Studies on polynuclear copper (II) complexes

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STUDIES ON POLYNUCLEAR

COPPER (II) COMPLEXES

by

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A Doctoral Thesis

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for the award of

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ABSTRACT

A study has been made of the copper catalyst employed in the

oxidative coupling of phenols and also of some polynuclear copper (II)

complexes which are closely related to the catalyst system.

The preparation of pyridine complexes of copper (I) halides and

their characterisation by infrared spectra is described and the nature

of these complexes in the solid state and in solution discussed.

The preparation and properties of several new tetranuclear

copper (II) complexes of the type Cu_4OX_64L, where X is Cl or Br and L

is a monodentate ligand, are described and, in addition, several of

these tetranuclear complexes containing mixed halide bridges have been

prepared for the first time and characterised. In theory, several of

these mixed halide complexes should exhibit structural isomerism, and

the two isomers of the complex $Cu_4OCl_2Br_44py$ have been positively

identified from physical measurements. Tetranuclear copper (II)

complexes have been shown to undergo halide exchange reactions in

solutions and from conductivity studies it is postulated that these

complexes may well be considerably dissociated in solvents such as

nitromethane. In addition, tetranuclear complexes with pyridine

ligands have been shown to undergo redox decomposition reactions at

temperatures above 150°C to yield copper (I) halide and a halopyridine.

The hydrolysis of three tetranuclear copper complexes has been

investigated and the products appear to be three new basic copper (II)

salts which readily dehydrate in solution to form the original

cluster complex.

The oxidation of copper (I) halide-pyridine complexes has been

studied in some detail and the relationship between the oxidation products

and tetranuclear copper (II) complexes is fully discussed. It is

(iii)

postulated that a cluster complex of the type $Cu_4O(OH)_2Cl_4 4py$

is initially formed from the oxidation of a copper (I) halide-pyridine

mixture or complex and that this tetranuclear compound is the active

catalyst for the oxidation of phenols. This catalyst complex has not

been isolated due to a fast hydrolysis reaction it apparently undergoes

in the presence of water vapour.

A reaction scheme for the oxidative coupling of phenols, involving

a tetranuclear copper (II) catalyst is discussed and shown to be viable

in terms of the known properties of the catalyst system, and the

kinetics of polymer formation.

In addition, a brief study of some mixed halide complexes of

copper (II) of the type $Cu_xCl_yBr_z$npy is described and possible

structures for these compounds are discussed.

PUBLICATION

The following paper has been published on the work described

in Chapter Four of this thesis:

"Preparation of $Cu_4OCl_3Br_34py$, a polynuclear copper complex

with mixed halide bridges". By D.S. Brown, T.G. Hopkins and

A.H. Norbury. Inorganic and Nuclear Chemistry Letters, 1973,
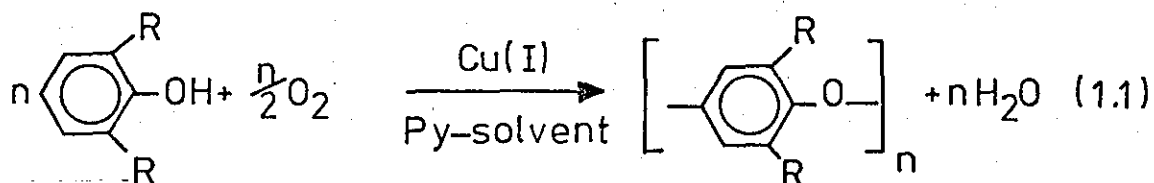
<u>9</u>, 971.

CONTENTS

CHAPTER ONE

INTRODUCTION

Amine complexes of copper salts have been used extensively as catalysts in oxidative coupling reactions ever since Hay reported the preparation of high molecular weight polyphenylene ethers using a copper (I)-pyridine catalyst in 1959(1). Hay found that 2,6-disubstituted phenols could be oxidatively coupled to yield polyethers (C-O coupling) according to equation 1.1.

$$ n\left(\right)\!\!\begin{array}{c}R\\-OH\\R\end{array} + \tfrac{n}{2}O_2 \quad \xrightarrow[\text{Py-solvent}]{\text{Cu(I)}} \quad \left[-\left(\right)\!\!\begin{array}{c}R\\-O-\\R\end{array}\right]_n + nH_2O \quad (1.1) $$

A side reaction involving C-C coupling results in the formation of some tetramethyldiphenoquinone.

Poly (2,6-dimethylphenylene oxide) (PPO) is now produced commercially (2) and has excellent electrical insulating properties and good resistance to chemical attack. Copper-amine catalyst systems have also been used to prepare poly (disulphides) (3), Poly (acetylenes) (4) and azo polymers (5) according to equations 1.2 to 1.4

$$ nHS\text{-}R\text{-}SH + n/2O_2 \xrightarrow[\text{amine}]{\text{Cu(I)}} (\text{-}S\text{-}R\text{-}S)_n + nH_2O \qquad (1.2) $$

$$ n \left(\right)\!\!\begin{array}{c}\text{-}C\equiv CH\\HC\equiv C\end{array} + \tfrac{n}{2}O_2 \xrightarrow[\text{py}]{\text{CuCl}} \left[\left(\right)\text{-}C\equiv C\text{-}C\equiv C\text{-}\right]_n + nH_2O \quad (1.3) $$

$$ nH_2N\text{-}Ar\text{-}NH_2 + nO_2 \xrightarrow[\text{amine}]{\text{Cu(I)}} [\text{-}Ar\text{-}N = N\text{-}]_n + 2nH_2O \qquad (1.4) $$
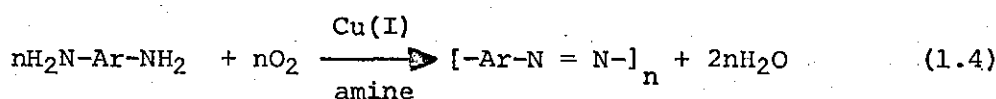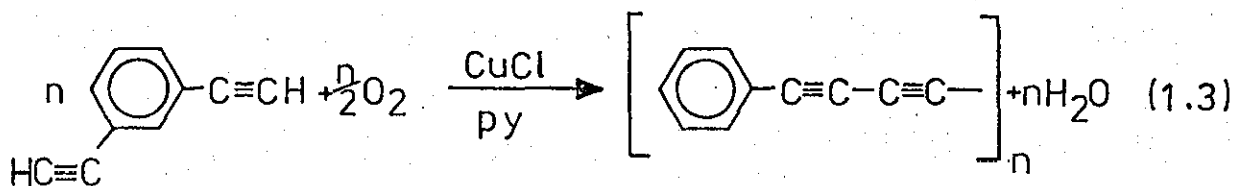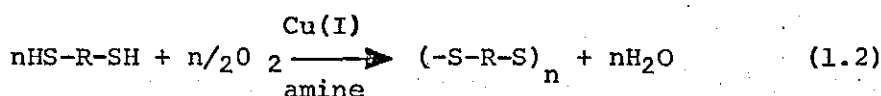
These polymers also find commercial applications in the plastics industry. In recent years oxidative coupling as a synthetic technique

has had considerable use, particularly in the field of natural product chemistry: the role of oxidative coupling in the biosynthesis of alkaloids and lignin has been recognised (6). In addition, the copper-amine catalyst system has kinetic and mechanistic similarities with the copper oxidases in enzymic oxidation reactions (7). Nigh (8) has recently reviewed the use of copper compounds as oxidative catalysts in organic chemistry.

It is not surprising, therefore, that due to the important industrial and biological role of copper catalysed oxidative coupling reactions, the kinetics and mechanisms of such reactions have been widely studied. However, although the role of the copper catalyst in such systems has been discussed at some length, no satisfactory explanation has been put forward as to the chemical composition or possible structure of the catalyst species involved. In general the problem of the nature of the catalyst has been approached with the emphasis on the purely organic aspects of the oxidative coupling reaction. Only limited attempts have been made to consider the catalyst in the context of the likely chemistry of copper complexes, and some of the stoichiometries and structures which have been proposed are not acceptable from the point of view of an inorganic chemist. This project was undertaken to study the catalyst system, in order to determine the stoichiometry and structure of the copper species involved in the phenolic coupling reaction. It was hoped that, if the structure of the catalyst was determined, this would lead to a greater understanding of the mechanism of the phenolic coupling in particular, and of oxidative coupling in general, so that more informed attempts could be made to eliminate unwanted side reactions and maximise yields of the desired product. A summary of kinetics, mechanisms, stoichiometries

and structures which have been proposed for the copper catalysed

oxidative coupling reaction over the past fourteen years is

discussed below.

An active catalyst species is produced by suspending a

copper (I) halide in a suitable solvent (benzene, nitrobenzene,

O-dichlorobenzene, etc.) containing an amine, and oxidising the

resulting species with molecular oxygen or air, to give a green

copper (II) complex. This active catalyst species is present

in solution. If, for example, a phenol monomer is added to the

solution whilst oxygen is being passed through it, an oxidative

coupling reaction takes place. The kinetics of the oxidation

reaction have been studied by several workers (7, 9-14) .

Finkbeiner (7), White and Klopfer (12) and Tsuchida et al. (10) have

shown that the role of oxygen in the system is to reoxidise copper

(I) to Copper (II) only, and that one quarter of a mole of oxygen

per mole of copper is consumed during the oxidation. Brooks (18),

Price and Nakaoka (9) and Tsuchida et al. (10, 14) have shown

that the rate of reaction was independent of momomer concentration,

but first order with respect to the copper (I) halide concentration

and the oxygen partial pressure. Tsuchida et al (10) have shown

that for the oxidation of copper (I) halide-pyridine mixtures in the

absence of monomer, the rate of oxygen consumption is a maximum

for a pyridine to copper ratio of 3:1. The quantity and type of

amine used in the catalyst system has a marked effect on both the

rate of oxidation of monomer and on the production of unwanted

by-products. White and Klopfer (11, 12) have studied the effect

of various amines on the polymerisation of 2, 6-diphenylphenol.

Using the intrinsic viscosity of the solution as a measure of the

rate of polymer production, they compared the activities of a

number of monodentate or bidentate primary, secondary and tertiary

amines, and found that the most effective polymerisation catalysts

for the production of high molecular weight polymers, occured at

a nitrogen to copper ratio of 1:1. They also found that with bistertiary

amines, high molecular weight polymers were not formed unless the

two nitrogen atoms were separated by either two or three carbon

atoms. Pyridine, tetramethylethylenediamine (TMED) and

tetramethyl-1,3-butanediamine (TMBD) appeared to be the most

effective ligands for the polymerisation. Endres et al. (13)

have shown that the extent of the C-O and C-C coupling reactions in

the oxidative coupling of disubstituted phenols, is determined in

part by the copper to nitrogen ratio of the catalyst species.

For a copper (I) chloride-pyridine catalyst, they found that at

low pyridine to copper ratios, C-C coupling predominated, whilst

at high pyridine to copper ratios (>10:1) the major product was

the polyphenylene oxide as a result of C-O coupling. White

and Klopfer (11) found that in general, the less active the amine

in promoting the oxidation of monomer, the smaller the carbon-

carbon coupled product. A notable exception to this, however, is

N,N' diethylethylenediamine, which is completely unreactive to

polymerisation, but does promote the C-C coupled reaction.

Hay (15), White and Klopfer (11, 12) and Price and Nakaoka (9)

have studied the effect of monomer structure on the rate of

oxidative coupling in disubstituted phenols. Their results

indicated that there are two factors connected with monomer

structure which are important in determining the rate of the

oxidation reaction. Firstly the presence of bulky substituents

in the 2,6-positions slows the rate of reaction by physically

preventing coordination to the catalyst species. Secondly the

absence of electron donating o-methyl groups or the presence of

electron with-drawing groups in the phenyl ring retards the oxidation reaction by raising the oxidation potential of the substituted phenol.

Brooks (18) has studied the oxidative coupling reaction using a copper (I) halide-pyridine catalyst at high pyridine to copper ratios, and proposed a mechanism for the reaction which was kinetically similar to enzyme reaction mechanisms. A very similar mechanism has been proposed by Tsuchida et al. (10, 14) who studied the polymerisation of 2,6-disubstituted phenols with particular reference to coupling selectivity (10) and the role of oxygen in the system (14). They found the oxidation kinetically similar to a Michaelis-Menton type reaction, well known in enzymatic systems. The proposed kinetic reaction scheme is shown in figure 1.1. Tsuchida et al. found the co-ordination stage (A in figure 1.1) to be dependent on the nature of the amine used in the catalyst. The value of the equilibrium constant for stage A was found to be very much greater for pyridine than for aliphatic amines. This was ascribed to steric effects; bulky amines physically preventing the phenol from co-ordinating. These workers also found that, whereas one equivalent of the copper (II) catalyst containing an aromatic amine would oxidise one equivalent of monomer in the absence of oxygen; in the presence of an aliphatic amine, even an excess of copper (II) catalyst was not sufficient for the coupling to occur in the absence of oxygen. It was concluded that oxygen promotes either the electron transfer from the co-ordinated monomer (Stage B in figure 1.1) to the metal ion, or the dissociation reaction of the activated monomer (Stage C), probably by forming a complex with the intermediate. These workers suggest that the π-electron accepting property of the

A. Coordination of monomer.

$$\text{Cu(II)L} + {}^{\ominus}\text{O} \overset{k_1}{\underset{k_{-1}}{\rightleftarrows}} \text{LCu(II)} \leftarrow {}^{\ominus}\text{O}$$
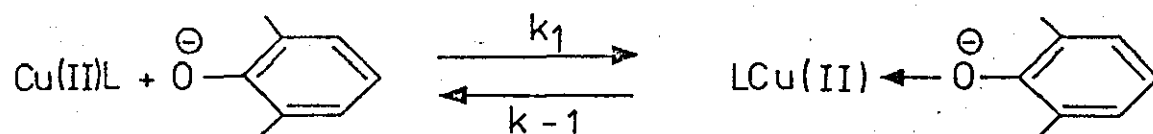
B. Electron transfer.

$$\text{LCu(II)} \leftarrow {}^{\ominus}\text{O} \overset{ke}{\longrightarrow} \text{LCu(I)} \leftarrow \overset{\bullet}{\text{O}}$$
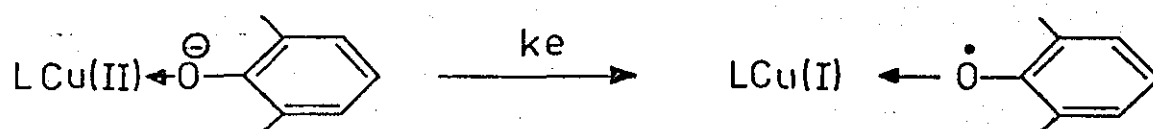
C. Dissociation of activated monomer.

$$\text{LCu(I)} \leftarrow \overset{\bullet}{\text{O}} \overset{kd}{\longrightarrow} \text{LCu(I)} + \overset{\bullet}{\text{O}}$$
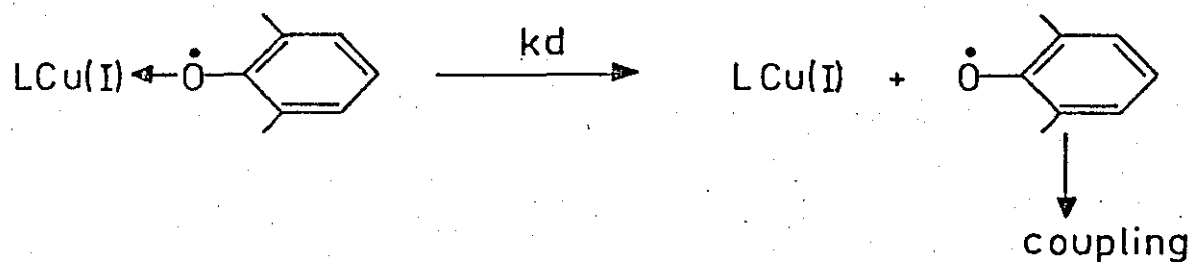
coupling

D. Recycling of catalyst.

$$\text{Cu(I)L} \overset{ko}{\longrightarrow} \text{Cu(II)L}$$
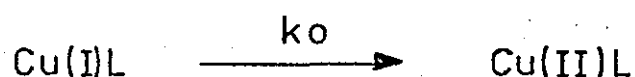
FIGURE 1.1. kinetic reaction scheme for oxidative coupling (Tsuchida et al.)

pyridine ring allows stage B to occur and thus the catalyst is active even in the absence of oxygen.

Concerning the coupling selectivity of the catalyst system, Tsuchida et al. studied the extent of C-O coupling using a catalyst with pyridine to copper ratios varying from 1:1 to 100:1. They found that the value of k_1, the rate constant for the polymerisation (equal to $\frac{k_1}{k_{-1}}$ $(1 - \frac{ke}{kd})$), increased with increasing selectivity of C-O coupling. This rate constant may be considered as a measure of the affinity of the copper complex for the phenol. Hence it is the electronic state of the co-ordinated radicals (determined by the nature of the amine ligand) which decides the coupling selectivity. These workers suggested that it is difficult to regard the coupling as a free radical mechanism, as had been proposed by many other workers (7, 15-17), for if the coupling occured between the free radicals themselves, there would be no need for it to be determined by the nature of the catalyst species. As C-O coupling occurs only in the presence of metal ions, the mechanism is considered to involve a co-ordinated radical; C-C coupling, they suggest, may occur through a very different mechanism. Tsuchida et al. also discussed the effects of different solvents on the rate of reaction, and explained the very slow rates in polar solvents, such as dimethylformamide, by the lowering of the electron transfer rate (stage B in figure 1.1) due to the stabilisation by the polar solvent of the complex before electron transfer.

Finkbeiner (7) studied the oxidation of a copper (I) chloride-pyridine mixture in benzene and o-dichlorobenzene and proposed stoichiometries for the reaction shown in equations 1.5 and 1.6 below. Equation 1.5 applies in the absence of water and 1.6 when water is present.

$$4CuCl + O_2 \xrightarrow[\text{Py.}]{C_6H_6} 2CuCl_2 : 2Cu\ O\ npy \qquad (1.5)$$

$$4CuCl + O_2 \xrightarrow[\text{py} - H_2O]{C_6H_6} 2CuCl_2 : 2Cu(OH)_2\ npy \qquad (1.6)$$
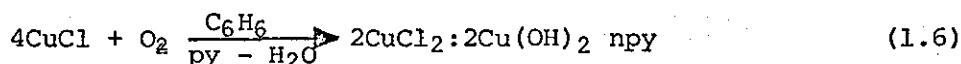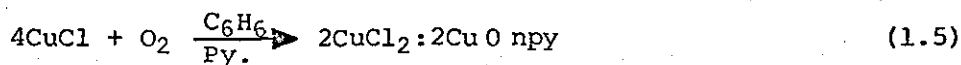
Due to the fact that Finkbeiner and other workers in this field

reported only the routine drying of solvents, and pretreatment

of pyridine with potassium hydroxide (which does not remove the

last 1% of water), water must be considered as a possible

reactant in the preparation of an active catalyst. Hence

equation (1.6) is more likely to be nearer the true stoichiometry

for the oxidation. Further work by Finkbeiner led him to

investigate the minimum pyridine to copper ratio that would

produce complete oxidation of the copper (I) species, as measured by

the amount of oxygen consumed in the reaction. He found that

below a pyridine to copper ratio of 2:3, oxidation was incomplete

and proposed the stoichiometry of equation 1.7 for the oxidation.

$$6CuCl + 3/2O_2 + 4py \xrightarrow{C_6H_6} 2CuCl_2\ 2py.CuCl_2 : 3CuO \qquad (1.7)$$
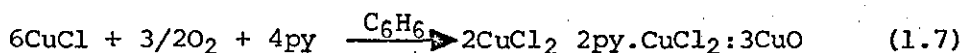
It is not clear whether the product in equation (1.7) was supposed

to be a complex salt or a mixture of bispyridinedichloro copper (II),

copper(II) chloride and copper (II) oxide. Finkbeiner claimed to

have attempted to isolate the active species, by precipitation of

the copper complex with hexane, but did not report any results as

to the catalytic activity or stoichiometry of the complex thus

obtained, apart from noting that it had a similar infrared spectrum

to bispyridine dichloro copper (II). Although Finkbeiner found

that the oxidation of a copper (I) chloride-pyridine mixture in benzene

or O-dichlorobenzene (referred to as "inert solvents") produced an

ill-defined amorphous copper (II) species, he reported that if the

oxidation was carried out in methanol, a deep green crystalline

material precipitated (7). This complex had the stoichiometry

Cu(OMe)Cl py and was a very active catalyst for the polymerisation

of disubstituted phenols. This catalyst species also promoted

different proportions of C-O and C-C coupled products, the relative

amounts depending on the pyridine to copper ratio in the reaction

mixture, as had been observed in the different catalyst system

prepared from an ": inert solvent". Hay (16) found that although

copper (II) hydroxide in pyridine was inactive as a catalyst,

treatment with one equivalent of hydrogen chloride generated an

active species. He concluded that the active catalyst was a

copper salt containing one hydroxide group per copper atom.

