	1510	1590	
1450		1430	1480
1310		1305	1290
1290	1295	1195	1200
1110	1125	1100	1100
1050	1060	1030	1050
1005	1025	950	
805	815	800	810
700			

* Samples produced weak spectra, therefore not all peaks could be detected

It was thought that the $M\{Ce(S_2CNRR')_4\}$ series of dithiocarbamates may be more air stable than the $Ce(S_2CNRR')_3$ series since the cerium centre is coordinatively saturated.

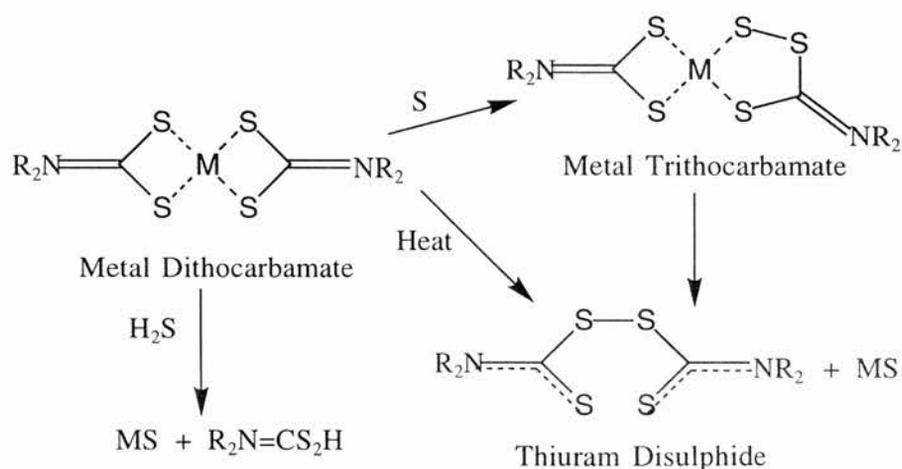
Thus sodium and ammonium salts of the cerium complex were synthesised, and as before these complexes were found to be air sensitive with the solid colour darkening upon exposure to air. However, their synthesis is easier with the complex having a better stability to air during the synthesis.

It had been reported that $[\text{NBu}^{\text{N}}_4\{\text{Ce}(\text{S}_2\text{CNHPh})_4\}]$ was stable in air, however, it was found that on exposure to air the colour of the compound darkened almost immediately.

Again the FTIR spectra of the complexes suggests that the desired product, $\text{M}\{\text{Ce}(\text{S}_2\text{CNRR}')_4\}$, has been synthesised with a similar spectra to those of the $\text{Ce}(\text{S}_2\text{CNRR}')_3$ series with extra stretches for the ammonium cation.

It is believed that the desired complexes have been formed and that thermal decomposition experiments to produce Ce_2S_3 and study the chemistry of cerium dithiocarbamates can be carried out. It is known that sulphur can insert into the M-S bond to give trithiocarbamates³⁴, and that dithiocarbamates can reductively eliminate to give thiuram disulphides and metal sulphide, see scheme 4.7. The metal dithiocarbamate can also react with H_2S to produce metal sulphide also shown in scheme 4.7 and these pathways have been studied as low temperature routes in the production of Ce_2S_3 .

Scheme 4.7 :- Possible Routes to Metal Sulphides from Dithiocarbamates



In many of the methods used to produce Ce_2S_3 there are problems in maintaining the exact stoichiometry, it is thought that the reactions between dithiocarbamate and sulphur or H_2S may help combat any stoichiometry problems that may be encountered.

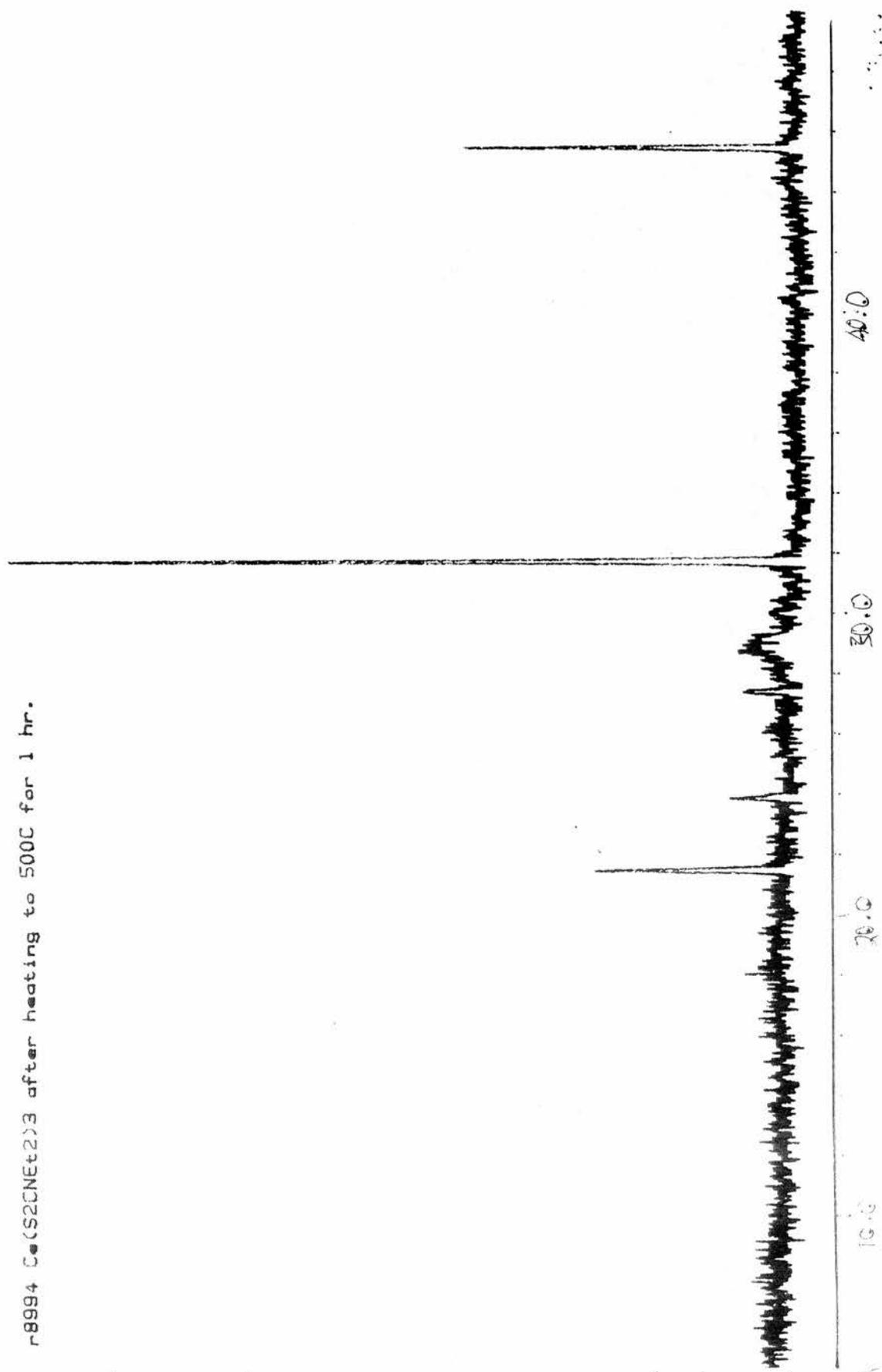
The tris dithiocarbamates, $Ce(S_2CNRR')_3$, were heated to $500\text{ }^\circ\text{C}$ in a stream of nitrogen to allow the complex to decompose and the organic residue to be volatilised and carried by the nitrogen into a cold trap. In all cases, the decomposition of $Ce(S_2CNRR')_3$ leads to a small amount of a black solid, regardless of the substituents, the majority of the organic material subliming away. The FTIR of the black solid shows no or very little organic material present in the samples thus suggesting that the dithiocarbamate has decomposed to leave a carbonised cerium compound. Powder XRD patterns showed an absence of Ce_2S_3 or any known cerium sulphide, figure 4.7 shows the PXRD pattern of the black solid obtained from $Ce(S_2CNHPh)_3$.