This supposition was supported by Tsuruya et al. (19) who oxidatively

coupled 2,6-dimethylphenol using a catalyst prepared from copper (II)

chloride, potassium hydroxide (1:1) and pyridine in methanol.

De Jongh et al. (20) used a complex of stoichiometry $[Cu(OH)TMED]_2Cl_2$

as an effective oxidative catalyst. This was prepared by the

oxidation of copper (I) chloride in a methanol-water solution

containing tetramethylethylenediammine. This complex was observed

by De Jongh to be identical (infrared spectrum, melting point

and colour) to $[Cu(OH)TMED]_2Br_2$ prepared by Wasson in 1968(21).

The crystal structure of this latter complex (22) showed the

two hydroxide groups bridging the two copper atoms. The data in

Wasson's papers, however, refers to the bromide complex only and

whilst the structures of the two complexes might be expected to be

similar, properties like melting point and infrared spectra are

not likely to be identical for a chloride and bromide complex.

Several structural forms have been postulated for the active

catalyst species. Finkbeiner (7) studied the visible spectra of

solutions of his copper methoxide chloride catalyst species at

different pyridine to copper ratios and, based on a small shift in

the absorption maxima between pyridine to copper ratios of 1:1 and 558:1, postulated the existence of two catalyst species, the structures of which are shown in figure 1.2. One species (A) is present at relatively low pyridine to copper ratios and catalyses the C-C coupling reaction; the other (B) exists at high pyridine to copper ratios (>100:1) and catalyses the C-O coupling reaction. The two competing coupling reactions for these catalyst species are shown in equations 1.8 and 1.9 below.

Low ligand to copper ratio:-

$$2[Cu(OMe)Cl\ py] + 2\ ROH \longrightarrow [Cu(OR)Cl\ py]_2 \longrightarrow diphenoquinone \quad (1.8)$$

High ligand to copper ratio:-

$$Cu(OMe)Cl(py)_2 + ROH \longrightarrow Cu(OR)Cl(py)_2 \longrightarrow polyphenylene\ oxide \quad (1.9)$$
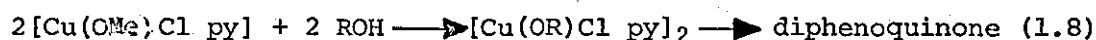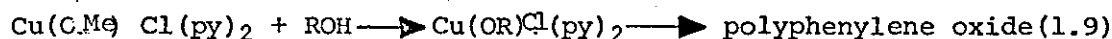
ROH = disubstituted phenol

In copper alkoxides, alkoxyhalides and co-ordination complexes of such compounds, it is the alkoxide groups that are thought to bridge the two coppers of a dimeric unit. Magnetic and spectral data indicate that bridging alkoxide groups are present in copper methoxide, copper methoxychloride and copper ethoxychloride (23, 24). Sterns (25) has reported the crystal structure of $[Cu(OMe)Cl\ 2\text{-mepy}]_2$. This complex consists of two centrosymmetric dimeric units, in which the copper atoms are linked by methoxide oxygen bridges, the dimers being joined into infinite chains through long copper-chlorine bonds. The methoxide complex prepared by Finkbeiner may well be structurally similar to that studied by Sterns; the presence of bridging methoxide groups in the former complex could well be confirmed by determining the magnetic moment of the complex. The magnetic moment of $[Cu(OMe)Cl\ 2\text{-mepy}]_2$ has been found to be lowered to 0.6 B.M. at room temperature, due to spin-coupling between the copper atoms

A   B
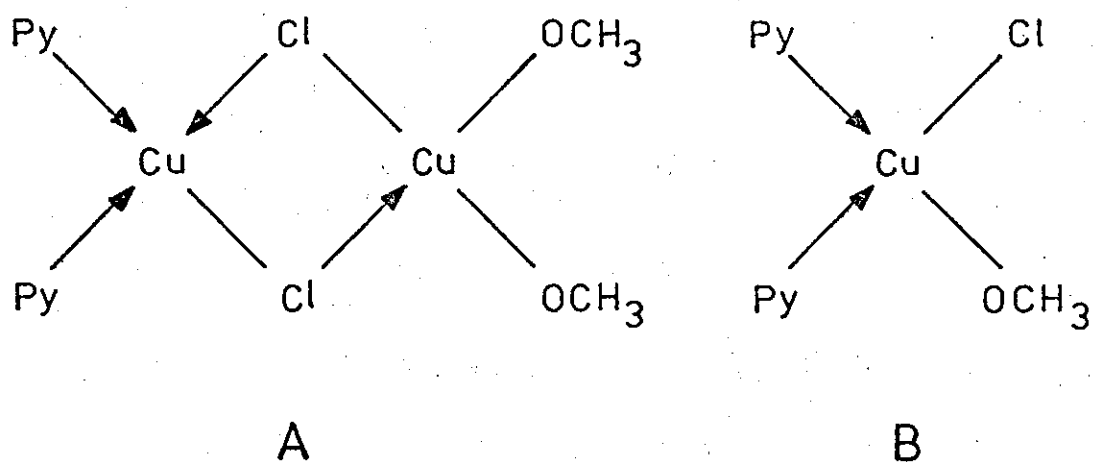
FIGURE 1.2.   Proposed methoxide catalyst
structures (Finkbeiner)
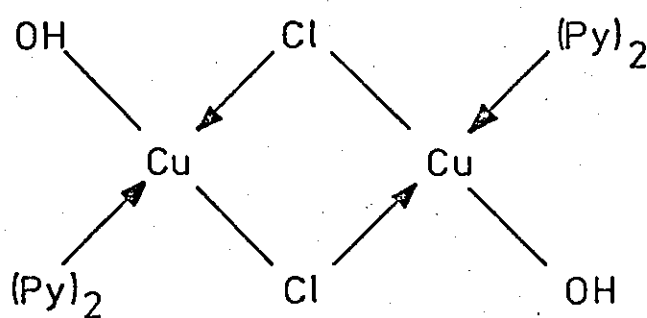
FIGURE 1.3.   Proposed catalyst structure
(Price and Nakaoka)

assisted by the orbitals of the bridging oxygen atoms of the methoxide

groups. Recently Roubaty et al. (26) studied the proton NMR of the

methoxide complex prepared by Finkbeiner, and suggested that it

contained the structural unit:-

$$Cu \overset{\displaystyle O}{\underset{\displaystyle \quad}{\diagup \diagdown}} Cu$$
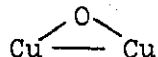
Apart from points already discussed, such as the effect on the

magnetic properties of this type of structure and inconsistency with

what is known of copper chemistry, this work is unsatisfactory in some

of the details of its analytical and NMR data. This paper will be

discussed in detail in Chapter Eight, in which present work on the

structure of the methoxide complex is evaluated.

When the oxidation of a copper (I) chloride-pyridine mixture was

carried out in the absence of methanol, Finkbeiner proposed that structurally

similar catalysts to those shown in fig. 1.2 were formed: in this case,

however, hydroxide groups replaced the terminal methoxide groups in the

figure. Co-ordination complexes of copper hydroxide species are similar

to the alkoxide complexes described above, to the extent that dimeric

structures with hydroxide bridges are favoured, as in the case of

$[Cu(OH)TMED]_2Br_2$ mentioned earlier. Complexes of the type $[Cu(OH)L_m]_2X$,

where L may be a monodentate (m = 2) or bidentate (m = 1) amine and X is

an anion, have been studied in detail by McWhinnie (L = 2-mepy, 2-amino py;

X = ClO_4, NO_3) (27,28) and Ferraro and Walker (29) and Harris et al. (30)

who each studied a similar series (L = bipy, phen: X = Cl, Br, I, NCS,

ClO_4, SO_4). In all cases dimeric hydroxy bridged complexes were

postulated. In addition, Leussing and Hansen (31) have reported the

existence of the dimeric species $py_2Cu(OH)_2Cupy_2^{2+}$ in solution. It is

clear that the structures proposed by Finkbeiner (fig. 1.2) are not in

accord with what is now known of the co-ordination chemistry of copper

methoxide and hydroxide complexes. Price and Nakaoka (9)

suggested that the structure shown in fig. 1.3 was the active

catalyst produced by the oxidation of copper (I) chloride and

pyridine in nitrobenzene. This differs from that proposed

by Finkbeiner (figure 1.2, A) only in the position of the terminal

hydroxide groups and in the number of pyridine ligands present,

and can be considered unlikely to occur for the reasons outlined

above.

The proposal that the catalyst species is dimeric in nature

seems to be derived from the supposition that copper (I) chloride

exists as the dimer Cu_2Cl_2: this dimeric structure with bridging

chloride atoms being retained in the oxidized copper (II) species.

Copper (I) chloride has been shown to be polymeric in the solid

state (32), with the Zinc Blende ($<407°C$) or Wurtzite ($>407°C$)

structure. There is evidence that, even at high temperatures, the

vapours of copper (I) chloride contain substantial amounts of the

cyclic trimer Cu_3Cl_3 (33) and the tetramer Cu_4Cl_4 (34, 35), with

smaller amounts of the pentamer Cu_5Cl_5 (35), there is little

evidence, however, for the dimer claimed by earlier workers.

Price and Nakaoka (9), however, have used evidence obtained

from the oxidation of copper (I) chloride in melts to support the

dimeric structure of the catalyst. Ruthven and Kenney (36) found

that the rate of oxidation of copper (I) chloride in a melt of

potassium and lanthanum chlorides, was proportional to the square

of the cuprous ion concentration. This was interpreted as arising

from a reaction involving the simultaneous oxidation of two cuprous

ions with one mole of oxygen, to give a peroxy bridged intermediate

species: the proposed reaction scheme is shown in figure 1.4.

The evidence for the peroxide species in Ruthven and Kenneys' paper

however, was very tentative and no substantiating evidence has been

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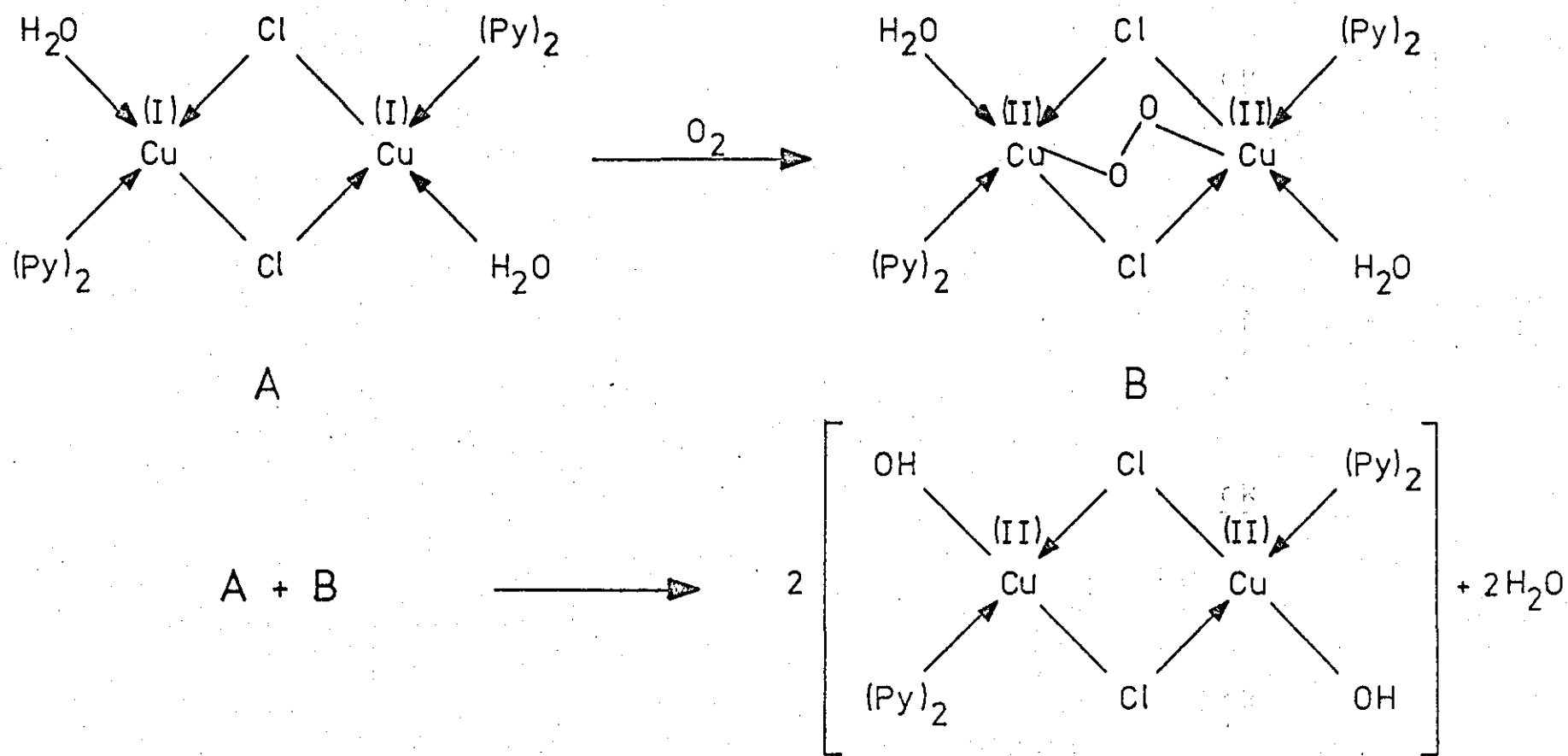
FIGURE 1.4. Preparation of the active catalyst species. (Price and Nakaoka)

put forward by Price and Nakaoka for the existence of this particular species in the catalyst system.

Complete mechanisms for the oxidative coupling reaction, involving a structural description of the copper catalyst species, have been postulated only by Price and Nakaoka (9) and Smith (37). The reaction schemes envisaged by Price and Nakaoka for the oxidative coupling of disubstituted phenols are shown in figures 1.5 and 1.6. Figure 1.5 is relevant for high pyridine to copper ratios which produces C-O coupling, and figure 1.6 for low pyridine to copper ratios, producing C-C coupling. At high pyridine to copper ratios, two pyridine molecules are co-ordinated to each copper atom (figure 1.5). This results in decreased bonding between the copper and aryloxy radical after electron transfer and causes the radicals to readily dissociate and participate in C-O coupling. At low pyridine to copper ratios, however (figure 1.6), only one pyridine molecule is co-ordinated to each copper atom and this results in the aryloxy radicals remaining co-ordinated to the copper atoms after the electron transfer reaction . This in turn leads to C-C coupling to form the diphenoquinone. As both of these reaction schemes require the presence of terminal hydroxide groups and a copper peroxide intermediate, they must be considered unlikely for the reasons stated above. Recently Smith (37) has suggested the same reaction mechanism for the oxidation of thiophenols, also involving a dimeric catalyst with terminal hydroxide groups and a peroxide type intermediate. This scheme must also be considered suspect for similar reasons.