The samples were then heated to $500\text{ }^\circ\text{C}$ in a flow H_2S with similar results being obtained. Due to the small amount of solid left it is thought that the cerium dithiocarbamates may have some volatility and therefore are subliming rather than decomposing. Reactions involving sulphur were not carried out at this temperature as it will sublime leaving the cerium dithiocarbamate to undergo a similar reaction to that first attempted. Therefore in an attempt to find out if these complexes are volatile and to produce a truly low temperature method to Ce_2S_3 , low temperature, ($<200\text{ }^\circ\text{C}$) reactions were carried out.

The tris dithiocarbamate solids were heated under vacuum to $180\text{ }^\circ\text{C}$ and the compounds appeared to decompose between $120\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$ slowly going a brown colour as the sample was heated and then turning black as the sample was further heated.

Upon heating $Ce(S_2CNPr^i_2)_3$ under vacuum a black solid appeared at around $130\text{ }^\circ\text{C}$. The initial colour of the solid is bright yellow and darkens in colour above approximately $70\text{ }^\circ\text{C}$ and continually darkens turning black close to $130\text{ }^\circ\text{C}$. The resultant solid still has organic material present as indicated by FTIR studies, figure 4.8.

Figure 4.7 :- Powder XRD Pattern of $Ce(S_2CNHPh)_3$ Heated to 500 °C



A similar result is obtained when $\text{Ce}(\text{S}_2\text{CNPr}^i_2)_3$ is heated in the presence of sulphur however the temperature at which the black solid forms has increase to 140 °C and again the FTIR shows the presence of organic material, figure 4.8.

When the temperature reaches about 120 °C a significant amount of the sulphur sublimes to the top of the vessel, thus leaving a dark yellow brown solid which on further heating turns black. When this reaction is carried out at lower temperatures, 120 °C, and in a closed system with occasional pressure release a different result is obtained. A yellow solid is left which before cooling has an orange tint to it. After the sample was cooled the yellow solid was then dissolved in carbon disulphide, to remove any excess sulphur, and this left a small amount of a black solid. This suggests that either the dithiocarbamate, or resulting product, possibly a thiuram disulphide, is soluble in CS_2 or that some of the dithiocarbamate has sublimed upon opening the flask to release the pressure. However, the most likely explanation is that the cerium complex has decomposed during heating and the organic material has dissolved in the CS_2 . The yellow colour apparent at the end of the reaction before dissolving in CS_2 arises from the presence of excess sulphur.

It is thought when heated in a flow of nitrogen or under vacuum the cerium complex is unstable towards the reductive elimination of thiuram disulphide and thus decomposes leaving a black solid. It was hoped that the presence of sulphur would allow the formation of Ce_2S_3 , perhaps via a trithiocarbamate complex, but this did not appear to be the case. It was also thought that the presence of H_2S gas would help to produce Ce_2S_3 , however, it would appear that higher temperatures are required.

Upon heating $\text{Ce}(\text{S}_2\text{CNPr}^i_2)_3$ to 180 °C in a flow of H_2S gas the solid went brown but never went black. The FTIR of this solid is shown in figure 4.9. When the cerium complex was stirred in toluene the solution was yellow in colour but on addition of H_2S it went immediately brown. After 15 minutes the solution had reverted back to the original yellow colour but on removal of H_2S and the stirring stopped a brown precipitate formed. On exposure to air the colour darkend slightly and a sulphury odour was emitted. The FTIR is similar to those previously obtained, figure 4.8, upon heating $\text{Ce}(\text{dtc})$ complexes.

Figure 4.8 :- FTIR Spectra of $Ce(S_2CNPr_2)_3$ Decomposed in N_2 and S

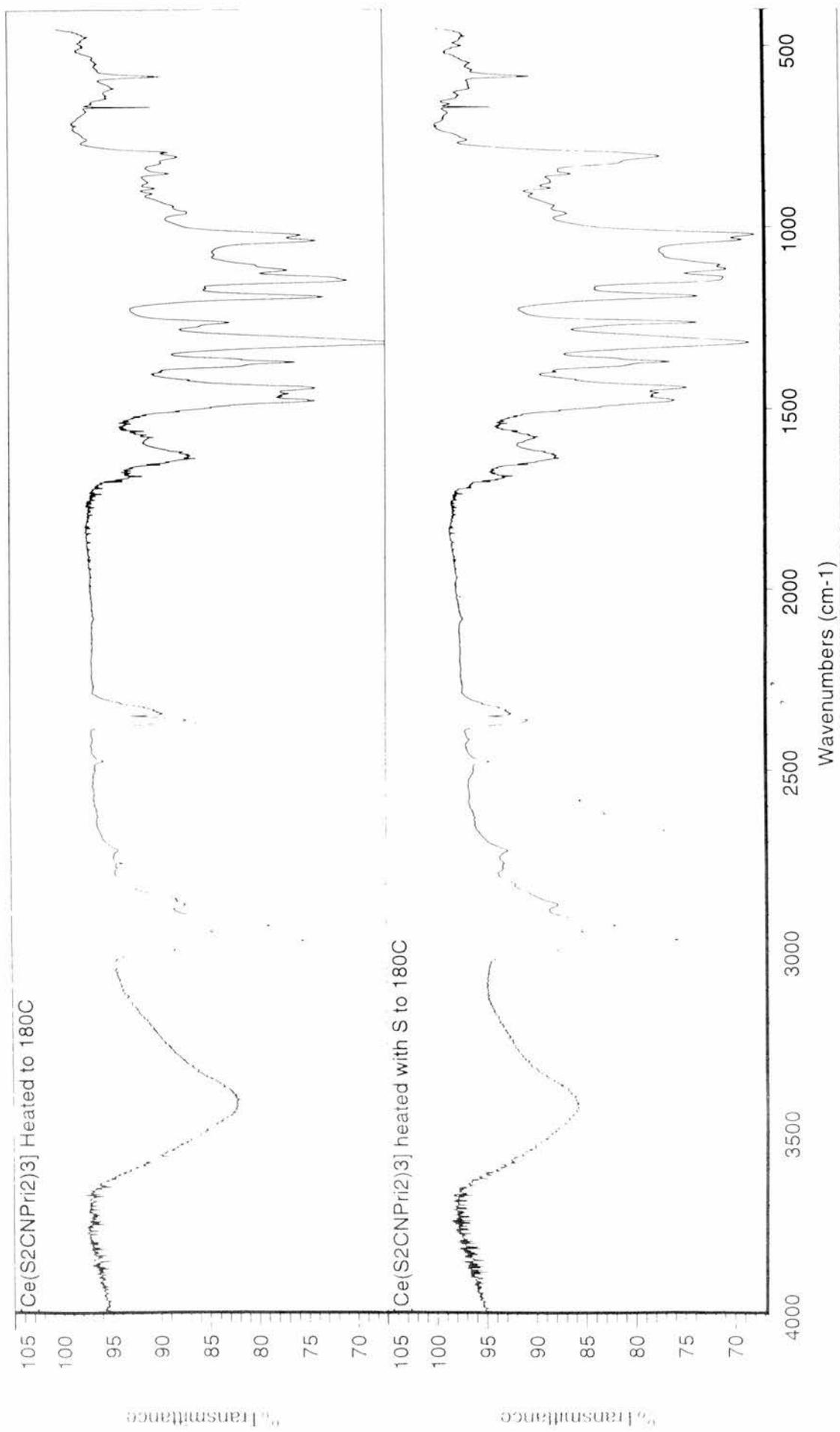
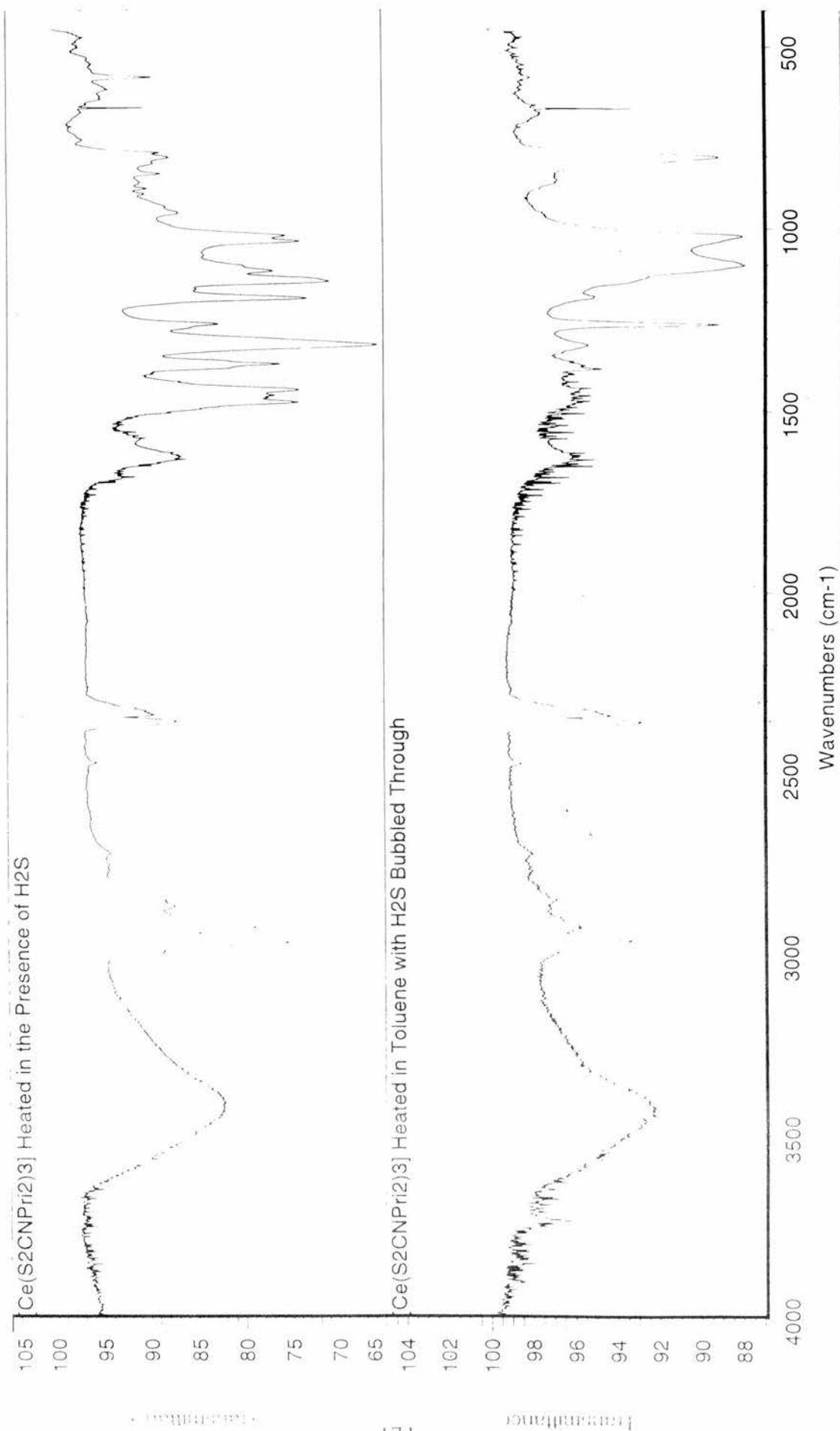