It can be seen on consideration of the above information, that the catalytic oxidative coupling reaction is very complicated and influenced by a large number of parameters. Any
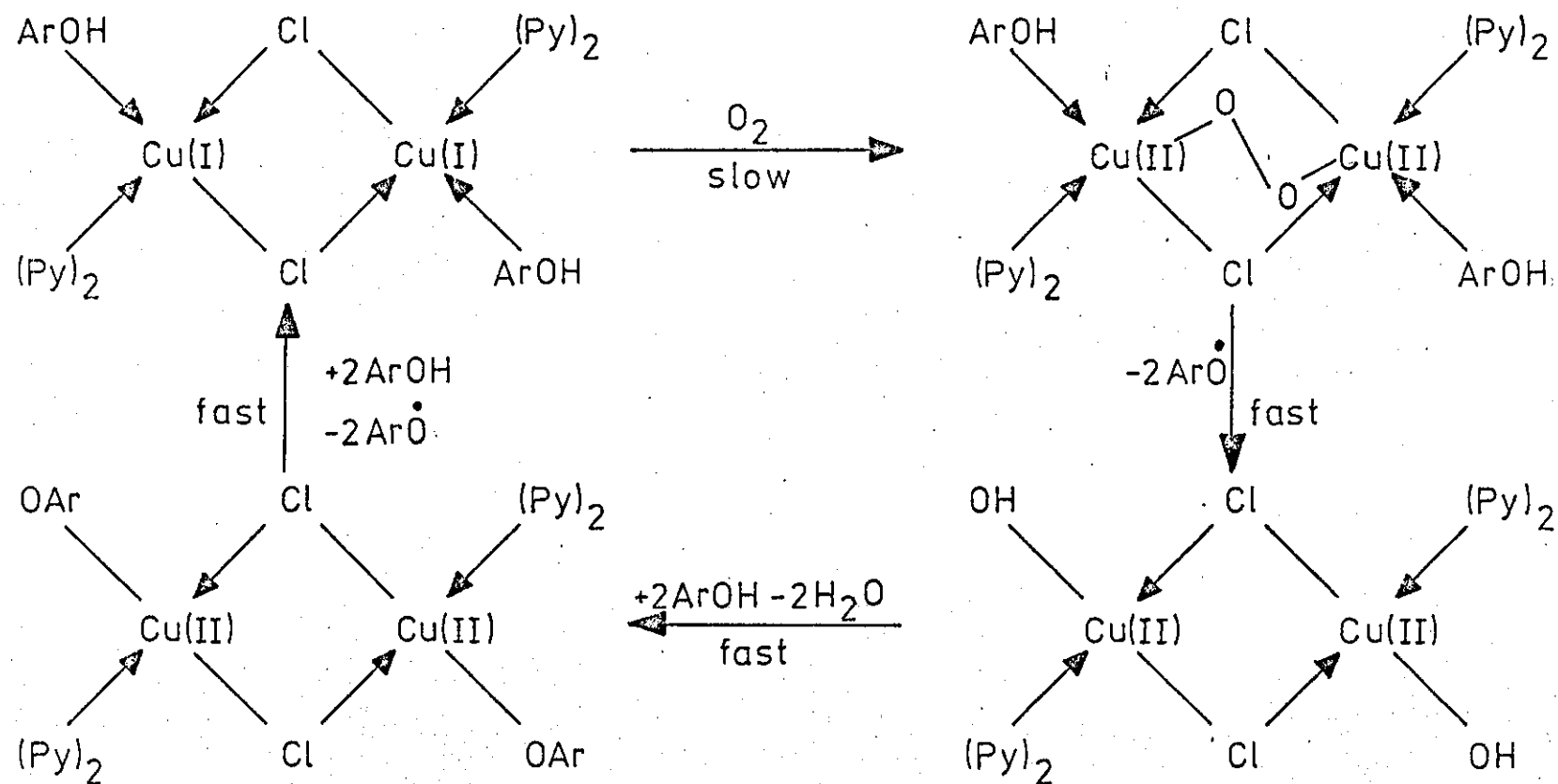
FIGURE 1.5.   C—O coupling scheme (Price and Nakaoka).
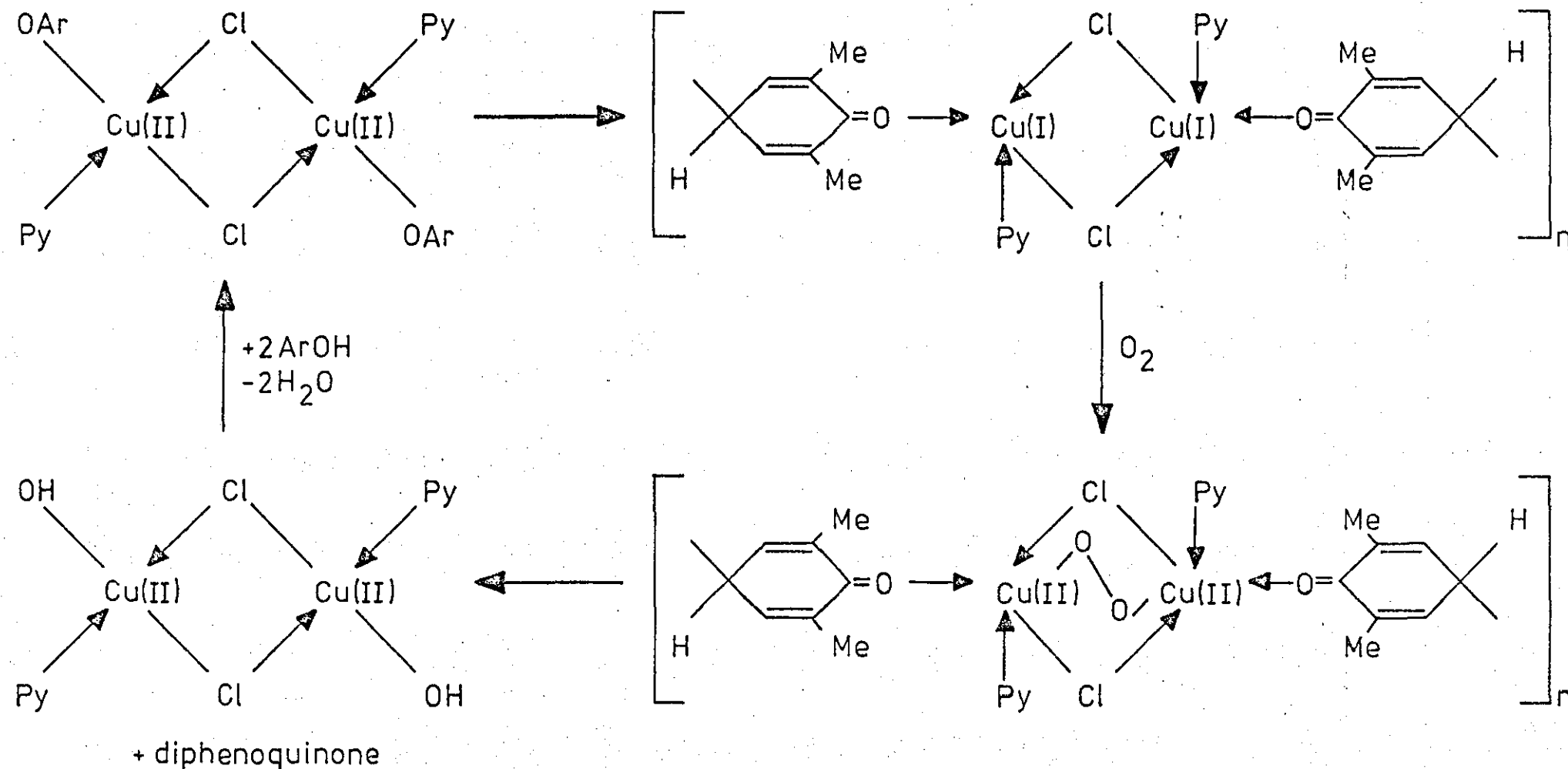
FIGURE 1.6.   C—C coupling scheme Price and Nakaoka.

structure. proposed for the copper catalyst would (apart from being realistic in terms of copper chemistry) have to agree with the kinetics of the oxidation and explain the effects of ligand ratios and structures, monomer structure and solvent effects, on the rate of oxidation and yields of specific products. The reason why the catalyst structure is unique to the oxidation products of copper (I) halides will also have to be satisfactorily explained.

During the initial stages of this study it became clear that polynuclear copper complexes were involved during the oxidation of a copper (I)halide-amine complex. The oxidation in wet air of a copper (I) chloride-pyridine complex of stoichiometry CuCl py was studied using a gravimetric technique. The results of this investigation (detailed in Chapter Eight) indicated that a reaction involving at least four copper atoms must be considered in order to account for the observed weight changes in terms of whole numbers of constituent atoms or molecules. The first stage in the oxidation appeared to be the gain of one mole of oxygen and one mole of water per four copper atoms, giving rise to the stoichiometry indicated in equation 1.10.

$$4CuCl \ py + O_2 + H_2O \longrightarrow Cu_4O(OH)_2Cl_4 \ 4py \qquad (1.10)$$
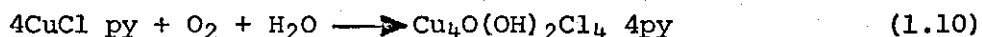
Tetranuclear copper (II) complexes of similar stoichiometry to the product in equation 1.10 have been studied since 1966. Coincidently they were first reported by Finkbeiner (7), who prepared the complex $Cu_4OCl_6 4py$, but thought it to be a mixture of basic copper (II) salts. He did, however, report that the complex had some catalytic activity. Little is known of the reactions and stabilities of such complexes and it was decided, on the strength of the results outlined above, to devote a large part of this project to the study of these polynuclear complexes.

Consequently this thesis describes the preparation and characterisation of new polynuclear copper (II) complexes with structural properties that could be related to the catalyst complex. Investigations into the stability and reactions of these complexes, as well as a study of the oxidation products from copper (I) halide-amine complexes both in the solid state and in solution are reported.

CHAPTER TWO

COPPER (I) HALIDE-PYRIDINE COMPLEXES

2.1 Introduction

As a preliminary to the study of the oxidation of copper

halide-pyridine mixtures, it was felt appropriate to investigate

and characterise the solid copper (I) halide-pyridine adducts, with

the aim of subsequently oxidising these complexes in the solid state.

Up to the time that the work on this particular aspect of the

project was initiated, some confusion existed in the literature

concerning the stoichiometrics and colours of copper (I) halide-

pyridine complexes. Lang in 1888 (38), Varet in 1897 (39) and

Murchjan in 1940 (40) all reported 1:2 adducts of copper (I) chloride

and bromide with pyridine. The complexes were described by these

workers as "green" or "golden green". No precautions were taken to

exclude oxygen from the preparations and, as pyridine solutions of

copper (I) chloride and bromide are very sensitive to aerial oxidation,

it seems likely that the complexes obtained by these workers were

wholly or partially copper (II) compounds. Complexes of copper (I)

will exhibit colours due to charge transfer effects rather than d-d

transitions, as the copper atoms have a d^{10} configuration. The

charge transfer bands attributable to the copper (I)-pyridine system

might be expected to occur near the ultraviolet end of the spectrum,

producing yellow or white complexes. Many copper (II) complexes are

green or blue, due to the d-d transitions of the d^9 copper (II)

configuration. A white 1:1 adduct of copper (I) bromide and pyridine

was reported by Wilkins and Burkin (41) who also prepared the

corresponding white iodide complex. Malik (42), however, reported

the 1:1 copper (I) iodide-pyridine complex as an amethyst crystalline

solid. He also reported potentiometric evidence for the existence of

1:1 and 1:2 adducts of copper (I) chloride and pyridine, but failed

to isolate those complexes. Due to this somewhat confused picture it

was considered necessary to isolate all possible adducts of copper (I) halides and pyridine, and characterise them by analytical and infrared data. After this work was completed, however, De Ahna and Hardt (43) published the preparation of complexes of copper (I) halides with pyridine, picolines, lutidines and collidines. These compounds had the stiochiometry $CuXL_n$, where X is chloride, bromide or iodide, L is pyridine or alkyl pyridine, and n is one or three, and they exhibited intense fluorescence which changed reversibly at low temperatures. Both 1:1 and 1:3 adducts were prepared using a vacuum technique similar to that described in 2.2 below. De Ahna and Hardt reported thermogravimetric data on the trisamine adducts which showed a one-step loss of two molecules of ligand to form the monoamine adduct. Bisamine complexes were not isolated. The decomposition of the monoamine adduct was reported to be a multistage process, the eventual product being the copper (I) halide. In addition to fluorescence and thermogravimetric data, they also tabulated x-ray powder diffraction lines for the complexes, but did not report infrared or analytical data.

2.2 Experimental and Results

2.2.1 Preparative methods

The pyridine adducts of copper (I) chloride and bromide were very sensitive to aerial oxidation, and so were prepared using a vacuum technique. After preparation these complexes were handled in a glove-box containing an atmosphere of dry nitrogen and analytical and infrared data obtained using standard techniques (46).

(a) preparation of copper (I) chloride and bromide complexes

Pyridine adducts of copper (I) chloride and bromide were prepared using a simple vacuum frame shown in figure 2.1. Pyridine (40ml) was degassed in tube B and cold distilled into tube A, which contained the copper (I) halide (ca.0.2 g) and a magnetic stirrer bar.

- 16 -
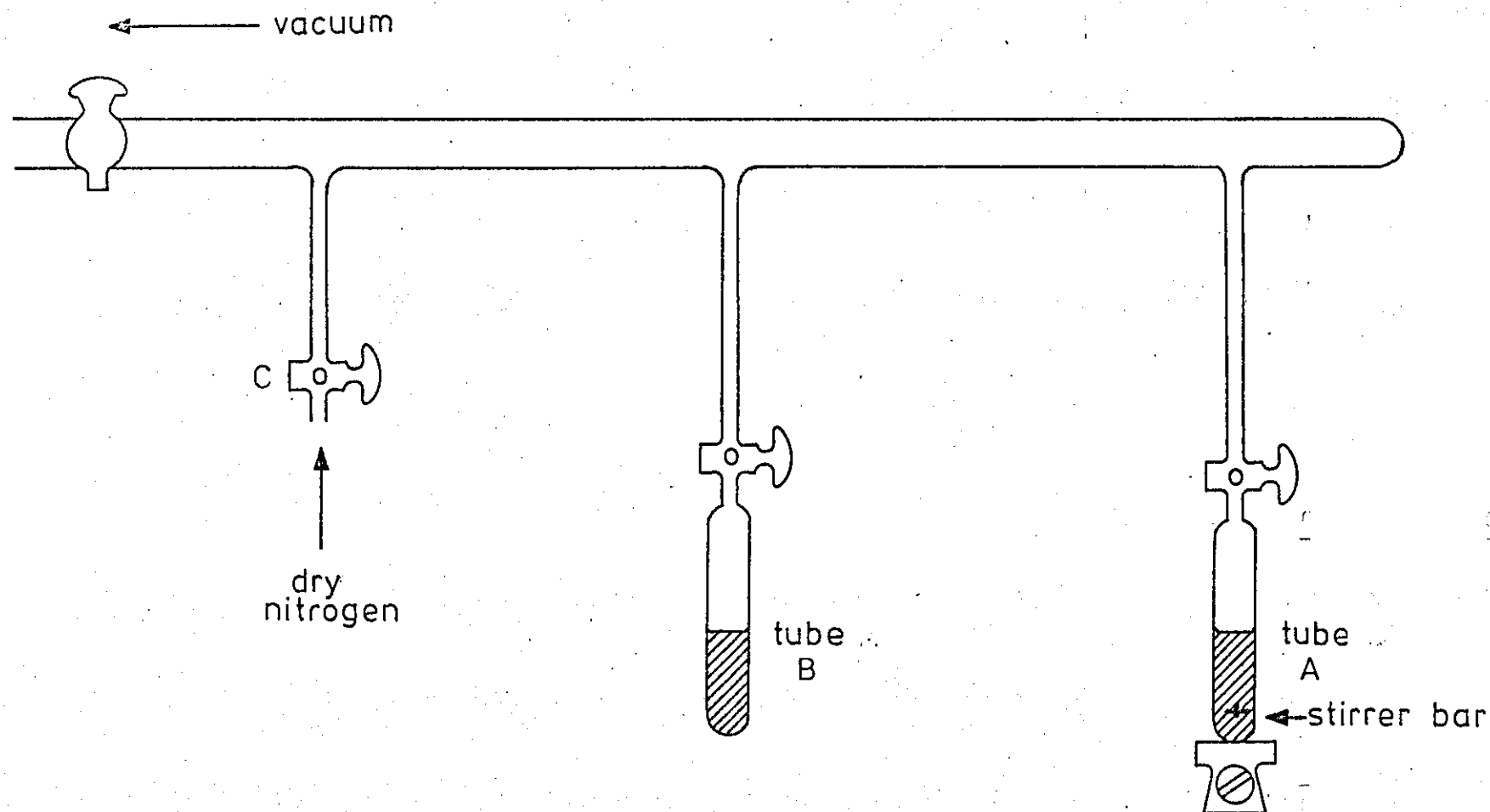
FIGURE 2.1. Vacuum frame used for the preparation of copper (I) halide—pyridine complexes.

The solution was allowed to reach room temperature and stirred until all the copper halide had dissolved. Pyridine was then cold distilled back to tube B with the temperature of tube A maintained at 0°C. This resulted in the formation of the yellow trispyridine adduct. The pale yellow (chloride) or white (bromide) monopyridine adduct was prepared by evacuating the trispyridine adduct for thirty minutes, whilst maintaining the temperature of tube A at 35°C.

Dry nitrogen was let into the apparatus by means of tap C, and the tube containing the copper (I) halide-pyridine complex transferred to the glove-box for analysis.

Attempts were made to prepare the bispyridine adduct of copper (I) chloride and bromide by two different methods. In the first of these, the general method of preparation of the monopyridine adduct was followed as described above, except that the temperature of tube A was varied between 0 and 30°C during several preparations. Analytical data indicated that the products contained between one and three molecules of pyridine. No complexes corresponding to the bispyridine adducts were obtained. In the second method of preparation, dry degassed diethyl ether was cold distilled to the copper (I) halide-pyridine solution. A creamy yellow complex precipitated, which was filtered on a filter stick, washed with degassed diethyl ether and transferred to a glove-box for analysis. Analytical data indicated that this complex contained between one and two molecules of pyridine.

(b) preparation of copper (I) iodide complexes

Copper (I) iodide (ca.4g) was dissolved in pyridine (Ca.50 ml) and the yellow solution filtered. About 20 ml of pyridine was removed under vacuum and dry diethyl ether (20 ml) added to the remaining solution. A pale yellow solid precipitated which turned white when washed with diethyl ether. The white product was collected and dried

TABLE 2.1

ANALYTICAL DATA FOR COPPER (I) HALIDE-PYRIDINE COMPLEXES

COMPOUND	COLOUR	% COPPER		% HALOGEN	
		FOUND	CALC.	FOUND	CALC.
CuClpy	Very pale Yellow	35.71	35.68	19.84	19.91
CuCl3py	Deep yellow	18.90	18.89	10.58	10.54
CuBrpy	White	28.66	28.55	35.94	35.91
CuBr3py	Deep yellow	17.01	16.69	21.25	20.99
CuIpy	White	23.33	23.57	46.87	47.08
CuI2py	Pale yellow	18.01	18.23	36.14	36.40

TABLE 2.2

INFRARED DATA (1700-250 cm^{-1}) FOR COPPER HALIDE-PYRIDINE COMPLEXES

FREE AMINE (50)	ASSIGN-MENT (50)	CuX$_2$2py (50) x=Cl	x=Br	CuClpy	CuCl3py	CuBrpy	CuBr3py	CuIpy	CuI2py
1583	8a	1603	1601	1596	1593	1596	1595	1596	1591
1572	8b	1572	1571	–	1569	–	–	–	–
1482	19a	1490	1490	1482	1482	1482	1480	1480	1480
1439	19b	1449	1448	1442	1442	1442	1442	1440	1440
1375	14	1365	1364	1352	1355	1352	1352	1353	–
1288	3	1240	1238	–	–	–	–	1235	–
1218	9a	1218	1219	1212	1215 1210	1212	1215 1209	1215	1210 1205
1148	15	1151	1158 1152	1156	1150	1155	1151	1150	1149
1068	18a	1079	1078	1076	1068	1075	1068	1068	1068 1062
1085	18b	1063	1061	–	–	–	–	–	–
1030	12	1042	1042	1039	1039	1039	1036	1040	1032
992	1	1016 1009	1015 1008	1009	1016	1009	1010	1009	1003
942	5	948	944	–	–	–	–	–	–
891	10a	876	870	889	890	888	890	–	–
749	4	764	759	747 752	755	747	742 757	751	748 758
700	11	691	689	704 692	705 700	702 693	699 694	698	706 690
605	6a	645	645	629	629	629	625	622	621
405	16b	444	444	412	422	413	420	410	416

in vacuo (2 torr). The product was analysed and found to be the monopyridine adduct. The monopyridine adduct of copper (I) iodide (1.0 g) was placed on a watch glass in a closed vessel containing pyridine, at 20°C. The complex was allowed to remain in contact with the pyridine vapour for several days, until no further gain in weight was observed. The product, a pale yellow solid, was analysed and its infrared spectrum recorded, it had the stoichiometry CuI2.4py. Thus if a trispyridine adduct of copper (I) iodide did exist, it was not stable with respect to loss of pyridine at this temperature. Dry nitrogen was passed over the yellow complex for two hours resulting in a pale yellow compound which, on analysis, was found to have a stoichiometry CuI2py. This complex did not lose any further pyridine at 20°C.

Analytical data for these copper (I) halide-pyridine adducts are contained in table 2.1. Infrared spectral data was obtained in the region $4000 - 250$ cm^{-1} using a Perkin Elmer 457 spectrophotometer. Spectral data for these complexes ($1700 - 250$ cm^{-1}) is contained in table 2.2. The only bands attributable to the compounds in the region $4000 - 1700$ cm^{-1} were due to the C-H vibrations of the pyridine ring ($3000 - 3100$ cm^{-1}). These bands were very weak and appeared at the same frequencies in all the complexes studied, and so are not tabulated. The copper (II) complexes, $CuCl_2 2py$ and $CuBr_2 2py$, are included for comparative purposes.

The spectrophotometer was calibrated in the region $4000 - 700$ cm^{-1} by means of polystyrene film, and from $700 - 250$ cm^{-1} using a paraffin oil mull of mercury (II) oxide between cesium iodide plates.

2.2.2 Vapour pressure measurements

The vapour pressures of the trispyridine adducts of copper (I) chloride and bromide were studied in the temperature range $18 - 90$°C,

in order to investigate the possible existence of Bispyridine

adducts of these copper (I) halides, using the apparatus shown in

figure 2.2. The spiral spring and optically flat window and holder

were obtained from C.W. Wingent Ltd., and incorporated into the

vacuum frame as shown in figure 2.2. The apparatus consists of a

hollow spiral spring connected directly to the container holding

the sample under investigation. The outer case is connected to a

vacuum system, via a mercury manometer. Any pressure difference

between the two halves of the apparatus, causes the spring to

distort, which in turn results in a deflection of the platinum

mirror attached to it. The deflection of the mirror is directly

proportional to the pressure difference between the two halves of

the apparatus, and so can be utilised to determine the vapour

pressure in the part of the apparatus containing the sample. In

practice, the filament of a lamp is focused onto the mirror and

reflected back to a scale fixed horizontally above the lamp.