Figure 4.9 :- FTIR Spectra of the Reactions Between H_2S and $\text{Ce}(\text{S}_2\text{CNPri}_2)_3$



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Similar results were obtained for all the $\text{Ce}(\text{S}_2\text{CNRR}')_3$ complexes as well as for the $\text{M}\{\text{Ce}(\text{S}_2\text{CNRR}')_4\}$. For $\text{M}\{\text{Ce}(\text{S}_2\text{CNRR}')_4\}$, the temperatures at which the solid decomposed under vacuum increased.

The reaction of $[\text{NEt}_4:\text{Ce}(\text{S}_2\text{CNHPh})_4]$ and sulphur produced a yellow/brown solid at a temperature of 260 °C and on cooling the colour of the solid darkened becoming more brown. The sample was then dissolved in carbon disulphide to leave a small amount of dark brown solid suggesting that the yellow colour is coming from excess sulphur present. The FTIR of this solid shows that some dithiocarbamate is still present suggesting that a higher temperature will be required to produce Ce_2S_3 than is being currently used.

It has been reported that the temperature regime at which calcium dithiocarbamates are decomposed plays a vital role in the purity of the product, CaS , obtained³². It is thought that a slower rate allows the organic remnants to volatilise before carbonisation of the metal sulphide can occur. The heating regime used in the previous experiments was extremely hard to control accurately and varied significantly depending upon the apparatus used.

TGA experiments were attempted on $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$, $\text{NBu}^n_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$, and $\text{Ce}(\text{S}_2\text{CNHPh})_3$ at a more controlled temperature regime of 10 °C min⁻¹, 5 °C min⁻¹, and 1 °C min⁻¹ in a flow, 100 cm min⁻¹, of nitrogen. Similar results were obtained for the three different heating regimes, figure 4.10 shows the traces of heating $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ at 1 °C min⁻¹ and 5 °C min⁻¹. The TGA spectrum of $\text{NBu}^n_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ is the same as that when the tetraethyl ammonium cation is used, figure 4.11, showing that the composition of the cation plays no role in the decomposition pathway of the cerium dithiocarbamate.

The weight lost from heating the samples is between 75 and 80 %, the exact amount varies slightly with the heating regime, the slower the rate slightly more weight is lost, see figure 4.10. The complex starts to lose weight at just below 100 °C and then falls rapidly tailing off just over 200 °C. The expected weight loss for the samples to produce Ce_2S_3 is approximately 80 % for $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ and 82 % for

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Figure 4.10 :- TGA of $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ Heated at 1 and 5 $^\circ\text{C min}^{-1}$

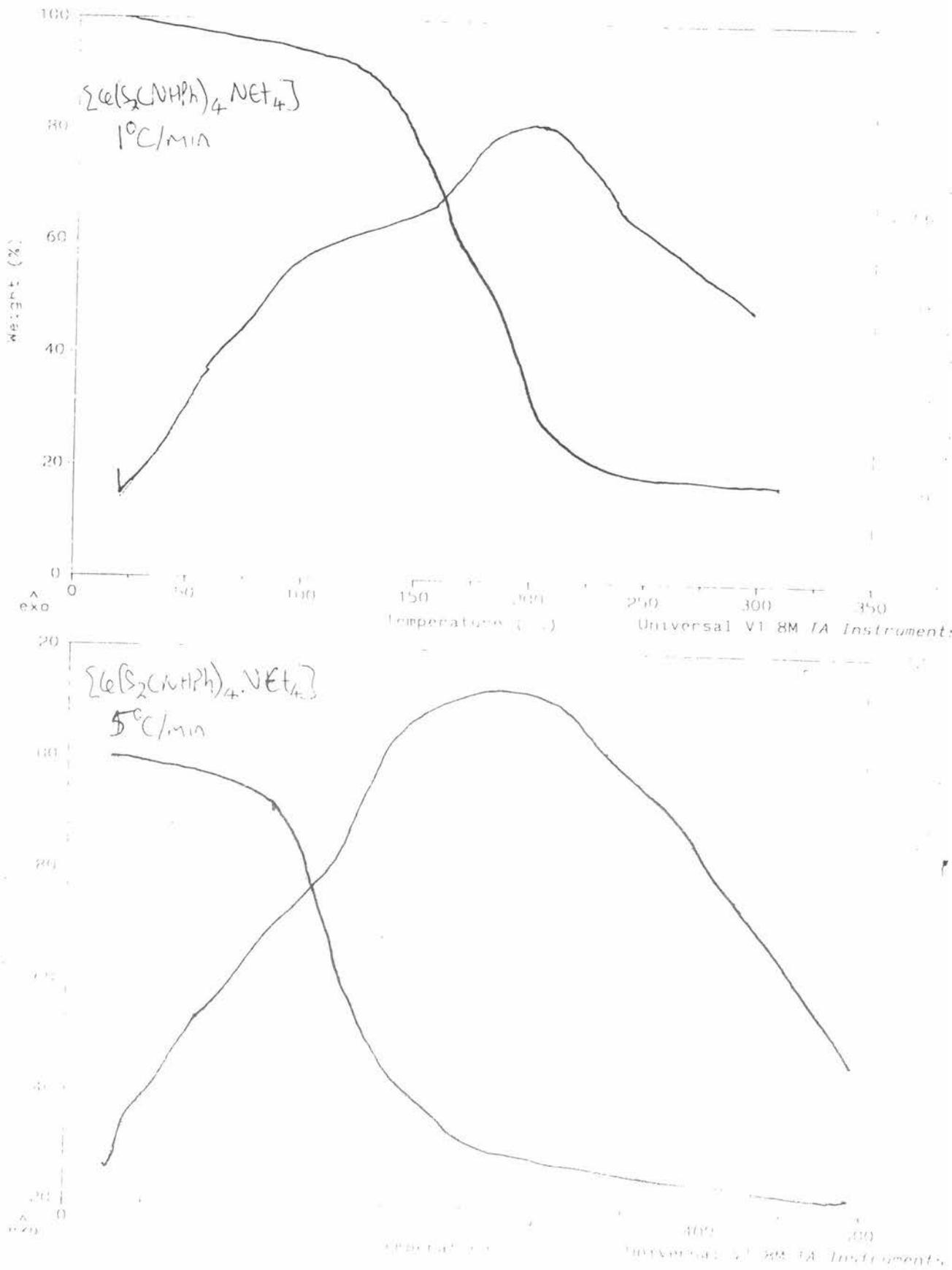
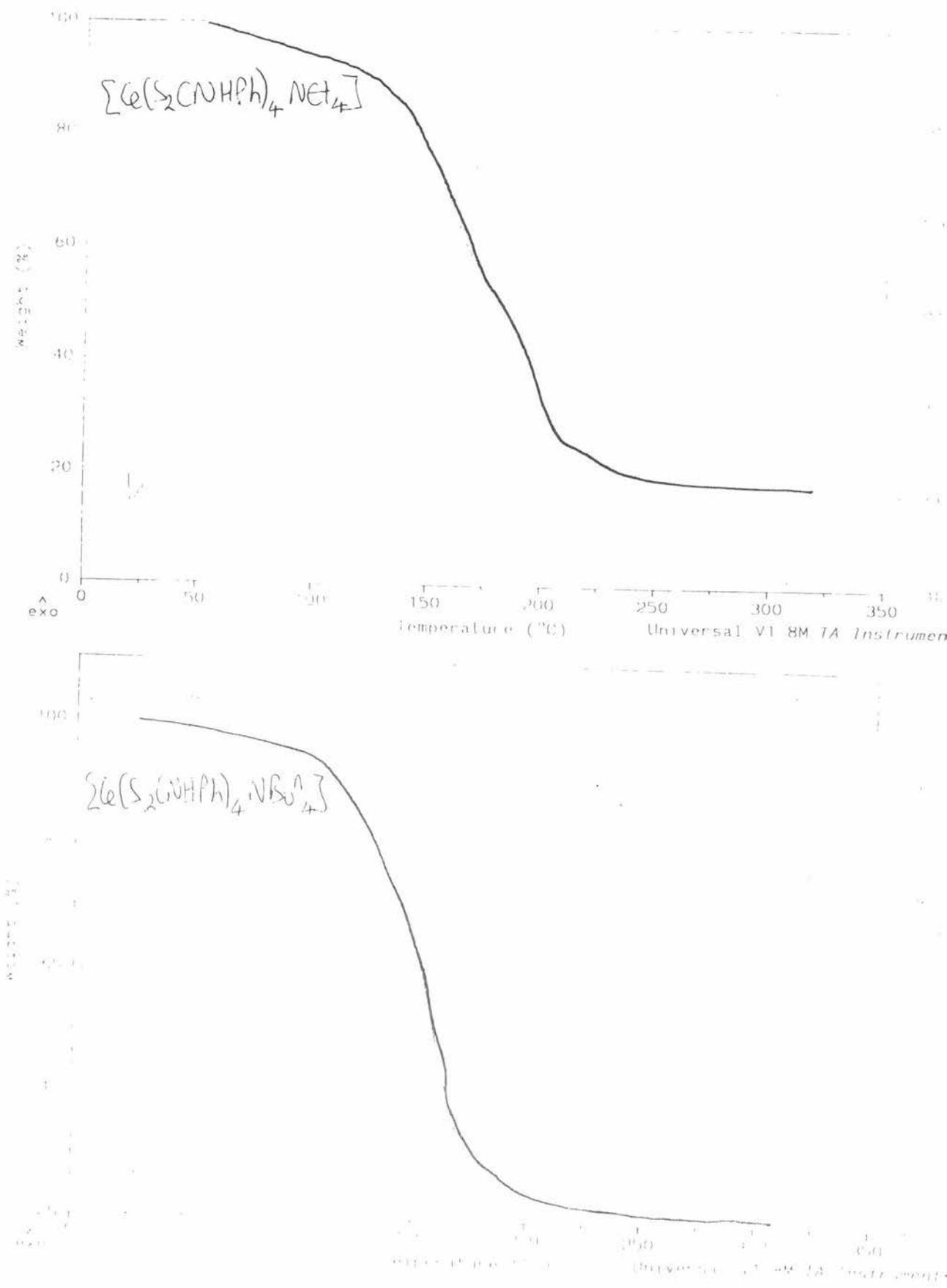


Figure 4.11 :- TGA of $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ and $\text{NBu}^n_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$



$\text{NBu}^n_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$. It can be seen that for the expected weight loss is almost equal to the observed weight loss. However, on removal of the solids from the TGA a black material was left not a yellow orange material as was expected. This result suggests that the ligand is decomposing giving a carbonised product. When heating within a furnace to similar temperatures a black material is formed but is not believed to be cerium sulphide. It is possible that the dithiocarbamate is volatile and sublimes giving rise to the weight loss and the black solid is the decomposed dithiocarbamate.

When $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ was heated in the presence of excess sulphur in the TGA the temperature at which weight loss started increased by 100 °C from just below 100 °C to just below 200 °C and levelling off just above 300 °C, see figure 4.12. In this case excess sulphur is added to the mixture and the weight loss observed is over 90 %. It is thought that the presence of sulphur has increased the decomposition temperature by either preventing the material subliming or by partially reacting with it. The end product is again black in colour.

Upon heating $[\text{Ce}(\text{S}_2\text{CNHPh})_3]$ in the TGA significantly less weight is lost from the sample, figure 4.13, and the rate of weight loss also appears slower than for the tetra dithiocarbamate complexes. The expected weight loss is around 70 % and the observed is only just over 30 %. As before the material removed is black.

These results suggest that either the dithiocarbamate selected is not suitable for producing Ce_2S_3 or that during the heating of the sample Ce_2S_3 is forming but then decomposing due to its poor thermal stability.

In light of the results obtained from the TGA, $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ was decomposed in a tube furnace and the decomposition products analysed by GC-MS. Figure 4.14 shows the GC-MS trace obtained upon heating $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ to 200 °C in a helium atmosphere. The first peak to be observed is attributed to carbonyl sulphide, this has formed due to a small amount of air being present in the system and despite all attempts could not be removed. The next and most intense peak is due to carbon disulphide, the presence of this peak suggests that the dithiocarbamate is decomposing back to its starting constituents and not forming Ce_2S_3 . The next two peaks are dimethyldisulphide and

Figure 4.12 :- TGA of $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ Reacted with Sulphur