Changes in the position of this reflected beam are used to evaluate

the changes in the vapour pressure due to raising the temperature

of the sample.

After confirming its analytical purity, 0.2 - 0.4 g of the

trispyridine complex was placed in a small sample holder in the

glove-box and then attached to the vacuum frame, using a blanket of

nitrogen. The frame had already been flushed out with dry nitrogen,

and directly the sample holder was attached, taps A and B were

opened and tap C turned to connect the frame to the vacuum pump.

The sample was cooled with liquid nitrogen to prevent loss of pyridine

during this initial evacuation; the whole system was then

pumped out to less than one torr. Tap A was then closed and remained

so for the rest of the experiment. The apparatus was lowered into

platinum mirror

optical flat

spiral spring

tap A

tap B

tap C

to vacuum

sample holder

thermostated water bath

mercury manometer
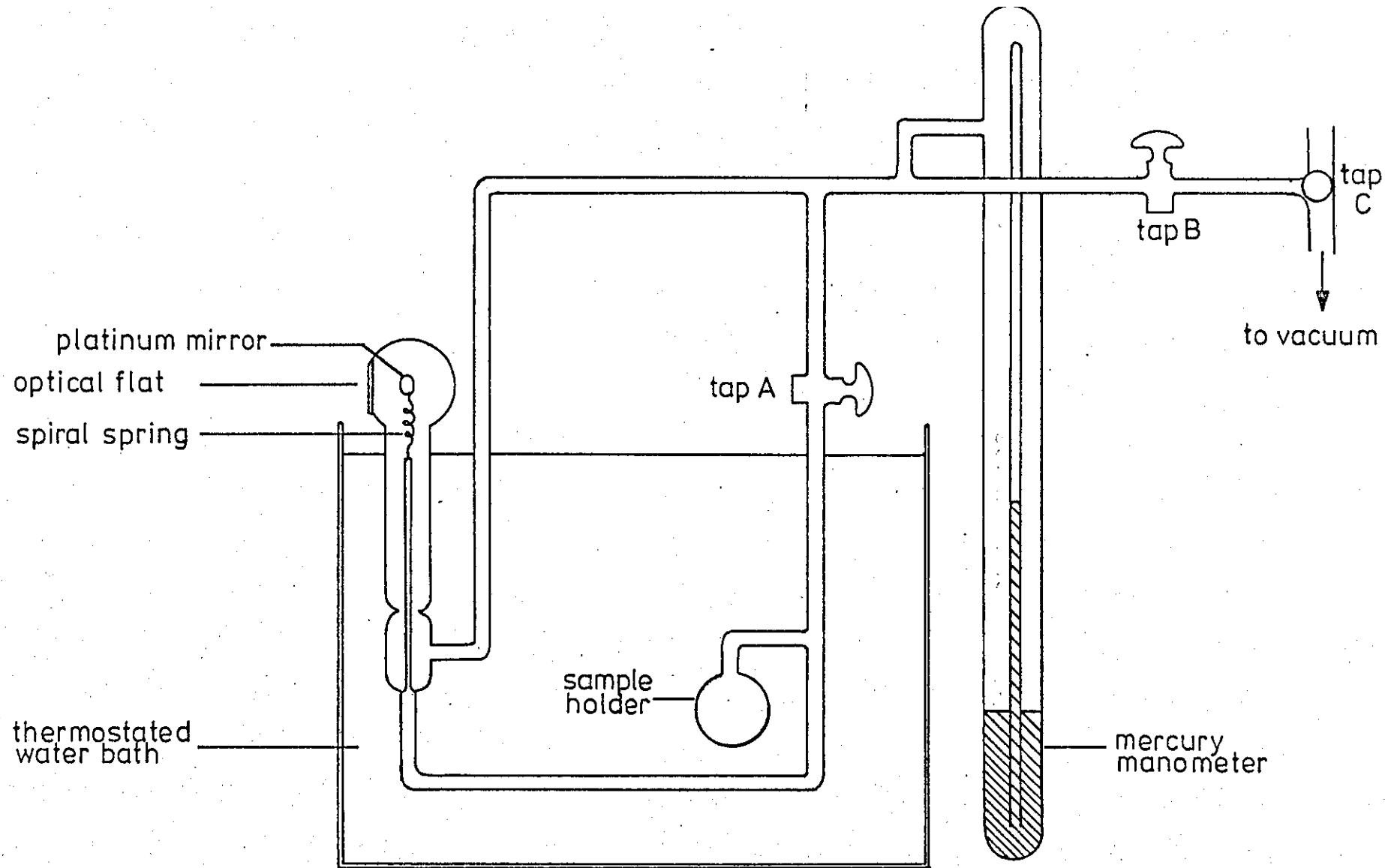
FIGURE 2.2.   Vapour pressure apparatus

a thermostatically controlled water bath, up to the base of tap A (figure 2.2). The system was allowed to reach thermal equilibrium (about two hours in this first instance). Tap B was then closed, the lamp filament focused on the centre of the scale, and this "zero" reading noted. After this, care was taken not to move the lamp, scale or apparatus in the water bath, as this would shift the "zero" position of the reflected filament. The temperature of the bath was recorded and raised by 3 - 4°C. After the apparatus had again reached thermal equilibrium (indicated by the position of the filament image on the scale remaining steady, about 40 minutes in all), tap C was opened to the air and tap B carefully opened. Air was let into the right-hand side of the apparatus until the image of the filament had returned to the "zero" position on the scale. At this point the pressure in both sides of the apparatus was equal, and so the pressure recorded on the manometer was equal to the vapour pressure of the sample in the other half of the apparatus. The manometer was read using a katharometer, and the temperature of the water bath noted. The manometer side of the apparatus was then evacuated and the temperature of the water bath raised prior to the next reading. The water bath could be heated from 18 to 90°C by means of an immersion heater, temperature control of better than $\pm$ 0.1°C being achieved by means of a 100 watt carbon filament lamp connected to an adjustable thermostat. For temperatures above 75°C, a 250 watt immersion heater replaced the carbon lamp. The temperature of the water bath was recorded by means of 0-50 and 50 - 110°C thermometers, whose accuracy was checked against a N.P.L. calibrated thermometer. Polystyrene spheres were used to reduce heat and water losses at the surface of the bath.

TABLE 2.3

CONDUCTIVITY DATA

COMPOUND	CONC^N g.eq./l	CONDUCTIVITY ohm^{-1}	CELL CONSTANT	SPECIFIC CONDUCTIVITY ohm^{-1} cm^{-2} (AV)	EQUIVALENT CONDUCTIVITY ohm^{-1} (AV)
AgNO$_3$	0.001	7.35×10^{-4}	0.123	9.04×10^{-5}	90.4
CuCl	0.001	4.14×10^{-5} to 5.14×10^{-5}	0.123	5.71×10^{-6}	5.7
pyridine	–	3.74×10^{-6}	0.123	4.6×10^{-7}	–

The results of the vapour pressure measurements are presented in figures 2.3 and 2.4 as graphs of $\log_{10}P$ versus $1/T^\circ$ K.

2.2.3 Conductivity measurements

Conductivity measurements were made on a copper (I) chloride-pyridine solution using the apparatus shown in figure 2.5, which was designed to measure conductivities under anaerobic conditions. The conductivity of a M/1000 solution of copper (I) chloride in pyridine was compared with that of a M/1000 solution of a 1:1 electrolyte, silver nitrate, at the same temperature. The procedure adopted is outlined below.

Dry copper (I) chloride (0.001 mole) was weighed into the conductivity cell and the apparatus flushed out with dry nitrogen. Dry degassed pyridine (50 ml) was added through the rubber septum using a syringe, and the solution was stirred magnetically until all the solid had dissolved. The cell was then placed in a thermostatically controlled liquid paraffin bath and allowed to reach thermal equilibrium. Liquid paraffin was used for a constant temperature bath as a water bath leads to spurious readings at very low conductivities. The temperature was maintained at 25 ± 0.2°C. After one hour in the constant temperature bath, the conductivity of the solution was measured by means of the platinum black electrodes attached to a Wayne Kerr conductivity bridge. The cell constant was determined both before and after the experiment with a M/1000 potassium chloride solution at 25°C.

The experiment was repeated with dry silver nitrate (0.001 mole), and then with pyridine alone.

During these studies, it was observed that the conductivity of the solutions did not remain constant over an extended period of time. Whilst this effect was relatively small (ca. ± 10%) at
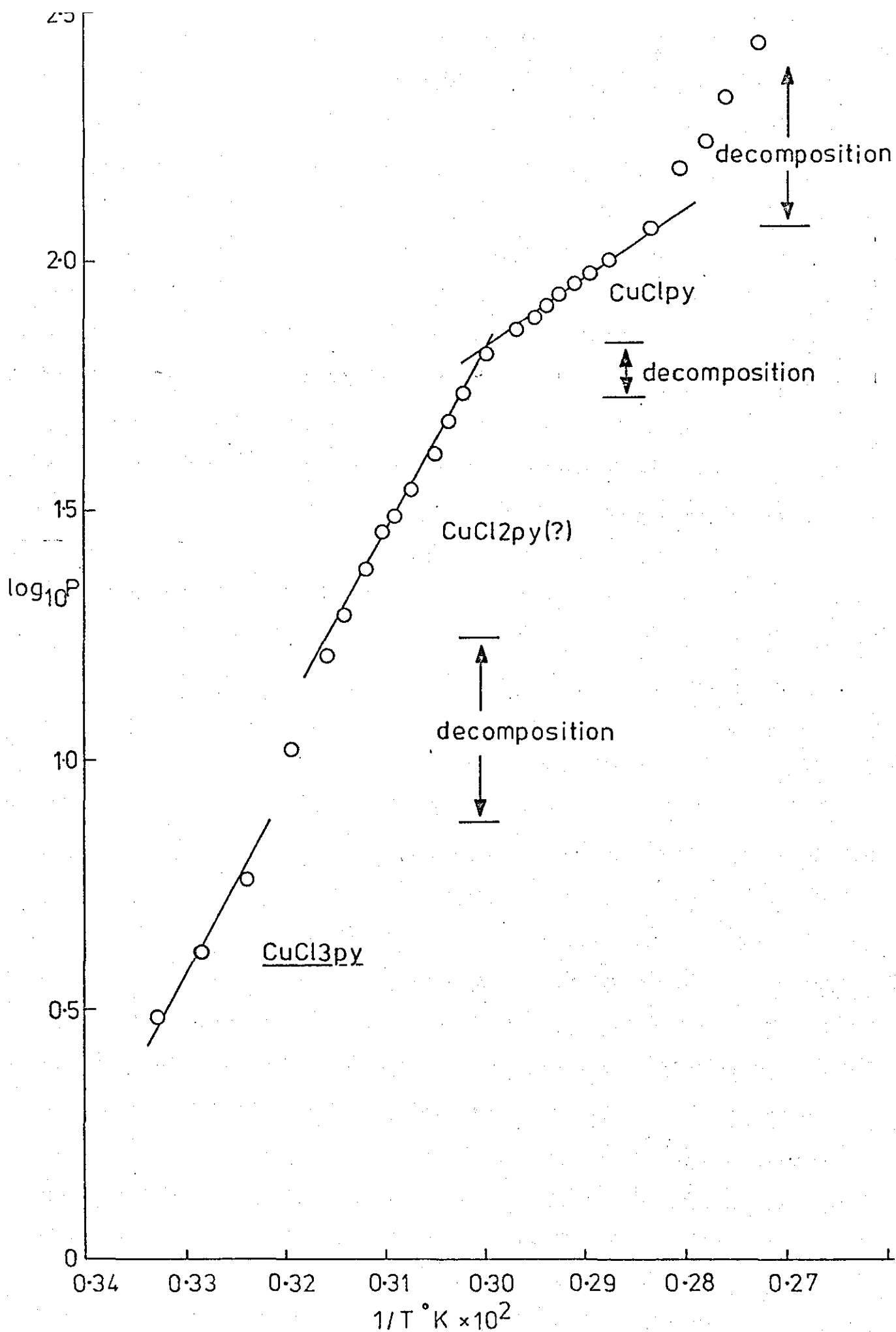
FIGURE 2.3. Graph of $\log_{10}P$ vs $1/T\,°K$ for CuCl3py.

FIGURE 2.4. Graph of $\log_{10} P$ vs $1/T^\circ K$ for CuBr3py.

to conductivity bridge

rubber septum

nitrogen

nitrogen

platinum black electrodes
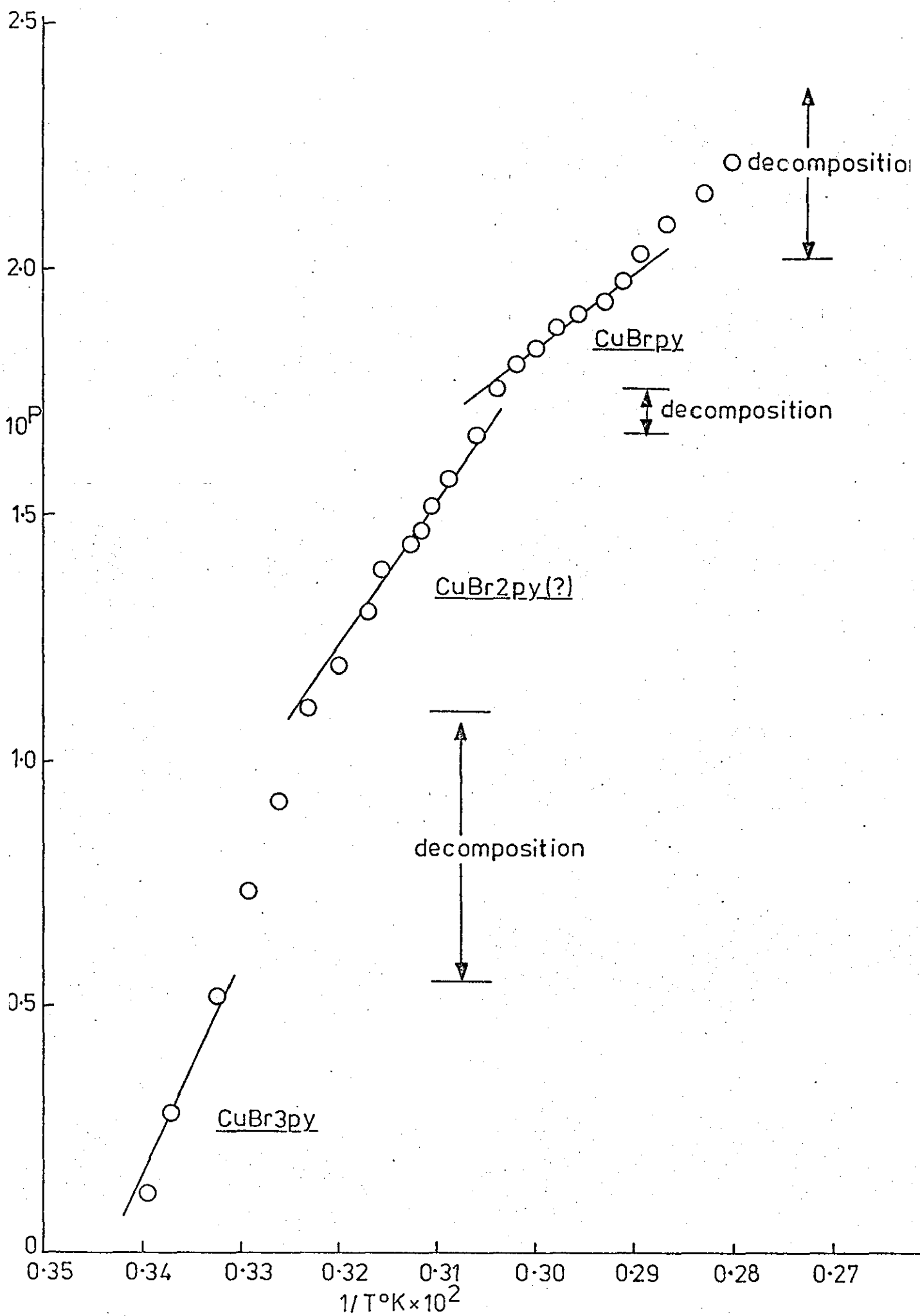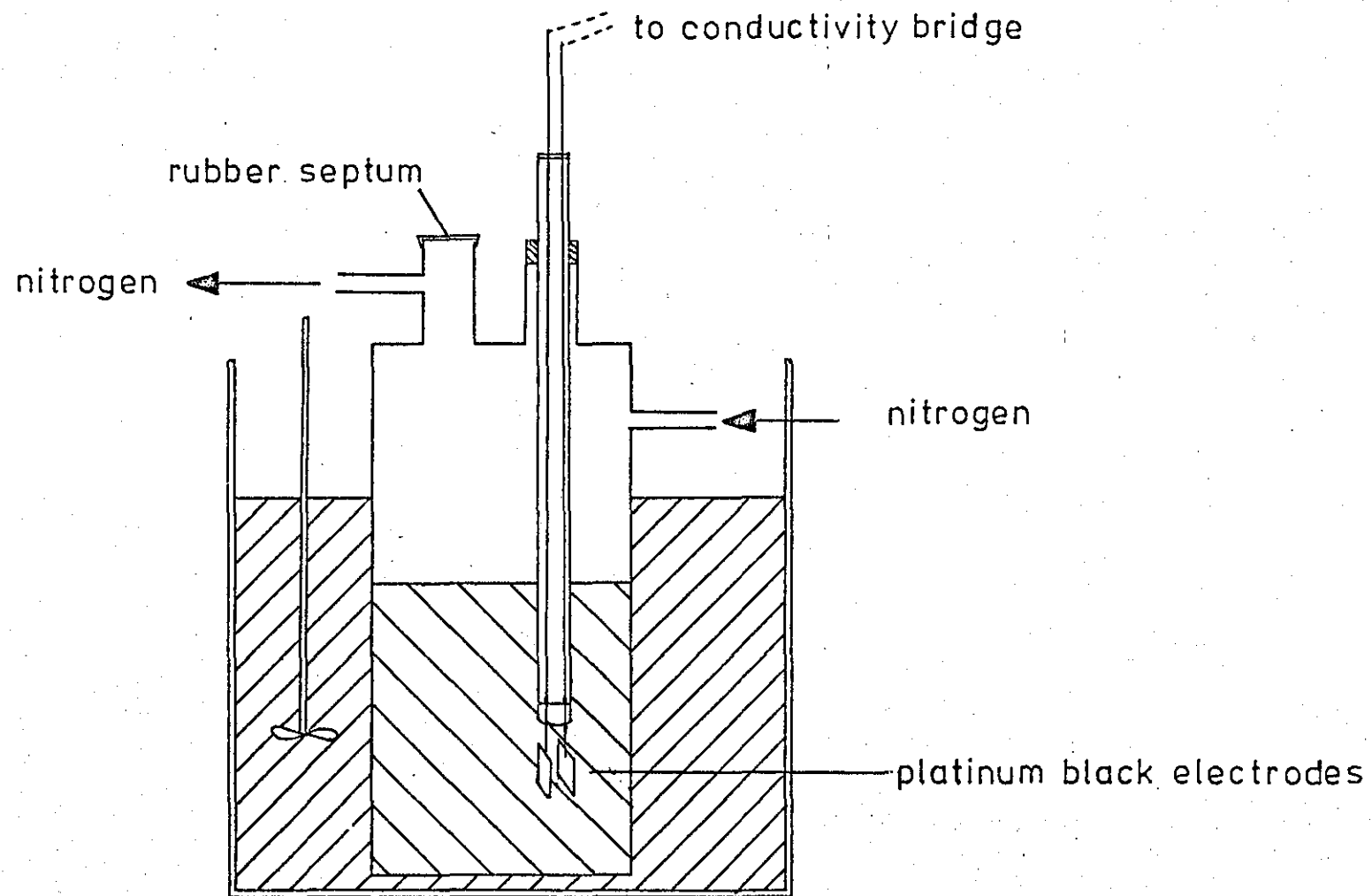
FIGURE 2.5. Conductivity apparatus

concentrations of solute in the order of M/1000, attempts to

measure the conductivity at solute concentrations of M/2000 and

lower, resulted in large fluctuations over a period of a few

hours (Ca. ± 100%). It was hoped to record conductivities at

various concentrations of copper (I) chloride in pyridine, in order

to investigate the electrolyte type by the method of Feltham and

Hayter (47). However, this had to be abandoned due to the large

fluctuation in conductivity observed at concentrations below

M/1000.