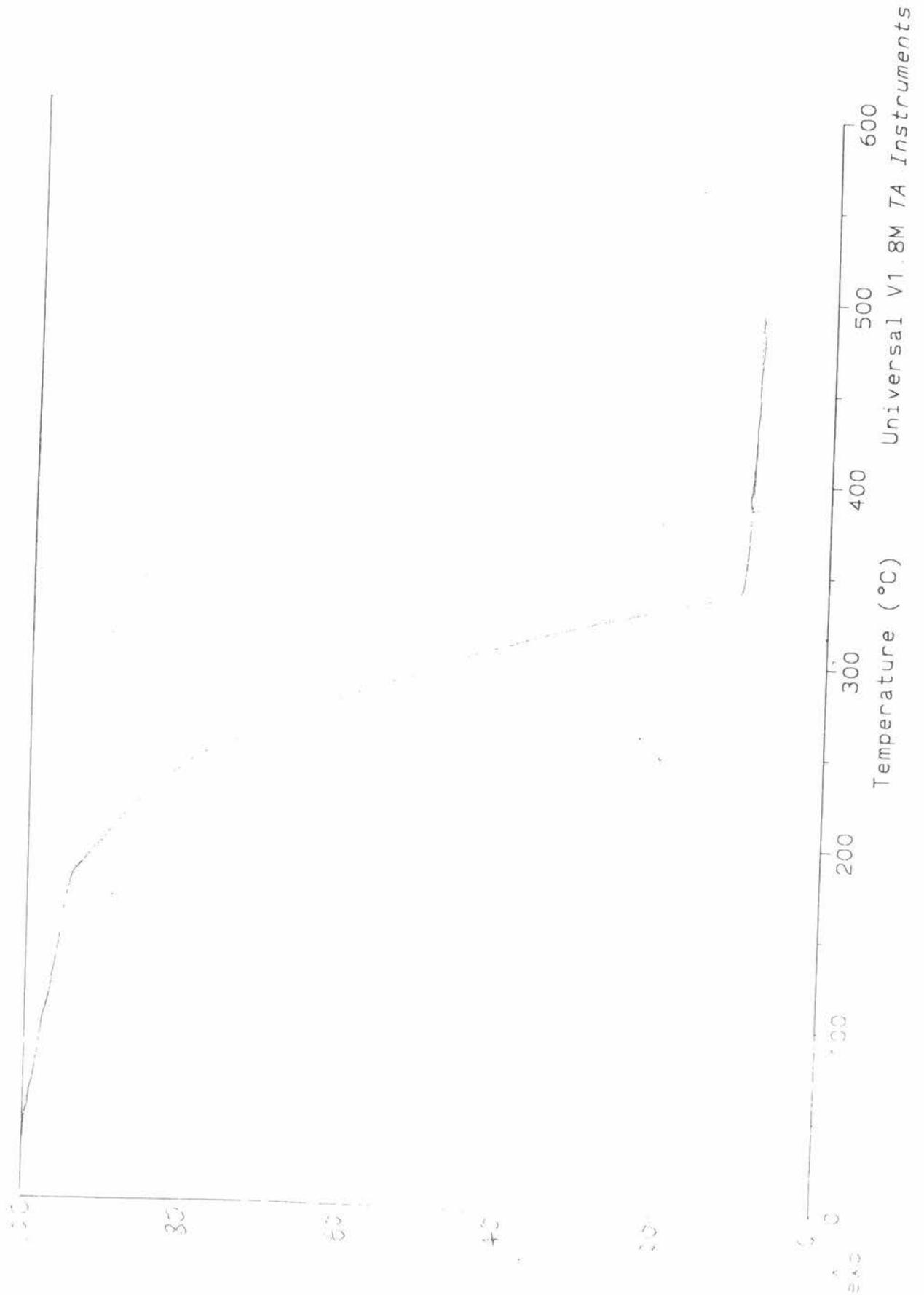
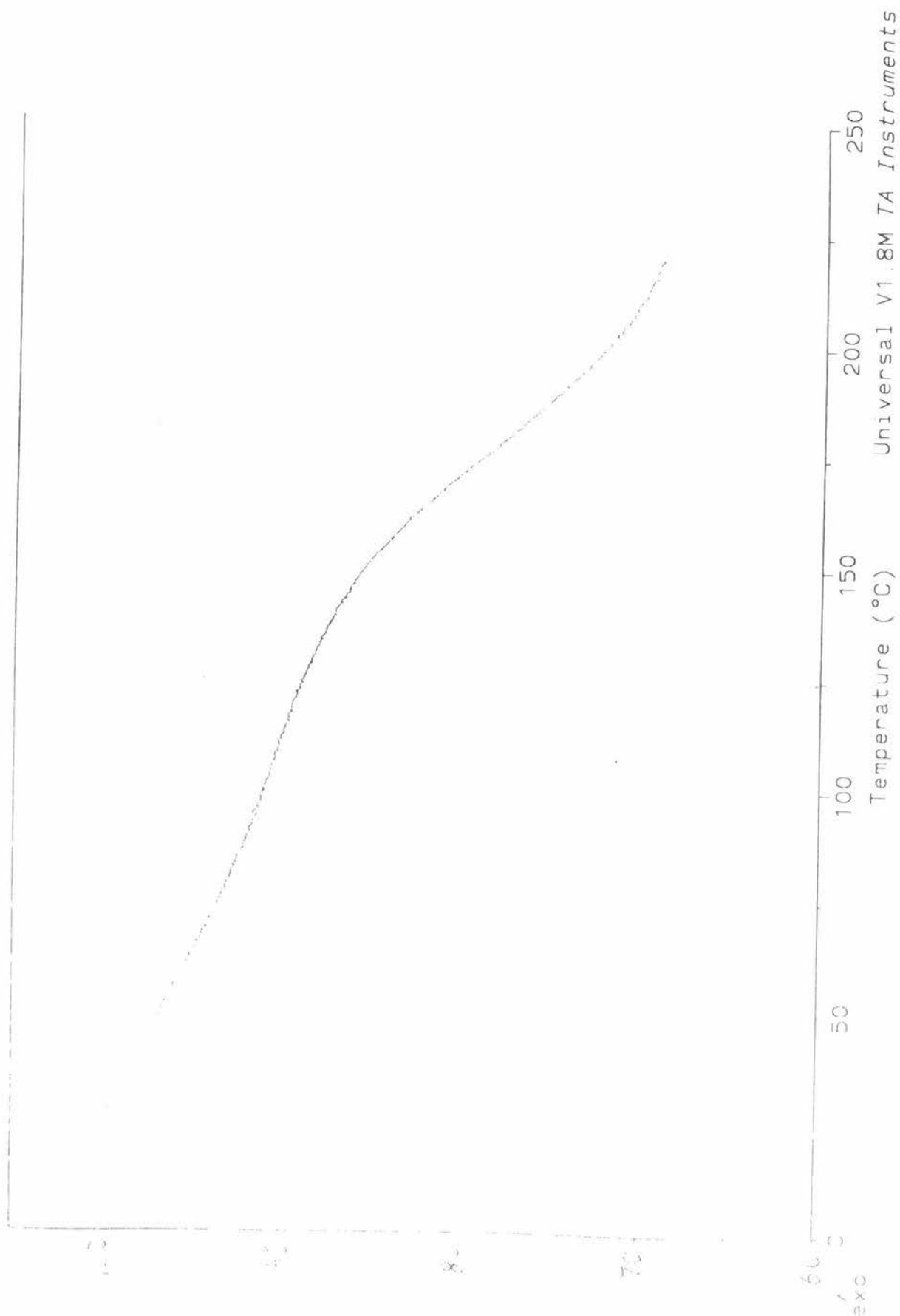
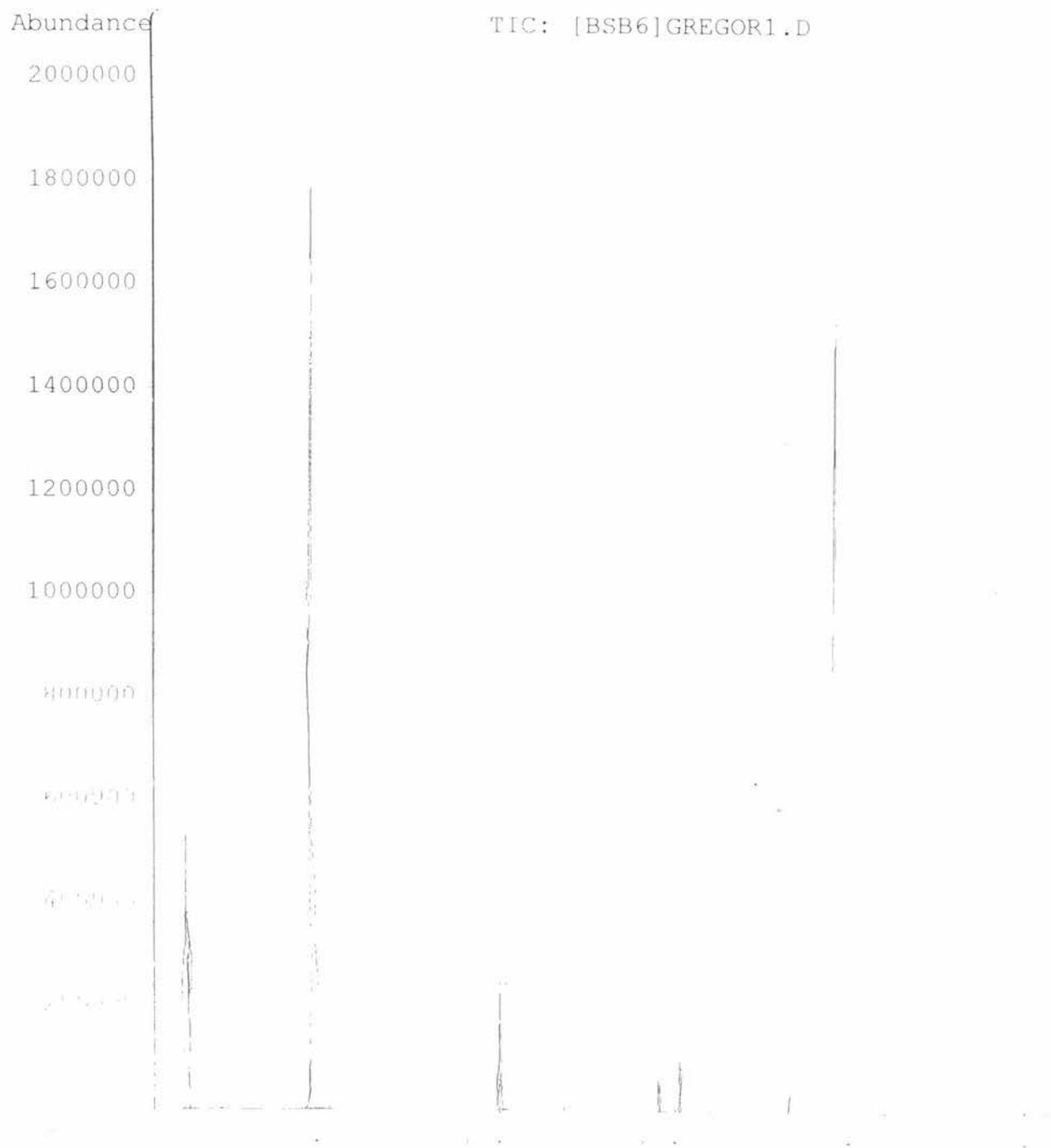