These variations in conductivity have not been satisfactorily

explained. However, pyridine has not been used and is not

recommended for use as a solvent in conductivity measurements, due

to its strong donor properties and low dielectric constant (48).

It may be that, due to the very low specific conductivities

encountered (ca. 1 x 10^{-6} ohm^{-1}) when working in pyridine at low

concentrations of solute, small changes in temperature may cause

large conductivity changes. Working with a liquid paraffin bath

means that the temperature can only be controlled to ± 0.2°C (due to

viscosity and heat transfer effects) and this may account for the

conductivity variations experienced. The results of the

conductivity measurements are contained in table 2.3.

2.2.4 Reagents

Copper (I) chloride and bromide were prepared by the reduction

of the corresponding copper (II) halide in aqueous solution, using

sulphur dioxide. The precipitated copper (I) halide was filtered

under a blanket of nitrogen. The white (chloride) or pale yellow

(bromide) product was washed with several portions of glacial

acetic acid, followed by absolute ethanol and anhydrous diethyl ether,

and dried in vacuo(2 torr) at 20°C. The products were stored under

vacuum.

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Copper (I) iodide was prepared from the reaction between an aqueous copper (II) sulphate solution, and a solution of potassium iodide and sodium thiosulphate (44). The precipitated copper (I) iodide was filtered, washed with several portions of water, followed by absolute ethanol and anhydrous diethyl ether, and dried in vacuo (2 torr) over phosphorus pentoxide for several days. The product, an off-white solid was stored over silica gel and away from direct sunlight.

All three copper (I) halides were analysed for copper and halogen and found to be 99.5 - 99.9% pure.

The pyridine used was a Fisons G.P.R. solvent which was distilled twice from solid potassium hydroxide, then refluxed for two days over 4A molecular sieve. The solvent was then redistilled, the fraction boiling between 114°C and 116°C being collected. The purified, dry solvent was stored in an amber bottle over molecular sieve.

All other solvents used were distilled and dried by standard methods (45).

B.O.C. "white spot" nitrogen was used throughout and dried by passing it successively through columns of silica gel, aluminium oxide and molecular sieve type 5A. No attempts were made to remove the traces of oxygen in the gas (<5 ppm) since copper (I) chloride-pyridine solutions could be stored in contact with the nitrogen for several months, without any visible signs of oxidation.

2.2.5 Analytical procedures;

(a) Copper

Copper was determined gravimetrically by dissolving the complex in a minimum quantity of dilute nitric acid, neutralising the solution, and precipitating the metal as the ethylenediammine mercuric iodide complex according to standard procedures (49).

(b) <u>Halide</u>

   Chloride was determined potentiometrically by dissolving the

complex in concentrated nitric acid and titrating with standard

N/10 silver nitrate solution, using calomel and silver metal

electrodes, and a potassium nitrate salt bridge.

   Bromide was determined by the Mohr titration (49) using

standard N/10 silver nitrate and N/10 ammonium thiocyanate.

   Iodide was determined gravimetrically by dissolving the complex in

"880" ammonium hydroxide solution and precipitating the halide as silver

iodide, using a N/100 silver nitrate solution according to a standard

method (49).

   Analar reagents and halide free conductivity water were used

throughout.

2.3 <u>Discussion</u>

   Table 2.1 shows that complexes of stoichiometry CuCl3py,

CuClpy, CuBr3py, CuBrpy, and CuIpy have been established,

confirming the work of De Ahna and Hardt(43). In addition,a

complex with apparent stoichiometry CuI2py has been prepared.

These complexes exhibit yellow or white colours as expected for

copper (I) compounds. A yellow complex of stoichiometry CuI3py was

reported by De Ahna and Hardt to be stable to loss of pyridine at

20°C, but the present work was unable to confirm this compound.

The chloride and bromide complexes are oxidised to copper (II)

compounds on exposure to the atmosphere: the monopyridine adduct

of copper (I) bromide is only slowly oxidised over a period of

several days exposure to the atmosphere, whereas the trispyridine

adduct of copper (I) chloride is completely oxidised after a few

seconds exposure to the air. A qualitative assessment of the

order of stability to oxidation results in the series:-

CuBrpy > CuClpy > CuBr3py > CuCl3py
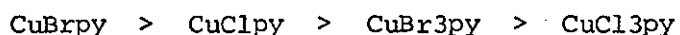
The infrared spectra of the copper (I) complexes (table 2.2)
are , in many respects, similar to copper (II)-pyridine complexes.
Co-ordinated pyridine can be readily distinguished from the free
amine by a shift in the strong 1583 cm^{-1} band to around 1600 cm^{-1};
and by shifts of the 605 and 405 cm^{-1} bands to 645 and 444 cm^{-1}
respectively for copper (II) complexes (50). In general there is a
tendancy for the fundamental modes of the amine to be at a slightly
higher frequency on co-ordination. This may be considered to arise
from the inductive effect consequent on co-ordination. The smallness
of these shifts has been attributed (51) to back donation which
weakens bonds by partially filling the ligand π^* orbitals. The
shifts tend to be greater for the chloride than the bromide
complexes of copper (II), which implies that the co-ordination of
the amine is stronger in the chloride than the bromide complex.
The frequencies of the ligand bands decrease as the negative
charge accumulated on the metal increases, or as metal ligand
π-bonding increases; thus the higher polarizability of Br$^-$
relative to Cl$^-$ explains why the ligand frequencies are generally
slightly lower in the bromide complexes.

The shift of the fundamental modes of pyridine on co-ordination
can be observed in the pyridine complexes of copper (I) halides.
However, it is noticeable that the shifts in those complexes are
much smaller than in the corresponding copper (II) compounds, indicating
that the co-ordinate bond is weaker in copper (I) complexes, as might
be expected due to the smaller charge on the metal atom. Where
there are noticeable differences between the positions of the bands in
chloride and bromide copper (I) complexes, these differences imply
a stronger co-ordinate bond, for the chloride complexes similar to

that observed for copper (II)-pyridine compounds. This trend is also

seen in CuIpy in which the pyridine is least strongly co-ordinated of

all the monopyridine adducts. Similar trends can be observed between

the various pyridine adducts of a particular copper (I) halide

where, in general, the greater the co-ordination number of the

copper species, the weaker the co-ordinate bond, as reflected in

the positions of the infrared bands. Hence it is now possible to

distinguish between not only copper (I) and copper (II)-pyridine complexes

by means of infrared data, but also to distinguish between copper (I)

halides with different amounts of pyridine ligand. The infrared

spectrum of the species with stoichiometry CuI2.4py (not tabulated)

showed the presence of unco-ordinated pyridine, with bands at 405,

605, 700 and 1583 cm^{-1}. This suggests that the complex of

stoichiometry CuI3py obtained by De Ahna and Hardt may well have

contained unco-ordinated pyridine. They did not report the x-ray

powder pattern of this particular complex, nor analytical

data for this or any other of the amine complexes prepared. Hence

there must remain some doubt as to the existence of a trispyridine

adduct of copper (I) iodide. The infrared spectra of the species

isolated during the attempted preparation of the bispyridine adducts of

copper (I) chloride and bromide (2.2.1 above), indicated that they

were mixtures of the mono- and trispyridine complexes. In a typical

preparation, a sample analysing as CuCl1.7py had bands at 692, 704,

747 and 1156 cm^{-1} due to CuClpy, and at 700, 755 and 1150 cm^{-1}

due to CuCl3py. No spectral data suggesting a bispyridine species

were obtained.

Preparations involving high vacuum techniques are not likely

to reveal the presence of bispyridine complexes that may be relatively

unstable to loss of pyridine. A similar argument can be applied to

the thermogravimetric work of De Ahna and Hardt (43), which was
conducted under a vacuum, and indicated a one step decomposition of
the trisamine adducts to give monoamine complexes. Consequently,
vapour pressure measurements were made to determine whether the
bispyridine adducts could be detected under higher vapour pressures
of pyridine than had existed under the experimental conditions
previously used. A graph of $\log_{10}$ vapour pressure versus reciprocal
temperature should reveal the presence of stable pyridine adducts
and their subsequent decompositions, by changes in the slope of the
graph. The results for the appropriate chloride and bromide
complexes, shown in figures 2.3 and 2.4 respectively, reveal smaller
changes in the slopes of the graphs than had been expected, but do
however indicate a multistage decomposition for both complexes.
From this present work and from the work of De Ahna and Hardt it
is clear that the monopyridine adducts of copper (I) chloride
and bromide are stable under high vacuum at temperatures in excess
of 40°C. Hence the highest temperature "plateau" on the vapour
pressure – temperature graph will correspond to these stable
monopyridine adducts. This is indicated in figures 2.3 and 2.4.
The decomposition of the monopyridine adducts at high temperature
is clearly visible as a large increase in vapour pressure, resulting
in a positive slope change. Two other "plateaux" at lower
temperatures are discernable on both figures, the one at lowest
temperatures will correspond to the trispyridine adducts, (since
that was the species at the beginning of the experiment) with
subsequent decomposition as indicated by a positive increase in the
slope of the graphs. The other 'plateau' occuring between the stable
tris- and monopyridine adducts may well correspond to the bispyridine
adducts or some other intermediate. The small changes in vapour

pressure corresponding to the decomposition of this complex is an
indication that it is very unstable to loss of pyridine, and probably
exists over a very limited temperature range.

The results of the conductivity measurements (table 2.4) must
be treated with caution for reasons already stated. They do, however,
indicate that copper (I) chloride is a non-electrolyte in pyridine
solution; there being a very large difference between the equivalent
conductivity of the copper (I) chloride solution and the slution of
the 1:1 electrolyte, silver nitrate. These differences cannot be
accounted for in terms of experimental error. Due to the insolubility
of the copper (I) halide-pyridine complexes in organic solvents,
it was not possible to measure the molecular weight of these
compounds and determine whether they were monomeric or polymeric in
nature. However,complexes of the type CuXR, where X is halide, and
R a monodentate ligand,have been shown by x-ray crystallography and
molecular weight studies to be tetrameric in form. Complexes such
as $[CuI(AsR_3)]_4$, (R = Me., Et., Bu.^{n}), and $[CuBr(AsPh_3)]_4$ are
well known (52, 53). De Ahna and Hardt's work on the thermal
decomposition of the monoamine adducts of copper (I) halides, which
showed a multistage decomposition, indicate that these complexes
could well be polymeric. The molecular weights of copper (I) chloride
and bromide in pyridine have been determined recently in these
laboratories (54), and shown to be 484 and 392 respectively
$[(CuCl)_4 = 396, (CuBr)_4 = 574]$·Copper (I) halides therefore
have polymeric structures in pyridine solution, and by analogy
with the above x-ray work, similar structures are probable for the
copper (I) halide-pyridine complexes in the solid as well.

CHAPTER THREE

TETRANUCLEAR COPPER (II) COMPLEXES —

PREPARATION AND PROPERTIES

3.1 Introduction

A relationship between tetranuclear copper complexes and the product from a reaction closely associated with the copper-amine catalyst system was mentioned in Chapter One. At this stage it is relevant to describe polynuclear copper (II) complexes containing the structural unit Cu_4O in more detail. This section describes the structure and properties of these complexes, as well as general methods of preparation. The number of known tetranuclear copper complexes has been extended by this present investigation and the preparation and properties of these complexes are described. In addition, the attempted preparation of tetranuclear complexes with various anions and involving other metals is reported.

3.1.1 Structural properties

The first preparation of a tetranuclear copper (II) complex of stoichiometry Cu_4OX_64L, where X is chloride or bromide, and L is a monodentate ligand, was reported by Finkbeiner in 1966 (7). He prepared the complex Cu_4OCl_64py by the oxidation of a copper (I) chloride-pyridine mixture in iso-propyl alcohol. Finkbeiner, however, did not realise the true nature of the complex, believing it to be a mixture of basic copper salts. The first crystal structure of a complex of this stoichiometry was reported by Bertrand and Kelley in 1966 (55, 56). Since then the crystal structure of a further seven cluster compounds of this type has been reported (57 - 63). These complexes contain the structural unit Cu_4OX_6, in which the central oxygen atom is tetrahedrally co-ordinated to four copper atoms, which are bridged in pairs by six halide atoms (chloride or bromide). The trigonal bipyramidal co-ordination of the copper is completed by the presence of an axial ligand. A perspective drawing of the structure is shown in figure 3.1. Copper (II) compounds of this type
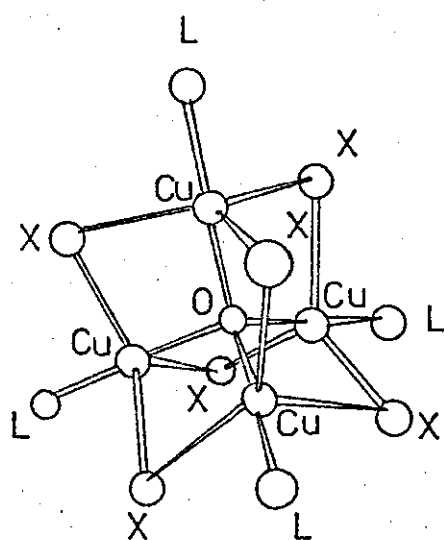
FIGURE 3.1. Structure of the tetranuclear copper (II)
complexes $Cu_4OX_6 4L$

are similar in structure to the basic beryllium and zinc acetates

(64, 65) and the Grignard oxidation product $Mg_4OBr_64(OC_4H_{10})$ (66)

and are unusual in that they contain five co-ordinate copper and

four co-ordinate oxygen. About forty of these copper cluster complexes

are now known, the majority of them reported by Bock et al.(67) and

Dieck and Brehm (68), and containing amine ligands in the axial

position. A few complexes are known with chloride or bromide atoms

in the axial position, and in these cases counter ions such as

potassium (62, 68) ammonium (68), tetramethyl ammonium, (55, 58, 68)

and NNN'N' tetraethylethylene diammonium (61) have been used.

Structural data from x-ray crystal studies (55-63) reveal that the

dimensions of the Cu_4O unit (Cu-O, $1.91\overset{o}{A}$; Cu-Cu, $3.12\overset{o}{A}$; Cu-O-Cu, 109°)

for all the reported structures, are almost identical to those of

the Cu_4O unit in copper (II) oxide (32). Although the tetrahedron

formed by the four copper atoms is fairly regular in all the reported

crystal structures, the halide octahedron of the Cu_4OX_6 unit is

distorted to some degree. Whereas this distortion is small for the

species $[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$ (55, 58), $Cu_4OBr_64(NH_3)$ (60), and

$Cu_4OCl_64(TPPO)(55, 56)$, it is considerable in the case of

$Cu_4OX_64py(57, 63)$ and $Cu_4OCl_64(2-mepy)$ (59). $Cu-Cl_{eq.}$ - Cu angles

for the decachloride complex vary from only 81.2° to 81.5° but

for the 2-methylpyridine complex, between 78.2 and 80.2° while the

corresponding $Cl_{eq.}$ - Cu - $Cl_{eq.}$ angles lie between 118.9° and

120.5° and 95.9° and 155.0° respectively. The cause of these

distortions has been suggested to be intermolecular hydrogen-chlorine

contacts in the case of the pyridine complex (57), and intramolecular

carbon-chlorine or hydrogen-chlorine contacts in the 2-methylpyridine

complex (59).

The magnetic moments for these cluster compounds lie between

1.9 and 2.2.B.M. per copper atom, within the range predicted for

trigonal bipyramidal copper (II) (69). There appears to be no

interaction between metal atoms. Since superexchange is usually

found in copper complexes containing a bridging oxygen (70), such an

interaction might have been expected. However, it has been suggested

(71) that superexchange involves coupling of spins through π-orbitals

on oxygen and, with the outer s and p orbitals used for σ-bonding,

there are no orbitals available on the oxygen for π-bonding in these

complexes. A recent study by Barnes et al. (72) and Lines et al. (73)

on the magnetic properties of tetranuclear copper complexes at

low temperatures, revealed evidence for antisymmetric exchange in

the pyridine and triphenyl-phosphine oxide complexes, but not in the

decachloride complexes.

The electronic spectra of these tetranuclear copper complexes

(56, 57, 59, 61, 67) show one broad band between 700 and 1000 nm,

sometimes with an associated shoulder. This band has been assigned

to d-d transitions (56). Apart from x-ray structural data, these

copper cluster compounds can be readily distinguished from other

copper (II) halide-ligand complexes, by means of their colour and

infrared spectra. Tetranuclear chloride complexes are yellow and

bromide complexes brown, whereas the majority of copper (II) halide-

ligand complexes are blue or green. The other major distinguishing

feature is the presence of a strong band in the infrared spectra

of the cluster compounds, which has been assigned to the assymmetric

Cu-O stretching vibration (67, 68). This band is sensitive to the

nature of the axial ligand, as well as the bridging halide and lies

between 500 and 600 cm^{-1}; it has been used to characterise many

of the known tetranuclear copper complexes (67, 68, 74, 75).

3.1.2 Preparative methods

The most important preparative method for these polynuclear copper complexes involves a reaction between copper (II) halide and copper (II) oxide. There are two main variations on this reaction. The method used by Dieck and Brehm (68) is to reflux a 3:1 mixture of anhydrous copper (II) chloride and copper (II) oxide in anhydrous methanol for 1-2 hours, filter the resulting solution and remove the methanol under vacuum. The product is the tetranuclear complex with axial methanol groups, which is slurried in anhydrous diethyl ether. A stoichiometric amount of the appropriate ligand is added, and the required tetranuclear complex formed by replacement of the axial methanol by the ligand. This reaction scheme is shown in equations 3.1 and 3.2 below.

$$3CuCl_2 \ + \ CuO \ \xrightarrow{\substack{(1) \ \text{reflux in MeOH} \\ (2) \ \text{remove MeOH}}} \ Cu_4OCl_6 \cdot 4MeOH \qquad (3.1)$$

$$Cu_4^{\flat}OCl_6 \cdot 4MeOH \ \xrightarrow{\substack{Et_2O \\ 4L}} \ Cu_4OCl_6 \cdot 4L \ + \ 4MeOH \qquad (3.2)$$
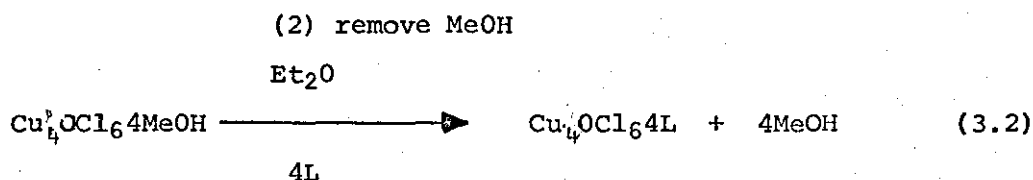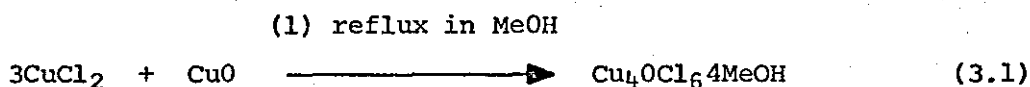
Dieck and Brehm did not extend this preparative method to the analogous bromide complexes.

The other common method of preparation involves simply refluxing a stoichiometric amount of copper (II) halide, copper (II) oxide and ligand in methanol or nitromethane for 24 hours, filtering the hot solution, and allowing the tetranuclear species thus formed to crystallise over a period of days (55, 56, 58).

One of the more unusual features of these copper cluster compounds is the variety of ways in which they can be prepared. It is possible to prepare them from reactants containing less than the required copper to chlorine ratio of 1:1.5, as well as from

TABLE 3.1

UNUSUAL PREPARATIVE METHODS FOR TETRANUCLEAR COPPER (II) COMPLEXES

COMPLEXES	PREPARATIVE METHODS	REFERENCE
$Cu_4OCl_64(TPPO)$	recrystallisation of $CuCl_22(TPPO)$ in methyl isobutyl ketone	55, 56
$Cu_4OCl_64(2-mepy)$	$CuCl_22H_2O + 2-mepy$	59
Cu_4OCl_64py	oxidation of a CuCl-pyridine mixture	7, 57
Cu_4OBr_64py	reflux $CuBr_22py$ in ethanol	63
$Cu_4OBr_64(NH_3)$	recrystallisation of Bromo [2 phenyl-2(diethylamino)ethoxo] copper (II) from nitromethane	60
$K_4Cu_4OCl_{10}$	oxidation of CuCl in a melt of K_2CuCl_4	62

TPPO = Triphenylphosphine oxide

systems where the source of the central oxygen atom is not
immediately obvious. In fact it is fair to say that the majority
of these complexes whose crystal structure has been determined,
were first prepared more by accident than design. A summary of
some of the more unusual preparations is contained in table 3.1.
Bock (67) has used the reaction between copper (II) chloride
dihydrate, sodium hydroxide and an amine to prepare several
tetranuclear species with substituted pyridines and quinoline,
according to equation 3.3.

$$4CuCl_2 2H_2O \ + \ 2NaOH \ + \ 4L \ \xrightarrow[20°C]{2 \ days} \ Cu_4OCl_6 4L \ + \ 2NaCl \ + \ 9H_2O \qquad (3.3)$$

$$L \ = \ amine$$
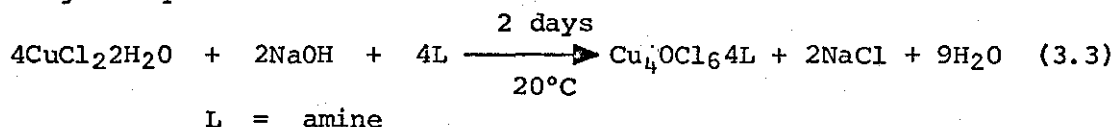
This reaction, however, is very slow and yields of tetranuclear
species are small (< 8%). Carr and Harrod (74) have prepared
several tetranuclear copper complexes as by-products, during the
preparation of low molecular weight polymers, by the thermal
decomposition of halophenoxycopper (II) compounds (equation 3.4).
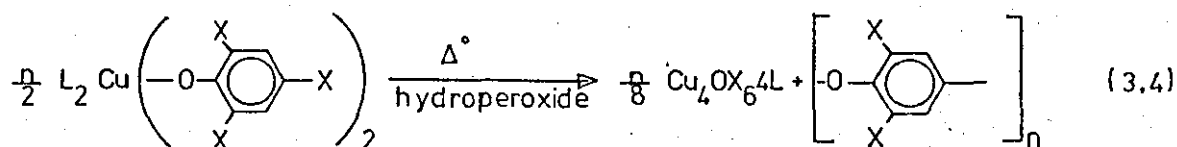
$$\begin{array}{ll}
L \ = \ C_5H_5N & X \ = \ Cl \\
\quad\ \ C_2H_5NH_2 & \quad\ \ Cl \\
\quad\ \ (C_6H_5)_3PO & \quad\ \ Cl \\
\quad\ \ NH_3 & \quad\ \ Cl \\
\quad\ \ (CH_3)_2N.CHO & \quad\ \ Cl \\
\quad\ \ (CH_3) SO & \quad\ \ Cl \\
\quad\ \ C_5H_5N & \quad\ \ Br
\end{array}$$

This decomposition reaction normally yields the bisligand
dihalo-copper (II) species, $CuX_2:2L$, but the addition of
hydroperoxides produces an almost 100% yield of tetranuclear complex

(based on copper). However this method of preparation is not of practicable value due to difficulties in preparing the starting material and separating the tetranuclear complex from the polymer.

There has been little work reported on the preparative reactions themselves. Gill and Sterns (59) have shown that the reaction between anhydrous copper (II) chloride and 2-methylpyridine in anhydrous methanol produces the methoxide complex [Cu(OMe)Cl2-mepy]$_2$, whereas the corresponding reaction with copper (II) chloride dihydrate yields the tetranuclear complex, even in the absence of oxygen. They suggested that the central oxygen atom in this latter complex comes from the water in the system. Belford et al. (61) have suggested that tetranuclear copper (II) complexes are formed by controlled base hydrolysis reactions, involving the aggregation of two binuclear hydroxy bridged copper (II) complexes, with subsequent condensation and dehydroxylation to form the Cu$_4$O unit.

TABLE 3.2

ANALYTICAL DATA FOR TETRANUCLEAR COPPER (II) COMPLEXES

LIGAND (L)	ANALYSES - Cu_4OX_64L								ν Cu - O asym. cm^{-1}	
	X = Cl				X = Br					
	% Cu		% Cl		% Cu		% Br			
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	X = Cl	X = Br
4-amino Pyridine	29.50	29.58	24.54	24.75	22.61	22.57	42.64	42.58	578	550
3,4-dimethyl Pyridine	27.55	27.88	23.15	23.34	21.41	21.57	40.65	40.69	572	530
3,5-dimethyl Pyridine	27.56	27.88	22.93	23.34	21.29	21.57	40.71	40.69	574	530
2,4 dimethyl Pyridine	27.60	27.88	23.08	23.34	21.19	21.57	40.40	40.69	575	534
4-Cyano Pyridine	28.36	28.26	23.89	23.65	21.60	21.90	41.32	41.12	580	538
Methanol	-	-	-	-	28.67	28.95	54.31	54.62	-	555
Piperidine	30.72	31.07	25.84	25.96	23.24	23.40	43.91	44.14	566	532

TABLE 3.3

ANALYTICAL DATA FOR TETRANUCLEAR COPPER (II) COMPLEXES

LIGAND (L)	ANALYSES – Cu_4OX_64L							
	X = Cl				X = Br			
	% Cu		% Cl		% Cu		% Br	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
Pyridine	31.55	31.80	26.48	26.61	23.80	23.84	44.92	44.98
2-methyl pyridine	29.60	29.71	24.85	24.87	–	–	–	–
3-methyl pyridine	29.84	29.71	24.88	24.87	22.40	22.65	42.45	42.73
4-methyl pyridine	29.92	29.71	24.91	24.87	22.60	22.65	42.45	42.73
Methanol*	39.64	41.59	33.20	34.81	–	–	–	–

* Isolated as Cu_4OCl_64MeOH: MeOH(Calc.%Cu, 39.52: %Cl, 33.07)

TABLE 3.4

ELECTRONIC REFLECTANCE SPECTRA FOR SOME TETRANUCLEAR COPPER (II) COMPLEXES

LIGAND (L)	λ MAX FOR Cu_4OX_44L (nm)	
	X = Cl	X = Br
4-aminopyridine	870, 775 (sh)	855
3,4-dimethylpyridine	850	850
3,5-dimethylpyridine	840	835
2,4-dimethylpyridine	825	820
4-cyanopyridine	–	874, 990 (sh)
piperidine	800,875 (sh)	825
3-methylpyridine	850, 800 (sh)	840
4-methylpryidine	860, 825 (sh)	850
pyridine	800	820, 900 (sh)

sh = shoulder

TABLE 3.5

THERMAL DATA FOR SOME TETRANUCLEAR CHLORIDE COMPLEXES WITH SUBSTITUTED PYRIDINES

COMPLEX	LIGAND pKa	DECOMPOSITION TEMPERATURES °C			WEIGHT LOSS %		PRODUCT
		T_s	T_m	T_f	Found	Calc. for loss of 4L	
$Cu_4OCl_6 4(pip)$	11.20	150	180	400	41.2	41.4	$3CuCl_2$ CuO
$Cu_4OCl_6 4(NH_2py)$	9.17	220	320	>400	33.0	43.8	?
$Cu_4OCl_6 4(2,4\text{-dimepy})$	6.72	150	300	350	47.6	47.0	$3CuCl_2$ CuO *
$Cu_4OCl_6 4(3,4\text{-dimepy})$	6.52	160	220	>400	34.8	47.0	?
$Cu_4OCl_6 4(3,5\text{-dimepy})$	6.14	160	230	400	46.2	47.0	$3CuCl_2$ CuO
$Cu_4OCl_6 4(4\text{-mepy})$	5.98	230	250	>400	39.2	43.6	?
$Cu_4OCl_6 4(2\text{-mepy})$	5.96	140	240	290	43.8	43.6	$3CuCl_2$ CuO
$Cu_4OCl_6 4(3mepy)$	5.63	230	320	340	43.0	43.6	$3CuCl_2$ * CuO

T_s = Temperature at start of decomposition.

T_m = Temperature at maximum rate of weight loss.

T_f = Temperature at end of decomposition.

* Product composition confirmed by x-ray powder diffraction data.

TABLE 3.6

THERMAL DATA FOR SOME TETRANUCLEAR BROMIDE COMPLEXES WITH SUBSTITUTED PYRIDINES

COMPLEX	LIGAND pKa	DECOMPOSITION TEMPERATURES °C			WEIGHT LOSS %		PRODUCT
		T_s	T_m	T_f	FOUND	CALC. FOR LOSS OF 4L	
$Cu_4OBr_6 4(pip)$	11.20	120	150	390	31.7	31.0	$3CuBr_2$ CuO
$Cu_4OBr_6 4(NH_2py)$	9.17	160	300	>400	32.0	33.4	?
$Cu_4OBr_6 4(2,4-dimepy)$	6.72	140	260	330	36.9	36.4	$3CuBr_2$ CuO *
$Cu_4OBr_6 4(3,4-dimepy)$	6.52	160	290	>400	29.6	36.4	?
$Cu_4OBr_6 4(3,5-dimepy)$	6.14	145	210	390	36.1	36.4	$3CuBr_2$ CuO
$Cu_4OBr_6 4(4-mepy)$	5.98	140	180	380	33.8	33.2	$3CuBr_2$ CuO

T_s = Temperature at start of decomposition.

T_m = Temperature at maximum rate of weight loss.

T_f = Temperature at end of decomposition

* Product composition confirmed by x-ray powder diffraction data.

3.2 Experimental and Results

3.2.1 Preparation of some tetranuclear complexes of the type Cu_4OX_64L

During the course of this present investigation, several new tetranuclear copper (II) complexes were prepared in order to study a wide range of these cluster compounds. Several other complexes, previously reported by other workers, were prepared for the same purpose. Analytical and infrared data for the former compounds are contained in table 3.2 and analytical data for the latter complexes in table 3.3. Table 3.4 details reflectance spectra between 1000 and 500 nm for many of these compounds, and tables 3.5 and 3.6 list thermogravimetric data.

With the exception of the 2-methyl pyridine and methanol complexes, all the tetranuclear complexes contained in tables 3.2 and 3.3 were prepared by a variation on the method of Dieck and Brehm (68). This new method was found to produce very pure products, it was quick and did not require anhydrous conditions. Copper (II) halide (0.1 mole, $CuCl_22H_2O$ or $CuBr_2$) and copper (II) oxide (0.033 mole) were refluxed in ethanol (150 ml) for two hours. The solution was cooled and filtered. To a portion of the filtrate, half the stoichiometric amount of ligand (based on $CuX_2 \rightarrow Cu_4OX_6$) was added and the tetranuclear complex precipitated. The complex was filtered, washed with absolute alcohol, followed by anhydrous diethyl ether, and dried in vacuo (2 torr) at 20°C. The addition of a greater amount of ligand to the filtered copper (II) solution (hereafter refered to as the "Cu_4OCl_6" or "Cu_4OBr_6" solution) resulted in the formation of appreciable amounts of the bisligand species, CuX_22L, identified by the appearance of bands due to the Cu-N and Cu-X stretching vibrations of these complexes in the infrared spectrum (76). The addition of enough ligand to precipitate

all the copper from solution resulted in the formation of a mixture of the bisligand species, the tetranuclear species and paratacamite $Cu_2(OH)_3Cl$. These products were identified by infrared and x-ray powder diffraction data (77, 78). Several of the pyridine and methyl-pyridine complexes were found to contain small amounts of the bisligand species. The tetranuclear complex was purified by treating the product with boiling ethanol; the bisligand species being more sluble in ethanol than the tetranuclear complex, was easily removed in this way.

If a 3:1 mixture of copper (II) chloride dihydrate and copper (II) oxide was refluxed in ethanol for a long period of time (ca. 24 hours), a light green compound slowly precipitated. The infrared spectrum and x-ray powder diffraction pattern of this complex was compared with reported data (77, 78), and the compound identified as a mixture of paratacamite, $Cu_2(OH)_3Cl$, and copper hydroxychloride $Cu(OH)Cl$.This strengthens the theory mentioned earlier that copper hydroxide species are formed as precursors in the formation of tetranuclear complexes. This precipitation of basic copper salts was not evident in the analogous bromide reaction.

The tetranuclear 2-methyl pyridine complex (table 3.3) was prepared by the method of Gill and Sterns (59). They reported that this complex crystallised as the monohydrate (the water was identified by infrared spectra and elemental analysis). However the present work does not confirm this; several preparations had identical analytical data and showed no evidence for water in the infrared spectra. The tetranuclear methanol complexes were prepared under anhydrous conditions by the method of Dieck and Brehm (68). It was noticed during these latter preparations, which involved refluxing 0.4 mole copper (II) halide with 0.13 mole copper (II) oxide (3:1) in anhydrous

methanol, nearly half the copper oxide remained unreacted after two hours. As subsequent removal of the methanol resulted in an almost 100% yield of tetranuclear complex (based on halide), molecular oxygen or a reaction with methanol must provide a substantial proportion of the oxygen required for the cluster complex.

3.2.2   Reactions of "Cu_4OX_6" solutions with other ligands

Attempts were made to prepare tetranuclear copper (II) complexes with many other ligands, including some bidentate ones. The results of these preparations are contained in table 3.7. In most preparations the ligand was added to the ethanolic "Cu_4OX_6" solution; the only exception to this being the triphenyl phosphine complexes, the preparation of which followed the method of Dieck and Brehm (68). The products were characterised by halide analysis and, where possible, by a comparison of the infrared spectra with that of reported species. In the case of p-chloro aniline and m-nitro aniline, no infrared data had been reported, and the species CuX_22L were prepared by adding a solution of the ligand in ethanol to an ethonalic solution of the copper (II) halide, and washing the precipitated product with ether. The tetranuclear complexes that were prepared, contained large amounts of the bisligand species and were not obtained in pure form. Dieck and Brehm (68) reported the species $Cu_4OX_64(PPh_3)$ X = Cl, Br, to be stable up to 60°C; however the present work was unable to confirm this. The reduction of copper (II) halide complexes in ethanol by triphenylphosphine, -arsine and -stibine has been reported by Jardine et al. (53, 79), and the present work indicates that the copper (II) ions in tetranuclear complexes have similar redox properties.

TABLE 3.7

RESULTS OF THE ATTEMPTED PREPARATION OF TETRANUCLEAR COPPER COMPLEXES WITH VARIOUS LIGANDS

LIGAND (L)	SPECIES PRODUCED ON ADDITION OF LIGAND TO "Cu_4OX_6" SOLUTION
triphenylphosphine	Reduction to copper (I) - $CuX(PPh_3)$ (79)
triphenylarsine	Reduction to copper (I) - $Cu_2X_2(AsPh_3)_3$ (53)
triphenylstibine	Reduction to copper (I) - $Cu_2Cl_2(SbPh_3)_3$; $CuBr(SbPh_3)_3$ (53)
thiourea	Reduction to copper (I) - $CuCl(Tu)_3$ (80)
2,6-dimethylpyridine	$CuX_2 2L$ (76)
2,5-dimethylpyridine	$CuX_2 2L$ (76)
ethylenediammine	$CuX_2 2L$ (81)
2,2-dipyridyl	$CuX_2 2L$ (82)
quinoxaline	$CuX_2 2L$ (83)
4-nitro pyridine N-oxide	mixture of $CuX_2 2L$ and $Cu_4OX_6 4L$ Cu-O: 578 cm^{-1}, x = Cl, 532 cm^{-1}, x = Br (84)
p-toluidine	$CuX_2 2L$ (85)
p-chloro aniline	mixture of $CuX_2 2L$ and $Cu_4OX_6 4L$ Cu-O: 565 cm^{-1}, x = Cl, 522 cm^{-1}, x = Br
m-nitro aniline	mixture of $CuX_2 2L$ and $Cu_4OX_6 4L$ Cu-O: 560 cm^{-1}, x = Cl; 525 cm^{-1}, x = Br

3.2.3 Attempted preparation of tetranuclear complexes with other bridging anions

It was considered likely that tetranuclear copper (II) complexes containing anions with known bridging properties such as thiocyanate, acetate, hydroxide, cyanate and iodide could be prepared by methods similar to those described in section 3.2.1. The results of these preparations are summarised in table 3.8. The reactants were refluxed in the particular solvent system shown for periods ranging from 2 to 24 hours. The only tetranuclear species produced were the Cu_4OCl_6 or Cu_4OBr_6 complexes when halide atoms were present in the reaction mixture. It may be that the insolubility of the copper (II) starting material in ethanol or methanol (with the exception of copper (II) acetate) prevented a reaction with copper oxide, and formation of a tetranuclear species. Other solvent systems were not tried, but they could produce better results. The reaction of copper hydroxychloride with copper oxide to produce a "Cu_4OX_6" solution is a further indication that hydroxy species may be involved in the preparation of tetranuclear copper (II) complexes.

Copper (I) iodide was prepared by the method described in Chapter Two; copper hydroxychloride by the method of Iitaka (86), copper (II) hydroxide by the reaction between copper (II) chloride and sodium hydroxide; copper (II) cyanate was prepared by heating the hexapyridine complex at 80°C under vacuum for one day, the latter complex was prepared by the method of Davis and Logan (87).

3.2.4 Attempted preparation of tetranuclear complexes of other metals

The existence of the tetranuclear beryllium and zinc acetates and the Grignard oxidation product $Mg_4OBr_64(OC_4H_{10})$, all cluster complexes containing the structural unit M_4O, has already been

mentioned. In addition, Blake (88) has reported the preparation

of $Co_4O\cdot6(OCO\cdot CMe_3)$ which he assumed to be of similar structure.

It seemed probable that tetranuclear complexes of other metals

could be prepared, using similar methods to those described above

for copper. Consequently attempts were made to prepare cluster

complexes of cobalt, zinc, cadmium, magnesium and nickel by

refluxing the metal (II) halide and metal (II) oxide in alcohol,

and adding pyridine to the filtered solution. The results of

these preparations are shown in table 3.9. The products were

identified by halide analysis, and by reference to the reported

infrared spectra of metal-pyridine complexes. No tetranuclear

complexes were prepared; it is possible that reactions carried out

under rigorously anhydrous conditions might be more successful.