Figure 4.13 :- TGA of $[\text{Ce}(\text{S}_2\text{CNHPh})_3]$



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Figure 4.14 :- GC-MS of $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$ Heated to 200°C



dimethyltrisulphide respectively, these are believed to have formed by carbon disulphide reacting with the remaining dithiocarbamate ligands or with the ammonium cation. The next two peaks in the GC-MS trace are unknown, but are possibly higher sulphides. The last peak observed in the trace is attributed to phenyl isothiocyanate, this product suggests that a sulphur molecule may still be coordinated to the cerium and hence that a cerium sulphide might form.

4.3.0 CONCLUSIONS

From this chapter of work the low temperature route to cerium sulphide is not as easy as was first thought. Due to the air sensitivity of the cerium complexes they are oxidised in the presence of extremely minute amounts of oxygen and, in the cases when the complexes are thermally decomposed, it appears that the presence of water causes a significant problem. For such a route to be possible the presence of oxygen and water must be excluded and even then it is not certain that the cerium complexes will be stable and react to form cerium sulphide. Literature suggests that the best chance of a low temperature route will be from the reaction with either sulphur or hydrogen sulphide. It was hoped that the presence of H_2S would help give a cleaner decomposition of the complexes and leave one form of cerium sulphide this, however, was not the case. In all cases when a temperatures above $400\text{ }^\circ\text{C}$ was used a black precipitate formed believed to be a carbonised product of cerium. When milder temperatures $< 200\text{ }^\circ\text{C}$ were used then a brown solid formed and upon exposure to air it darkened thus the products of the cerium dithiocarbamates with H_2S are air sensitive suggesting that the reaction has not gone to completion. When the reaction mixture is left for longer the same results are obtained. The TGA work carried out on the decomposition despite giving the expected weight loss resulted in a black material forming. The GC-MS of this material suggests that the dithiocarbamates may be decomposing back to their original starting components and that the cerium possibly becomes coordinated to nitrogen rather than sulphur.

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Even if a low temperature route can be formulated there still may be stoichiometric problems to overcome which will probably require another reaction step most likely at an elevated temperature.

4.4.0 EXPERIMENTAL

4.4.1 GENERAL PROCEDURES

All operations, unless stated, were performed under a dry deoxygenated nitrogen atmosphere purified by passing through a series of columns consisting of Cr^{2+} on silica. Manipulations were carried out using standard Schlenk and catheter tubing techniques. All hydrocarbon and ethereal solvents were dried and distilled over sodium diphenylketyl at atmospheric pressure prior to use. Cerium chloride heptahydrate was purchased from Avocado and dried, when necessary, using a literature method³⁶. Hydrogen sulphide gas was purchased from Matheson Gas Products and used neat without purification. All other chemicals used were purchased from Aldrich, Avocado, BDH, Fluka, Strem or Lancaster and in the case of liquids they were degassed prior to use.

Infrared data were recorded on a Nicolet 460 Protege spectrometer, NMR data were recorded on a Bruker AM 300 spectrometer in 5 mm glass tubes. Elemental analysis data were obtained at the University of St. Andrews. Thermogravimetric analysis (TGA) were carried out on a Thermal Analyst 3100, SDT 2960 simultaneous DTA-TGA, with a flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$. GC-MS data were collected by heating the sample in a carbolite MTF 12/38A tube furnace with a flow rate of helium at $200\text{-}300 \text{ cm}^3 \text{ min}^{-1}$, the volatile products passed immediately into the gc via a gas sampling valve and were separated on a HP5MS column. The products were identified on a Hewlett-Packard HP5890 series II mass spectrometer. All data were compared with the literature, where possible.

4.4.2 SYNTHESIS OF CERIUM COMPLEXES

Synthesis of $[\text{Ce}(\text{thd})_3\text{phen}]^{21}$

1,10-Phenanthroline (0.87 g, 4.4 mmol) was added to a solution of cerium chloride heptahydrate (1.49 g, 4 mmol) in ethanol (50 cm³). To this solution a second solution, of 2,2,6,6-tetramethyl-3,5-heptanedione (thd) (2.14 g, 11.6 mmol) in ethanol (50 cm³) and aqueous sodium hydroxide (2.9 cm³, 4 mol dm⁻³) was added slowly. The products were filtered and dried under reduced pressure. Synthesis of $[\text{Ce}(\text{fdh})_3\text{phen}]$ was carried out using the above procedure by replacing the thd with 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (fdh) (2.28 g, 11.6 mmol).

FTIR data for $[\text{Ce}(\text{thd})_3\text{phen}]$, KBr disc, 2960, 2898, 2855, 1580, 1540, 1505, 1450, 1410, 1360, 1230, 1190, 1130, 870, 820, 790, 760, 710, 600, 480, 410 cm⁻¹.

FTIR data for $[\text{Ce}(\text{fdh})_3\text{phen}]$, KBr disc, 2980, 2900, 2870, 1610, 1580, 1535, 1510, 1480, 1420, 1390, 1360, 1300, 1245, 1220, 1190, 1160, 1130, 1100, 960, 930, 860, 850, 790, 770, 730, 725, 680, 575, 475 cm⁻¹.

Synthesis of $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]^{40}$

Potassium bistrimethylsilylamide (60 cm³ of 0.5 mol dm⁻³, 30 mmol) was added slowly to a stirred suspension of dried cerium chloride (2.465 g, 10.0 mmol) in THF. The mixture was then left to stir for 16 h before removal of the solvent in vacuo. The solid was then extracted with pentane and filtered before removing the solvent under vacuum to leave a yellow/brown solid.

4.4.3 ATTEMPTED SYNTHESIS OF CERIUM SULPHIDE, PART I¹⁹

The cerium complex, $[\text{Ce}(\text{thd})_3\text{phen}]$, $[\text{Ce}(\text{fdh})_3\text{phen}]$, $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]$, or $[\text{Ce}(\text{iPrCp})_3]$, (1 mmol), was dissolved in toluene, (10 cm⁻³), and the solution stirred

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rapidly. If required the solution was heated to temperature using an oil bath and then H₂S gas was slowly bubbled through. Copper sulphate bubblers were used to prevent any excess H₂S polluting the atmosphere, when all the bubblers had turned black the reaction was stopped assuming that any reaction would be complete.

In all the reactions carried out a precipitate formed shortly after exposure to H₂S. In the room temperature reaction using the cerium complex, [Ce(thd)₃phen] or [Ce(ⁱPrCp)₃], a yellow precipitate formed. However on removal of the solvent the colour deepened and eventually turned brown. In all other cases, even when elevated temperatures were used for [Ce(thd)₃phen] or [Ce(ⁱPrCp)₃] the precipitate was brown. In most cases the FTIR of the brown precipitate formed resembles that of the starting material, except when very air sensitive starting materials are used.