The copper salts used throughout these experiments were

Fisons G.P.R. chemicals. Pyridine was purified as described in

Chapter Two. The other amines used were B.D.H. or Koch Light

products, and were fractionallydistilled or recrystallised before

use. Copper and halide analyses, and infrared spectra were determined

as described in Chapter Two. Reflectance spectra in the region

1000 - 500 nm were obtained at 20°C on a Beckman DK2A spectrophotometer

equipped with a standard reflectance attachment. Thermogravimetric

data were determined on a C.I. Microforce electro balance, under an

atmosphere of nitrogen which had been rendered carbon dioxide free

and dried by means of successive columns of soda asbestos and

4A molecular sieve. A heating rate of 2°C per minute was used, and

the furnace temperature controlled by means of a Stanton-Redcroft

linear temperature programmer. The furnace had a maximum temperature

of 400°C. The temperature was recorded with a copper-constantan

thermocouple pair, with the reference thermocouple in an ice bath

The output was fed to the X-axis of the recorder. X-ray powder

TABLE 3.8

RESULTS OF THE ATTEMPTED PREPARATION OF TETRANUCLEAR COPPER COMPLEXES
WITH VARIOUS BRIDGING ANIONS

REACTANTS	SOLVENT SYSTEM	PRODUCT
$CuO + CuI + I_2$ (1:3:2)	ethanol	no reaction
$CuO + CuOHCl$ (1:3)	ethanol	$Cu_4OCl_6 4py$ produced on addition of pyridine to solution
$CuO + Cu(NCO)_2 6py$ (1:3)	ethanol and methanol	no reaction
$CuO + Cu(NCO)_2$ (1:3)	anhydrous methanol	no reaction
$CuO + Cu(OH)_2$ (1:3)	ethanol	no reaction
$CuO + KNCS + CuX_2$ (1:3)	ethanol and anhydrous methanol	$Cu_4OX_6 4py$ produced on addition of pyridine to solution
$CuO + Cu(OAc)_2$ (1:3)	ethanol	no reaction

TABLE 3.9

RESULTS OF THE ATTEMPTED PREPARATION OF M_4OX_64py SPECIES

REACTANTS	PRODUCT ON ADDITION OF PYRIDINE TO FILTERED SOLUTION
CoO + $CoCl_26H_2O$ (1:3) in EtoH	$CoCl_22py$ (blue and violet forms) $CoCl_24py$ (76, 89, 90)
NiO + $NiCl_26H_2O$ (1:3) in EtOH	$NiCl_22py$ $NiCl_24py$ (76, 90)
ZnO + $ZnCl_2$ 1:3) in EtOH	$ZnCl_22py$ (76, 90, 91)
CdO' + $CdCl_2$ (1:3) in EtOH	$CdCl_22py$ (79, 91)
MgO + $MgCl_2$ (1:3) in EtOH	$MgCl_2XH_2O$
ZnO + $ZnBr_2$ (1:3) in EtOH	$ZnBr_22py$ (90, 91)
CoO + $CoBr_2$ (1:3) in EtOH	$CoBr_22py$ (90)
NiO + $NiBr_2$ (1:3) in EtOH	$NiBr_22py$ (90)

diffraction lines were recorded using a standard Phillips

diffraction apparatus and filtered Cukα radiation. Samples were

powdered, and pressed onto a glass microscope slide.

3.3 Properties of Tetranuclear Copper (II) Complexes

The new complexes prepared during this investigation (table 3.2)

all show the characteristics of tetranuclear copper (II) compounds.

The chloride complexes were yellow and the bromides brown. The

copper-oxygen assymmetric stretching vibration occurs at similar

frequencies to those reported for other tetranuclear compounds (67,

68). All the complexes, with the exception of the 4-cyano pyridine

and methanol compounds, were stable at room temperature. The

4-cyanopyridine complexes decomposed rapidly on exposure to the air

forming black oils. The methanol complexes reacted very readily with

water in the atmosphere, but were stable at room temperature in a

dry-box. Reflectance spectra (table 3.4) show one broad absorption

for all the complexes, sometimes with an associated shoulder;

the main band lying between 750 and .1000 nm as observed by other

workers (56, 57, 59, 61, 67).

For the copper (II) ion in a trigonal bipyramidal crystal field

(figure 3.2) two absorptions due to d-d transitions are expected,

namely d_{xz}, $d_{yz} \rightarrow d_{z^2}$ and d_{xy}, $d_{x^2} - d_{y^2} \rightarrow d_{z^2}$. It is noticeable

when comparing the x-ray structural data (56-61) with the electronic

spectra (56-58, 61, 67) for tetranuclear copper complexes, that for

compounds such as $[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$ and $Cu_4OCl_64(TPPO)$, in

which the copper atoms are in a strict trigonal bipyramidal

environment, two bands are clearly observed in the electronic spectrum .

For complexes such as $Cu_4OCl_64(2\text{-mepy})$ and Cu_4OCl_64py, where intra-

molecular or intermolecular interactions result in a distortion of the

halide octahedra, causing the copper atoms to experience a crystal

$d_{x^2-y^2}$

dz^2

d_{z^2}

dxy, dx^2-y^2

d_{xy}

d_{yz}, d_{zx}

dxz, dyz
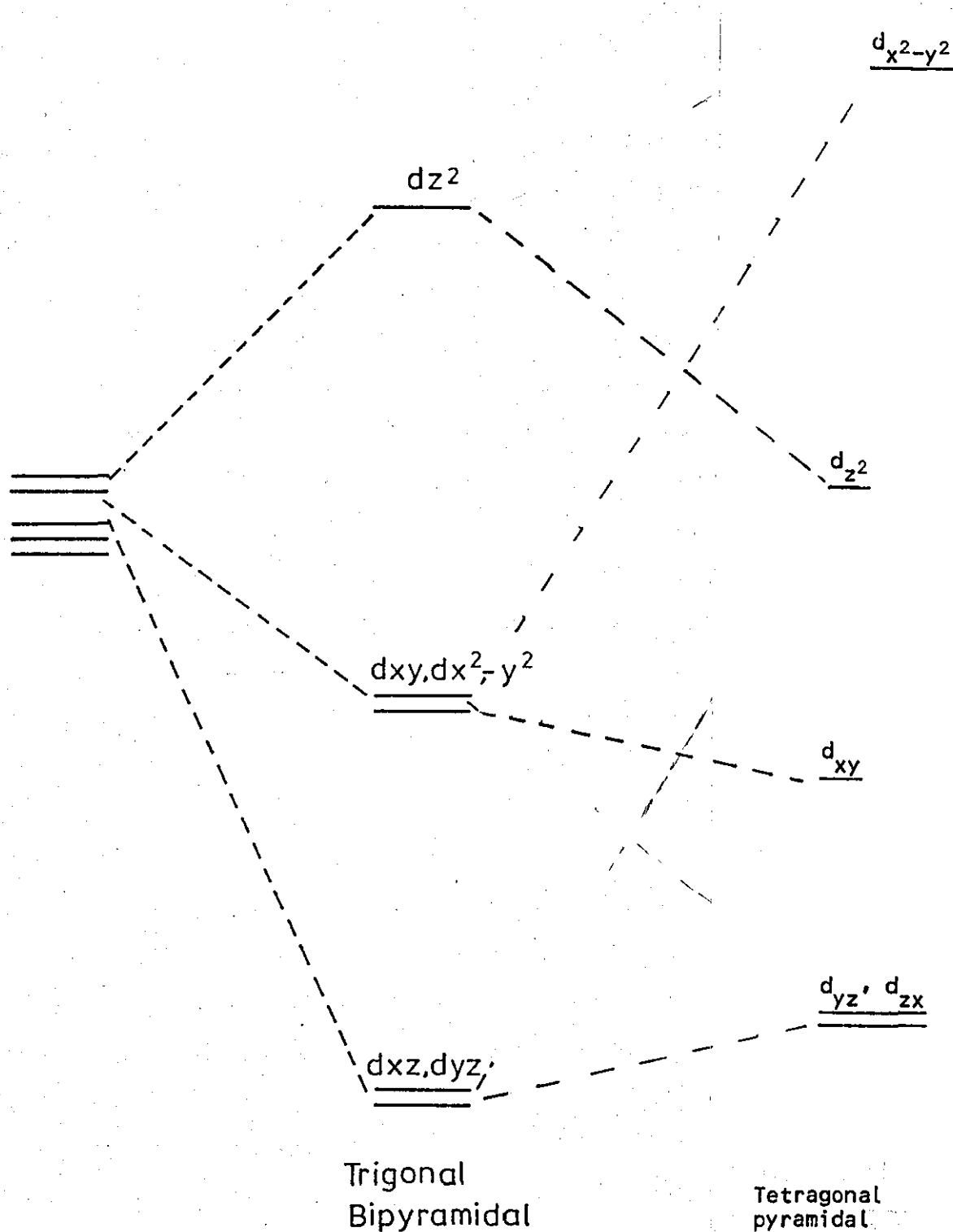
Trigonal
Bipyramidal

Tetragonal
pyramidal

FIGURE 3.2.   The splitting of the one-electron energy
levels of the Copper(II) ion in various
crystal fields.

field between trigonal bipyramidal and tetragonal pyramidal

symmetry, only one broad band is observed. Distortions of this

type from trigonal bipyramidal co-ordination result in a

destabilization of the $d_{x^2-y^2}$ orbital and a stabilization of the d_{xz},

d_{yz} and $d_{x^2-y^2}$ energy levels (figure 3.2). Under these circumstances,

the appearance of a broad band in the reflectance spectrum of $Cu_4OCl_6 \cdot 4py$

at 800 nm (table 3.4) in contrast to the two bands at 780 and 870 nm in

solution (57) probably reflects the lack of resolution in the former case.

Thermal gravimetric studies on fourteen of the tetranuclear

complexes indicate that on the basis of weight losses, the majority

of them lose four ligands to form a mixture of copper (II) halide and

copper (II) oxide (tables 3.5 and 3.6). Several of the complexes

however, still contained appreciable amounts of ligand at 400°C,

the maximum temperature of the furnace. The presence of copper (II)

halide in the decomposition product was confirmed by dissolving it in

ethanol and adding pyridine. This resulted in the precipitation of

the bispyridine dihalo copper (II) species which was characterised

by its infrared spectrum. In several cases (indicated in tables 3.5

and 3.6) the composition of the decomposition product was confirmed

by x-ray powder diffraction data, with reference to standard powder patterns (77). All the complexes with the exception of the 2-mepy species showed evidence for the formation of intermediates during the decomposition. In most cases these corresponded to the loss of one or two molecules of ligand; it is not clear however, at what stage during the decomposition the tetranuclear cluster collapsed to form copper (II) halide and copper (II) oxide. Figure 3.3 shows typical decompositions for three of these complexes. The thermal stability of chloride complexes was found to be greater than bromide complexes, containing the same ligand. This order is probably a consequence of the greater polarizability of the bromide anion, which effectively reduces the extent of metal-ligand π-bonding in these complexes, thus reducing the strength of the metal ligand bond. The relative thermal stabilities of the tetranuclear complexes can be estimated from the decomposition temperatures (tables 3.5 and 3.6). One might expect the basicities of the ligands, as judged by their pKa values, to give an indication of the strength of the σ-bond between the ligand and metal, and for this to be reflected in the thermal stability of the complexes. This relationship has been found for many transition metal-amine complexes, where trends have been observed which indicate that thermal stability increases with increasing ligand basicity (92-100). Several workers, however (83, 96, 101), have found that copper complexes do not follow this trend, in fact Bowman and Rogers (96) found that the thermal stability of copper (II) complexes with 4-substituted pyridines followed a reverse trend, and proposed an oxidation-reduction reaction occuring during the decomposition to explain this. During this study it was found that the complexes $Cu_4OX_6 4py$ and $Cu_4OBr_6 4(3-mepy)$ did undergo redox decomposition reactions and these, and other copper complexes which undergo similar reactions, will be
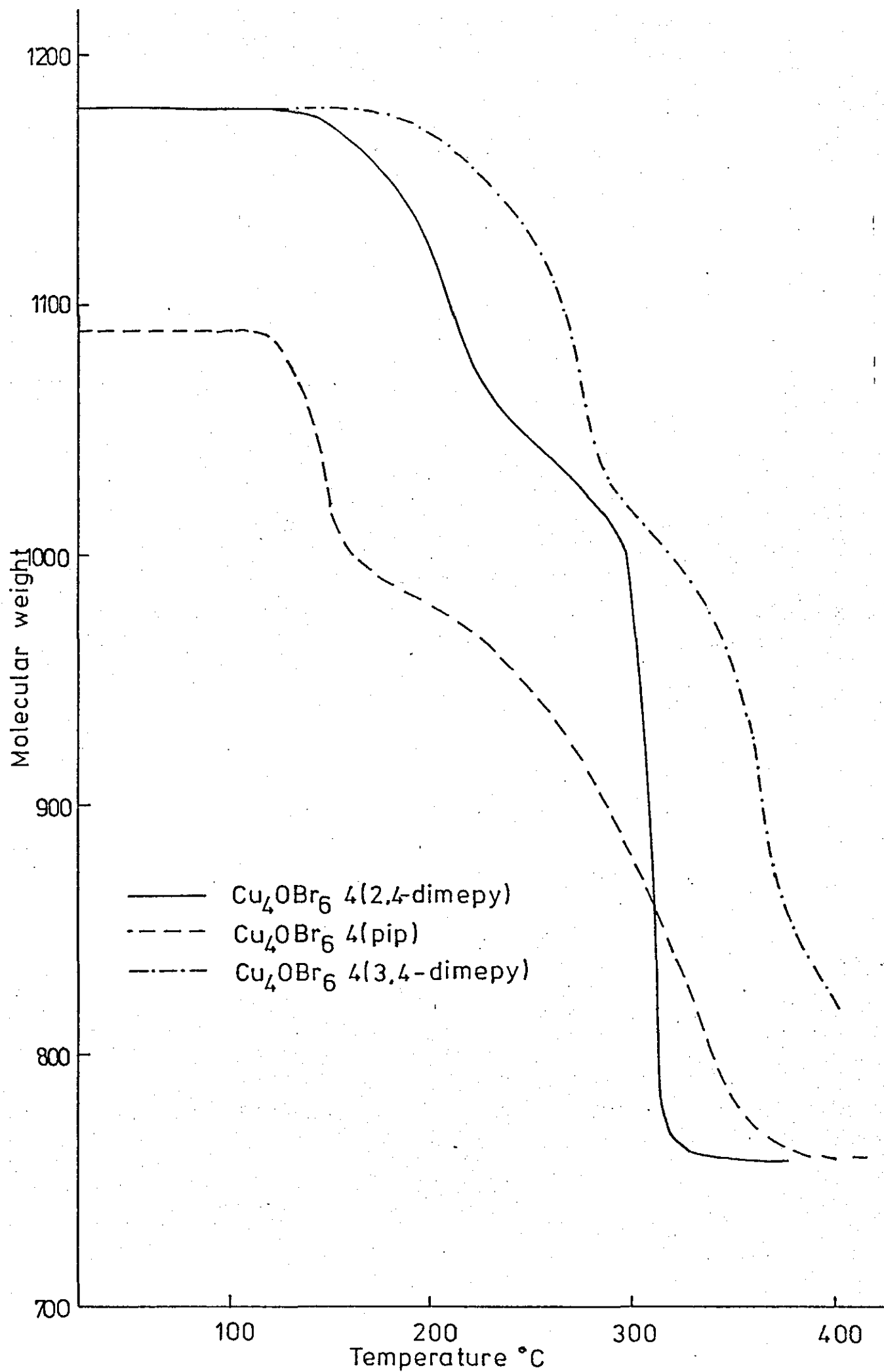
FIGURE 3.3. Thermograms for some tetranuclear complexes

Legend:
- Cu₄OBr₆ 4(2,4-dimepy) — solid line
- Cu₄OBr₆ 4(pip) — dashed line
- Cu₄OBr₆ 4(3,4-dimepy) — dash-dot line

discussed in the next chapter. However the tetranuclear complexes

under discussion at present did not appear to undergo redox

reactions during thermal decomposition (although data are incomplete

on several of the complexes that were still losing weight at

400°C),and little correlation between ligand basicity and thermal

stability can be found (tables 3.5 and 3.6). Beech (92), who

studied the decomposition of pyridine and substituted pyridine

complexes of cobalt (II) halides also found little correlation

between these factors. This lack of correlation in both systems can

be explained by steric interactions involving substituents in the

2-position in the pyridine ring, which will weaken the metal-nitrogen

bond whilst different charge densities and charge distribution in

the pyridine ring caused by substituents in the 3-or4-positions, will

tend to inhibit or encourage π-bonding, thus altering the strength

of the metal-nitrogen bond. The relatively weak bond in the

piperidine complexes (considering the high ligand basicity) is

probably a consequence of the lack of π-bonding in these complexes.

CHAPTER FOUR

TETRANUCLEAR COPPER (II) COMPLEXES WITH MIXED HALIDE BRIDGES

4.1 Experimental and Results

It was mentioned in the previous chapter that many tetranuclear copper (II) complexes of the type Cu_4OX_64L are known. These complexes all contain an octahedron of bridging bromine or chlorine atoms around the central Cu_4O unit. If complexes containing mixed chloride and bromide bridging anions could be prepared, these would be of considerable interest with respect to the structural and physiochemical properties of these cluster compounds, and of possible assistance in spectroscopic assignments. Due to the ease of formation of tetranuclear chloride or bromide complexes, by the reaction of copper (II) halide with copper (II) oxide in ethanol, an attempt was made to prepare the complex $Cu_4OCl_3Br_34py$ by refluxing copper (II) chloride, copper (II) bromide and copper (II) oxide (1.5:1.5:1) in ethanol, following the general preparative method outlined in Chapter Three. The success of the preparation led to attempts to prepare the series $Cu_4OCl_nBr_{6-n}4py$, where n = 1-5, by using different ratios of copper (II) chloride to bromide These preparations were also successful. A general preparative method is as follows:-

Copper (II) chloride dihydrate and copper (II) bromide in the appropriate molar ratios (total halide, 0.1 mole) were refluxed with copper (II) oxide (0.033 mole) in absolute ethanol (150 ml) for two hours. The resulting solution was cooled and filtered.To a portion of the filtrate, about half the stoichiometric amount of pyridine (based on total halide in solution) was added, which precipitated the required tetranuclear complex. The product was filtered, washed with absolute ethanol,   , followed by anhydrous diethyl ether and dried in vacuo (2 torr) at 20°C. A "work up" procedure similar to that described for the hexachloride and hexabromide complexes was found to be unnecessary. Analytical data are contained in table 4.1. The piperidine complex $Cu_4OCl_3Br_34(pip.)$ was prepared by the same method. The mixed halide-methanol complex $Cu_4OCl_3Br_34MeOH$, was prepared

TABLE 4.1

ANALYTICAL DATA FOR TETRANUCLEAR MIXED HALIDE COMPLEXES

COMPOUND	ANALYSES								COLOUR
	% COPPER		% CHLORINE		% BROMINE		%TOTAL HALIDE*		
	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.	
Cu_4OCl_5Br4py	30.10	30.12	20.90	21.01	9.07	9.47	30.13	30.48	deep yellow
$Cu_4OCl_4Br_24py$	28.58	28.62	15.76	15.97	17.74	17.99	–	–	yellow-brown
$Cu_4OCl_3Br_34py$	27.03	27.25	11.54	11.40	25.95	25.71	–	–	light brown
α-$Cu_4OCl_2Br_44py$	26.10	26.01	7.16	7.26	32.46	32.71	–	–	brown
β-$Cu_4OCl_2Br_44py$	26.21	26.01	7.14	7.26	32.61	32.71	–	–	brown
Cu_4OClBr_54py	24.80	24.88	3.80	3.47	38.48	39.11	42.59	42.58	dark brown
$Cu_4OCl_3Br_34(Pip)$	26.41	26.67	11.02	11.16	24.99	25.16	–	–	light brown
$Cu_4OCl_3Br_34(MeOH)$	34.05	34.14	14.28	14.29	31.96	32.20	–	–	red-brown

Pip = piperidine

* Where applicable

from anhydrous reagents by a method similar to that of Dieck and

Brehm (68), who prepared the hexachloride complex. The

two isomers of $Cu_4OCl_2Br_4 4py$ were obtained by two slightly different

preparative methods. α -$Cu_4OCl_2Br_4 4py$ was prepared as described

above; β-$Cu_4OCl_2Br_4 4py$ was prepared from $Cu_3Cl_2Br_4$ (see below) and

copper (II) oxide.