Varying concentrations and solvents, the cerium complexes were found to have low solubility in most solvents, were used with similar results.

It appears that on addition of H₂S gas it displaces the cerium complex, which has low solubility in most solvents. The precipitation of the cerium complex therefore does not allow enough time for a complete reaction to produce cerium sulphide, only a partial reaction can take place.

4.4.4 SYNTHESIS OF CERIUM DITHIOCARBAMATES

Synthesis of NH₄S₂CNRR' salts²⁵

Carbon disulphide (6 cm³, 7.6 g, 0.1 mol) was added to a mixture of ice cold amine (0.1 mol), (aniline, dipropylamine, diisopropylamine), and concentrated aqueous ammonia (30 cm³) with stirring over a 30 min period. The mixture was then stirred for a further 1 h during which time a yellow white solid precipitated. The solid product was collected by filtration, washed with small portions of ethanol and then dried over phosphorous pentoxide under vacuum.

NMR data were obtained for the samples;

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^1H , CD_3OD , $\text{NH}_4\text{S}_2\text{CNHPh}$; δ 7.35 (m, aromatic H), 7.2 (m, aromatic H), 7.08 (m, aromatic H), 6.7 (m, aromatic H), 4.9* (s, N-H) ppm.

^1H , CD_3OD , $\text{NH}_4\text{S}_2\text{CNPr}^i_2$; δ 4.9* (s, N-H), 3.45 (m of 7, C-H), 1.35 (d, 2 CH_3) ppm.

^1H , CD_3OD , $\text{NH}_4\text{S}_2\text{CNPr}_2$; δ 4.9* (s, N-H), 3.95 (m), 2.85 (m), 1.75 (m), 1.0 (t), 0.9 (t?) ppm.

* This peak is believed to be due to an exchange process between water and the ammonium ion.

Elemental analysis of the samples is listed in the table below with the expected values given in parenthesis.

Sample	% C	% H	% N
$\text{NH}_4\text{S}_2\text{CNHPh}$	45.13 (44.90)	5.38 (5.38)	14.90 (15.04)
$\text{NH}_4\text{S}_2\text{CNPr}^i_2$	43.24 (43.26)	9.57 (9.33)	14.16 (14.41)
$\text{NH}_4\text{S}_2\text{CNPr}_2$	44.20 (43.26)	9.66 (9.33)	14.38 (14.41)

Synthesis of $\text{NH}_2\text{RR}'\text{S}_2\text{CNRR}'$ salts

Carbon disulphide (6 cm^3 , 7.6 g, 0.1 mol) was added to a mixture of ice cold amine (0.2 mol), (aniline, t-Butylamine, diisopropylamine, methylhexylamine) with stirring over a 30 min period. The mixture was then stirred for a further 1 h during which time a yellow white solid precipitated. The solid product was collected by filtration, washed with small portions of ethanol and then dried over phosphorous pentoxide under vacuum.

NMR data were obtained for the samples;

^1H , CD_3OD , $\text{H}_3\text{NPh:S}_2\text{CNHPh}$; δ 7.37 (m, aromatic H), 7.19 (m, aromatic H), 4.9* (s, N-H) ppm.

^1H , CD_3OD , $\text{H}_3\text{NBu}^t\text{S}_2\text{CNHBU}^t$; δ 4.9* (s, N-H), 1.5 (t, 3 N-C- CH_3), 1.2 (s, 3 S_2C -N-C- CH_3) ppm.

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^1H , CD_3OD , $\text{H}_2\text{NPr}^i_2\text{S}_2\text{CNPr}^i_2$; δ 4.9* (s, N-H), 3.0 (m of 7, C-H), 1.1 (d, 2 CH_3) ppm.

* This peak is believed to be due to an exchange process between water and the ammonium ion.

Elemental analysis of the samples is listed in the table below with the expected values given in parenthesis.

Sample	% C	% H	% N
$\text{H}_3\text{NPhS}_2\text{CNHPh}$	59.09 (59.51)	4.99 (5.38)	11.01 (10.68)
$\text{H}_3\text{NBu}^t\text{S}_2\text{CNHBu}^t$	48.05 (48.60)	10.16 (9.97)	12.14 (12.60)
$\text{H}_2\text{NPr}^i_2\text{S}_2\text{CNPr}^i_2$	56.19 (56.06)	10.42 (10.86)	9.98 (10.06)

Synthesis of $\text{NaS}_2\text{CNRR}'$ salts³⁵

Sodium hydroxide (0.1 mmol) was dissolved in methanol (20 cm^3) and then the amine, (aniline, methylhexylamine 0.1 mol), was slowly added to the solution. Carbon disulphide (6 cm^3 , 7.6 g, 0.1 mol) was then added to the solution with stirring over a 30 min period. The mixture was then left to stir for a further 1 h before removal of the solvent under vacuum to leave a yellow white solid. The solid was washed with small portions of ethanol and then dried over phosphorous pentoxide under vacuum.

NMR data were obtained for the samples;

^1H , CD_3OD , NaS_2CNHPh ; δ 7.25 (m, aromatic H), 6.85 (m, aromatic H), 5.1* (s, N-H) ppm.

^1H , CD_3OD , $\text{NaS}_2\text{CNMeHex}$; δ 5.1* (s, N-H), 4.3 (t), 3.65 (s), 1.9 (m), 1.55 (s), 1.1 (t) ppm.

Synthesis of Ce(S₂CNRR')₃**Part I**

To a solution of cerium chloride heptahydrate (0.373 g, 1 mmol) in methanol (50 cm³) was added a solution of the ammonium or sodium dithiocarbamate (3 mmol) in methanol (50 cm³). Shortly after addition of the dithiocarbamate the solution went rapidly black. The experiment was repeated using degassed solvents but the same result occurred. On using a closed system a yellow precipitate formed, however, on removal of the solvent it turned black, decomposing very rapidly in the presence of air.

Part II^{23,24}

To a solution of anhydrous cerium chloride (1 mmol) in ethanol (5 cm³) was added by catheter to a solution of the ammonium or sodium dithiocarbamate (3 mmol) in ethanol (5 cm³). The mixture was stirred for 5-10 min before removal of the solvent under vacuum. The product was then extracted into cold acetonitrile and the solution filtered using catheter techniques to remove the chloride salt. The product was then precipitated by adding ether to the solution and then the solvent removed by catheter techniques before drying the solid under vacuum. The solid was then stored in a glove box in an argon atmosphere.

It is extremely important at all stages to exclude oxygen from the system. The formation of the cerium dithiocarbamate does occur in the presence of water but on removal of the solvent the material becomes unstable and slowly turns black.

FTIR data, neat material, [Ce(S₂CNHP_h)₃]; 2980, 2920, 1520, 1450, 1310, 1290, 1110, 1050, 1005, 805, 700 cm⁻¹. Elemental Analysis data, (expected in parenthesis, % C 39.11 (39.11), % H 2.791 (2.81), % N 6.79 (6.52).

FTIR data, neat material, [Ce(S₂CNHBu^t)₃]; 2975, 2905, 1295, 1125, 1060, 1025, 815 cm⁻¹, very weak spectrum.

FTIR data, neat material, [Ce(S₂CNPrⁱ)₃]; 2980, 2910, 1590, 1430, 1390, 1305, 1195, 1130, 1100, 1030, 950, 860, 800, 595 cm⁻¹.

FTIR data, neat material, $[\text{Ce}(\text{S}_2\text{CNMeHex})_3]$; 2960, 2910, 1290, 1200, 1100, 1050, 810 cm^{-1} , weak spectrum.

Synthesis of $\text{M}\{\text{Ce}(\text{S}_2\text{CNRR}')_4\}^{25}$

Where $\text{M} = \text{NR}_4$

To a solution of cerium chloride heptahydrate (0.373 g, 1 mmol) in methanol, (20 cm^3) was added a solution of the ammonium dithiocarbamate (4 mmol) and tetraethyl or tetrabutylammonium iodide (1 mmol) in methanol (20 cm^3). As with the trisdithiocarbamate cerium complexes, the addition of the two solutions results in a black coloured solution. This is due to the presence of oxygen.

For $\text{M} = \text{NH}_2\text{RR}'$ or Na

To a solution of cerium chloride heptahydrate (0.373 g, 1 mmol) in methanol (20 cm^3) was added a solution of the $\text{NH}_2\text{RR}'\text{S}_2\text{CNRR}'$ or $\text{NaS}_2\text{CNRR}'$ (4 mmol) in methanol (20 cm^3). After 10 min the mixture was filtered, the solid washed with methanol and dried under vacuum over P_4O_{10} . The solid was then stored in a glove box in an argon atmosphere.

It is noted that in some cases this reaction was successful especially in the case where $\text{R}=\text{R}'=\text{Pr}^i$. However, in most cases upon removal of the solvent from the precipitate it turned black, with the area touching the glass flask staying yellow showing that the surface is being oxidised.

Anhydrous Synthesis of $\text{M}\{\text{Ce}(\text{S}_2\text{CNHPh})_4\}$

To a solution of anhydrous cerium chloride (1 mmol) in ethanol (20 cm^3) was added a solution of the ammonium or sodium dithiocarbamate (4 mmol) in ethanol (20 cm^3). Tetraethyl or tetrabutylammonium iodide (1 mmol) was added if $\text{NH}_4\text{S}_2\text{CNHPh}$ was used. If NaS_2CNHPh or $\text{H}_2\text{NRR}'\text{S}_2\text{CNHPh}$ were used then no ammonium salt was

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required. The mixture was stirred for 5-10 min before removal of the solvent under vacuum. The product was then extracted into cold acetonitrile and the solution filtered using catheter techniques to remove the sodium or ammonium salt. The product was then precipitated by adding ether to the solution and then the solvent removed by catheter techniques before drying the solid under vacuum. The solid was then stored in a glove box in an argon atmosphere.

FTIR data, KBr disc of $\text{NEt}_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$; 3400, 3280, 3120, 2990, 2860, 1705, 1595, 1545, 1499, 1460, 1400, 1310, 1250, 1190, 1110, 1005, 930, 790, 725, 660, 590 cm^{-1} .

FTIR data, KBr disc of $\text{NBu}^n_4[\text{Ce}(\text{S}_2\text{CNHPh})_4]$; 3425, 3295, 3210, 3180, 3110, 3050, 3020, 2980, 2920, 2880, 1600, 1540, 1499, 1465, 1305, 1265, 1185, 1105, 1010, 950, 810, 790, 715, 700, 610 cm^{-1} .

4.4.5 ATTEMPTED SYNTHESIS OF CERIUM SULPHIDE, PART II

In a Nitrogen Atmosphere

The cerium dithiocarbamate salt was placed in a flask and slowly heated to 180 °C. The yellow solid darkened slowly turning brown and then black around 130 °C, depending upon the substituents. The resultant solid was filtered and washed with ethanol.

Upon heating the cerium dithiocarbamate to 500 °C a black solid was obtained.

In a Sulphur Atmosphere

The cerium dithiocarbamate, (2 mmol), was ground together with excess sulphur and placed in an evacuated flask. The flask was slowly heated up to 180 °C and the yellow coloured powder slowly turned darker going brown around 140 °C and then turning black just before 180 °C.

When $\text{NH}_4:\text{Ce}(\text{S}_2\text{CNHPh})_4$ was rapidly heated to 260 °C the solid remained a dark yellow in colour but is believed to be mainly sulphur.

In a Hydrogen Sulphide Atmosphere

The cerium dithiocarbamate, (2 mmol), was placed in a quartz boat within a furnace. The furnace was evacuated and then heated to 500 °C, H_2S gas was passed over the cerium complex for 1 h. The set up was then cooled and the resultant product removed and washed with ethanol leaving a black solid.

When the cerium complexes were heated to 180 °C the solid obtained was brown in colour and the FTIR showed the presence of some organic material.

By Bubbling Hydrogen Sulphide Through a Solution

Upon heating the cerium complex in a solution of toluene and then bubbling H_2S gas, the yellow solution immediately went brown. After 15 min the solution turned slowly yellow but, upon stopping the flow of H_2S and bubbling nitrogen, a brown precipitate forms. This precipitate darkens in colour upon removal of the solvent or contact with air and releases a sulphury odour. The FTIR is similar to that of the sample heated to 180 °C when no solvent is used.

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CHAPTER 5

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SUMMARY OF CONCLUSIONS

5.1.0 SUMMARY OF AIMS AND ACHIEVEMENTS

The initial aims were to devise a method of production of copper phthalocyanine (CuPc), to produce a form suitable for pigmentation and at the same time allow control of particle size. The reasons for this are to remove costly and time consuming finishing processes and with the hope of changing the colour to increase the profitability of CuPc as a pigment.

A gas phase reaction for the production of CuPc was devised which involved the designing of new apparatus to allow such a reaction to proceed, see chapter 2. Taking into consideration all the reaction conditions, low pressure, high flow rate, volatility and different sublimation rates of the starting materials, the design of the apparatus and getting five molecules in the right place at the right time it was an ambitious undertaking to attempt a gas phase reaction. Despite the difficulties success was achieved and CuPc was produced by a gas phase reaction although in very low yields and impure.

Solid state reactions should the oxidation state of the copper plays an important role in the reaction. It was shown that a small amount of copper (II) is required in the absence of oxygen. The role of the ammonium molybdate catalyst is believed to catalyse the reaction between phthalic anhydride and urea although it may help with cleaner decomposition of the copper source thus accounting for the purer samples produced when the catalyst is employed.

It had been hoped that a successful gas phase reaction would have allowed additives to be added in the gas phase to allow control of the particle size. As is this was not the case alternative methods were studied. In nanometre sized particles capping methods are used to control the particle size and one such method is zeolite capping. Zeolites were selected because it was hoped that only one or two molecules would fit within the cage structure thus controlling the size of the CuPc particles.

In all nine different zeolite-CuPc samples were produced from using three different zeolites, (sodium zeolite-X and Y-2 and protonated zeolite-Y), and three different synthetic techniques, (ship in a bottle, sublimation of CuPc onto the zeolite and grinding

all the starting materials together in a solid state type reaction). In eight cases the resultant product obtained was green in colour with only one being blue.

A vast number of different analytical techniques were used to determine whether the CuPc formed within the zeolite and if any structural or electronic changes had occurred which might explain the resultant colour change.

Transmission electron microscopy, powder X-ray diffraction and thermogravimetric analysis results showed that some CuPc was present on the surface. Resonance Raman spectroscopy showed that the CuPc was structurally intact and that the colour did not result from either substitution on the ring or from protonation. The visible spectrum of the samples showed that for the zeolite-CuPc1 (ship in a bottle method), and for zeolite-CuPc3 (solid state method), a splitting of the Q-bands resulted. The splitting gap was a result of a deviation from D_{4h} symmetry and was found to be dependant upon the environment in which the CuPc was in. For the zeolite-CuPc2 (sublimation method), samples only a single band was observed in the visible spectrum. It is thought that this arises from the formation of a thin film of CuPc only a few molecules thick coating the zeolite. It is thought that this is what gives rise to the green colour in all cases and that for the cases where a splitting of the Q band occurs small lumps of CuPc have formed giving rise to the spectrum. This is backed up by the photographs taken from the resonance Raman samples.

It had been hoped that the control of CuPc particle sizes would have led to other colours of CuPc being produced, namely towards the yellow, orange and red end of the colour range.

Cerium sulphide is a new orange/yellow pigment which is currently replacing the heavy metal cadmium red pigments. It was hoped that a low temperature route for its production would be achieved thus reducing its production costs.

Other metal sulphides, such as CdS, ZnS and CaS can be produced at relatively low temperatures by the decomposition of the metal dithiocarbamate. Cerium analogues were synthesised with great difficulty, complexes are extremely air sensitive. The samples are

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water stable however water was excluded as much as possible so that no oxygen was present upon decomposition of these samples.

The cerium dithiocarbamates were decomposed in three different environments, nitrogen, sulphur and hydrogen sulphide. In all cases when temperatures above 400 °C were used a black precipitate formed and when milder temperatures < 200 °C were used then a brown solid formed and upon exposure to air it darkened thus the products of the cerium dithiocarbamates are air sensitive suggesting that the reaction has not gone to completion. Even if a low temperature route can be formulated there still may be stoichiometric problems to overcome which will probably require another reaction step most likely at an elevated temperature.