The preparation of the mixed halide complex copper (II)

bromidechloride was reported by Batsanov et al. in 1968 (102). They

oxidized copper (I) chloride with a 50% excess of bromine in ethanol;

the ethanolic solution was allowed to evaporate at room temperature,

which resulted in the dark brown complex CuClBr. The product was

characterised by Batsanov et al. using X-ray, infrared and

thermogravimetric studies, all of which indicated that the product

was a true compound and not a mixture of copper (II) halides. This

preparation was repeated in the present investigation, but resulted in

a complex of stoichiometry $Cu_3Cl_2Br_4$ (Found Cu, 32.46%; Br, 55.58%;

Cl, 11.89%: Calc. Cu, 32.80%; Br, 55.00%; Cl, 12.20%: Calc. for

CuClBr Cu, 35.51%; Br, 44.67%; Cl, 19.82%). This compound was

presumably formed by some further oxidation of CuClBr by the excess

bromine present, and could be a 2:1 mixture of CuClBr and $CuBr_2$.

All other attempts to obtain pure samples of CuClBr, by the oxidation of

copper (I) chloride with varying amounts of bromine were unsuccessful.

In the preparation of the tetranuclear complex β-$Cu_4OCl_2Br_4 4py$,

the species $Cu_3Cl_2Br_4$ (6g) was refluxed with copper (II) oxide (1g)

in ethanol (150 ml) and, on the addition of pyridine (2g) to the

resulting solution, the cluster complex was obtained in a similar

manner to the complexes described above.

Crystals of the trishalide complex, $Cu_4OCl_3Br_3 4py$, were obtained

as 1 mm needles by adding a few drops of the "$Cu_4OCl_3Br_3$" solution

to 25 mls of absolute alcohol in a boiling tube. One drop of pyridine was then added, and the crystals allowed to form over a period of days at room temperature.

X-ray powder diffraction data and infrared spectra for all these mixed halide complexes are contained in tables 4.2 and 4.3 respectively. Table 4.4 contains thermogravimetric data. Reflectance spectra are shown in fig. 4.1, while figs. 4.2 and 4.3 contain the thermogravimetric decomposition curves for these complexes. The two hexahalide compounds, $Cu_4OX_6 4py$ (X = Cl, Br), are included in several of these tables and figures for comparative purposes.

Figure 4.4 shows the thermal decomposition curves for the bispyridine dihalo copper (II) species. Some confusion existed in the literature concerning the decomposition of the chloride complex, and the analogous bromide complex had not been studied by this technique. These two complexes were prepared by the methods of Lang (38) and Pfeiffer and Pimmer (103) respectively and recrystallised from DMF. Satisfactory analyses were obtained for both compounds.

To obtain information on the volatile products from the thermal decompositions of the hexahalide complexes, several decompositions were carried out using a Carbolite muffle furnace. Temperatures of 270°C for $Cu_4OCl_6 4py$ and 220°C for $Cu_4OBr_6 4py$ were used, the samples being contained in a glass tube. The volatile decomposition products were swept into a "U" trap, cooled with liquid nitrogen, by means of a stream of dry nitrogen gas. After the decompositions were complete, the volatile products were analysed by mass spectrographic techniques. The major peaks in the mass spectra are listed by mass number in Table 4.5.

The copper reagents, amines and solvents used for these preparations were prepared and/or purified as previously described. The bromine, a Fisons product, was used without further purification.

X-RAY POWDER DIFFRACTION LINES FOR TETRANUCLEAR HALIDE AND MIXED HALIDE-PYRIDINE COMPLEXES

$Cu_4OCl_6$4py		Cu_4OCl_5Br4py		$Cu_4OCl_4Br_2$4py		$Cu_4OCl_3Br_3$4py		α-$Cu_4OCl_2Br_4$4py		β-$Cu_4OCl_2Br_4$4py		$Cu_4OClBr_5$4py		$Cu_4OBr_6$4py		$Cu_4OBr_6$4py*	
d Å	I	d Å	I	d Å	I	d Å	I	d Å	I	d Å	I	d Å	I	d Å	I	d Å	I
10.72	80	10.88	90	10.82	100	10.72	50	10.97	100	8.46	100	8.51	100	10.97	90	11.87	30
9.99	5	10.15	5	10.12	5	10.02	5	10.24	10	6.33	5	6.71	5	10.40	5	10.84	15
8.47	40	8.55	15	8.54	10	8.43	100	8.58	20	4.14	5	4.02	5	8.58	30	10.65	80
8.04	100	8.08	100	8.08	60	8.01	50	8.15	90	3.79	5	3.82	5	8.16	100	7.97	100
7.83	80	7.89	80	7.87	50	7.83	50	7.95	85	3.65	5	3.66	5	7.97	70	7.60	30
6.66	20	6.70	10	6.67	15	6.66	30	6.71	15	3.37	5	3.38	5	6.66	10	6.19	10
5.37	20	5.39	30	5.39	40	5.25	20	5.42	30					5.41	20	5.93	20
5.05	20	5.11	10	5.09	15	5.08	50	5.11	25					5.14	10	5.28	10
4.85	20	4.90	10	4.93	15	4.90	5	4.97	10					4.53	10	4.07	20
4.46	10	4.72	5	4.87	15	4.15	50	4.19	5					4.09	30	3.89	10
4.02	10	4.05	10	4.04	20	4.02	5	4.05	25					3.97	40	3.79	50
3.92	10	3.95	10	3.91	15	3.93	50	3.96	30					3.89	60	3.74	30
3.85	10	3.81	5	3.80	30	3.79	5	3.83	35					3.65	15	3.36	15
3.75	10	3.29	10	3.43	15			3.36	10					3.38	20		
2.90	5	2.88	10	3.28	30	3.26	5	3.30	20					3.88	20		
				2.87	30			2.89	30					3.33	30		
														2.92	30		

*see text

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TABLE 4.3

INFRARED SPECTRA (1700 – 400 cm^{-1}) of mixed halide – pyridine complexes

FREE AMINE (50)	ASSIGNMENT (50)	Cu_4OCl_6	Cu_4OCl_5Br	$Cu_4OCl_4Br_2$	$Cu_4OCl_3Br_3$	$Cu_4OCl_3\overset{*}{B}r_3$	α-$Cu_4OCl_2Br_4$	β-$Cu_4OCl_2Br_4$	Cu_4OClBr_5	Cu_4OBr_6
		1610	1609	1611	1610	1610	1610	1610	1609	1609
15.83	8a	1600	1600	1601	1600	1600	1600	1600	1600	1600
1572	8b	1575	1572	1574	1574	1572	1572	1574	1573	1572
		1490		1491	1490		1491			1490
1482	19a	1488	1485	1488	1488	1485	1489	1489	1488	1488
1439	19b	1452	1450	1451	1450		1451			1446
		1448	1446	1449	1445	1445	1448	1448	1448	1450
1375	4	1368	1366	1366	1366	1366	1368	1366	–	1368
1288	3	1240	1240	1240	1239	1238	1239	1239	1239	1239
1218	9a	1217	1218	1219	1218	1218	1218	1218	1216	1219
		1157	1157	1158	1156	1156	1157			1157
1148	15	1146	1146	1147	1146	1145	1146	1156	1155	1146
1085	18b	–	1080	1080	1080	–	–	–	–	–
1068	18a	1070	1070	1070	1069	1069	1069	1072	1070	1069
1030	12	1040	1049	1049	1049	1048	1048	1049	1048	1048
992	1	1020	1019	1020	1019	1019	1019	1020	1019	1019
		956			950					
942	5	950	956	956	953	–	953	–	–	952

* single crystals from ethanol solution

TABLE 4.3 (cont'd)

FREE AMINE (50)	assignment (50)	Cu_4OCl_6	Cu_4OCl_5Br	$Cu_4OCl_4Br_2$	$Cu_4OCl_3Br_3$	$Cu_4OCl_3Br_3$*	$\alpha\text{-}Cu_4OCl_2Br_4$	$\beta\text{-}Cu_4OCl_2Br_4$	Cu_4OClBr_5	Cu_4OBr_6
891	10a	883	–	880	875	–	879	877	873	880
749	4	766 761 756	766 760 756	766 761 756	759	764 760 756	765 760 756	759	758	766 760 756
–	?	–	–	–	738	738	–	738	–	–
–	?	–	724	724	725	725	723	723	723	–
700	11	700 695	700 695	700 696	694 688	700 692	698 694	691	690	698 693
605	6a	651 648	652 648	651 649	647	646	647	647	646	646
–	νCu–Oasym.	576	569	562	553	551	544	541	537	536
405	16b	440 438	440 438	440 437	437	440 437	438	437	437	438

* single crystals from ethanol solution

TABLE 4.4

THERMAL DATA FOR TETRANUCLEAR HALIDE AND MIXED HALIDE COMPLEXES

COMPOUND	T_s °C	T_m °C	T_f °C	PRODUCT	WEIGHT LOSS %	
					FOUND	CALC.
Cu_4OCl_64py	200	265	295	4CuCl	50.1	50.5
Cu_4OCl_5Br4py	160	215	240	3CuCl: CuBr	47.0	47.8
$Cu_4OCl_4Br_24py$	166	222	248	3CuCl:CuBr	49.5	50.4
$Cu_4OCl_3Br_34py$	190	255	283	2CuCl: 2CuBr	48.3	48.0
$\alpha-Cu_4OCl_2Br_44py$	185	240	271	2CuCl: 2CuBr	50.2	50.4
$\beta-Cu_4OCl_2Br_44py$	190	240	278	CuCl: 3CuBr	45.8	45.8
Cu_4OClBr_54py	130	185	215	4CuBr	44.1	43.8
Cu_4OBr_64py	184	210	240	4CuBr	46.4	46.2
$Cu_4OBr_64(3-mepy)$	140	280	320	4CuBr	48.7	48.9

T_s = temperature at start of decomposition

T_m = temperature of maximum rate of weight change

T_f = temperature at finish of decomposition

TABLE 4.5

MASS SPECTRAL DATA FOR THE DECOMPOSITION PRODUCTS OF TETRANUCLEAR COPPER (II) COMPLEXES

COMPOUND	MASS NO.	ION	COMMENTS
Liquid product	79	$C_5H_5N^+$	-
from decomposition of	113)		contains chlorine,
		$C_5H_4NCl^+$	(intensities of
Cu_4OCl_64py	115)		peaks 1:0.3)
Solid product	79)	Br^+	
	81)	(and $C_5H_5N^+$)	
from decomposition of			
Cu_4OBr_64py	127	?	No bromine
	158)		intensities of peaks
	160)	Br_2^+	1:2:1
	162)		
	206)		Contains bromine,
	208)	?	(intensities of peaks
			1:1)
	253	?	No bromine

a) Cu_4OCl_5Br4py

b) $Cu_4OCl_2Br_44py$ (α and β)

c) $Cu_4OCl_4Br_24py$

d) Cu_4OClBr_54py

e) $Cu_4OCl_3Br_34py$
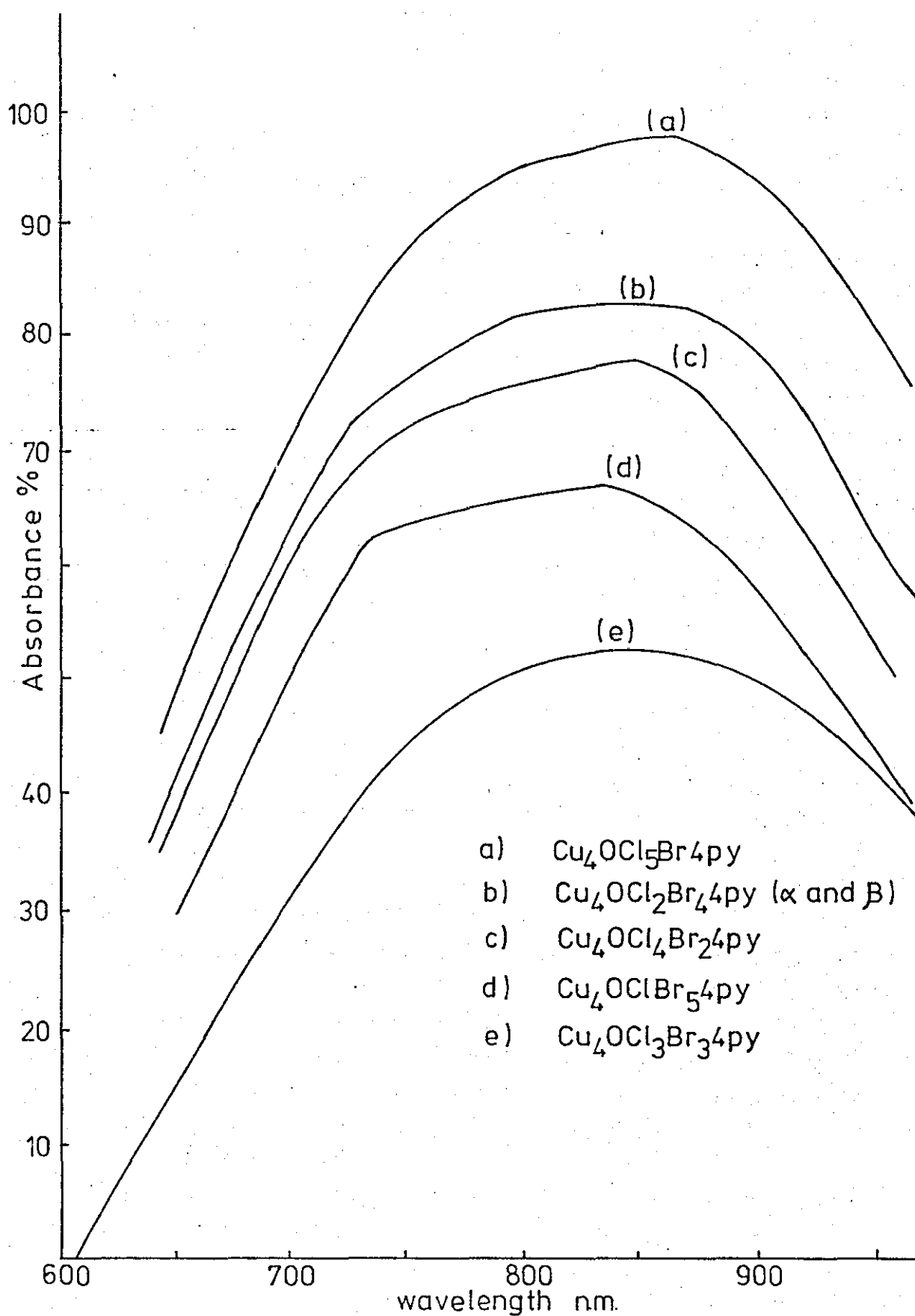
FIGURE 4.1.   Reflectance spectra for tetranuclear mixed
halide complexes

Legend for the figure:

(a) Cu_4OBr_64py

(b) $\beta\text{-}Cu_4OCl_2Br_44py$

(c) $Cu_4OCl_3Br_34py$

(d) Cu_4OClBr_54py
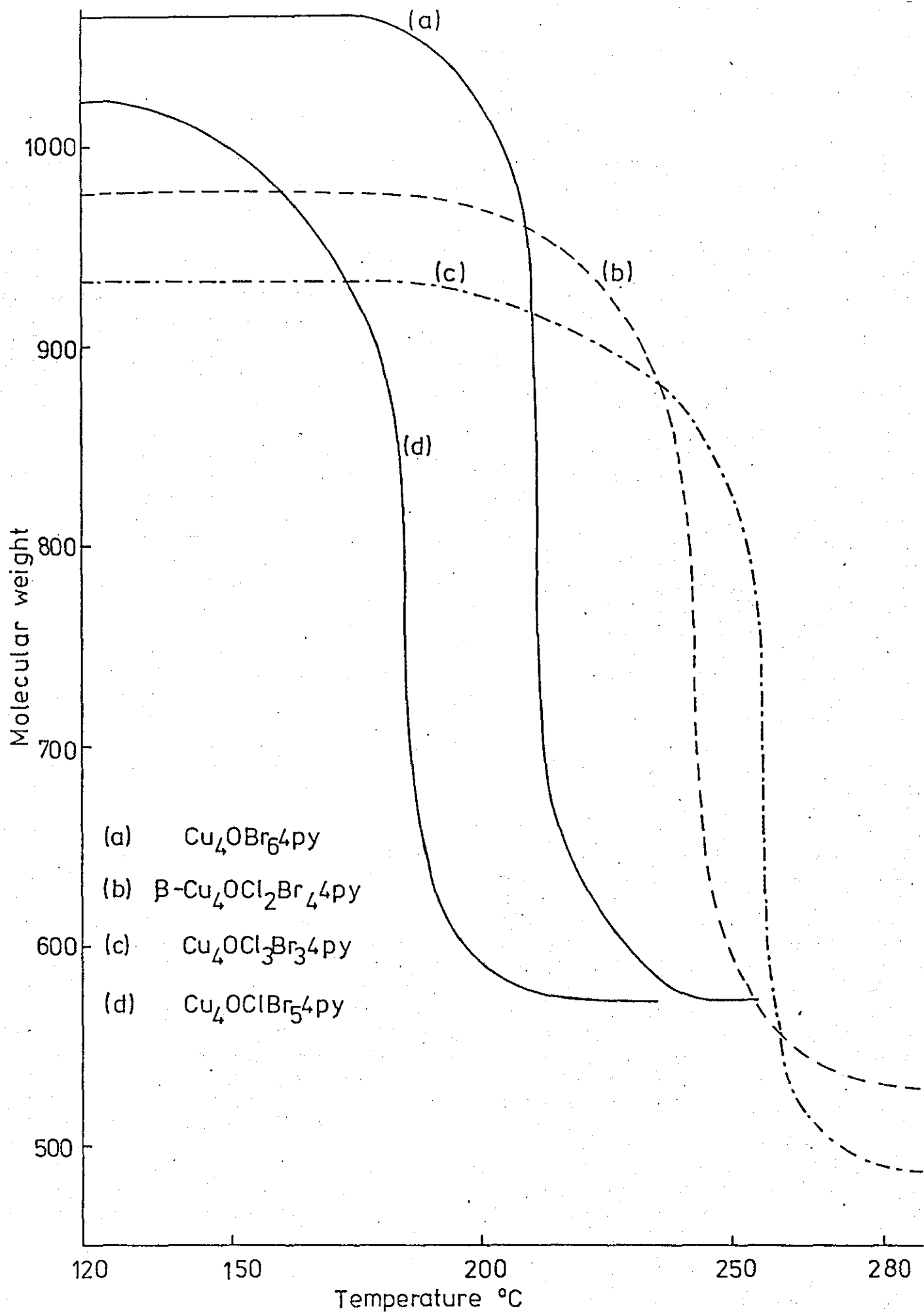
FIGURE 4.2.   Thermogravimetric decomposition curves for tetranuclear complexes
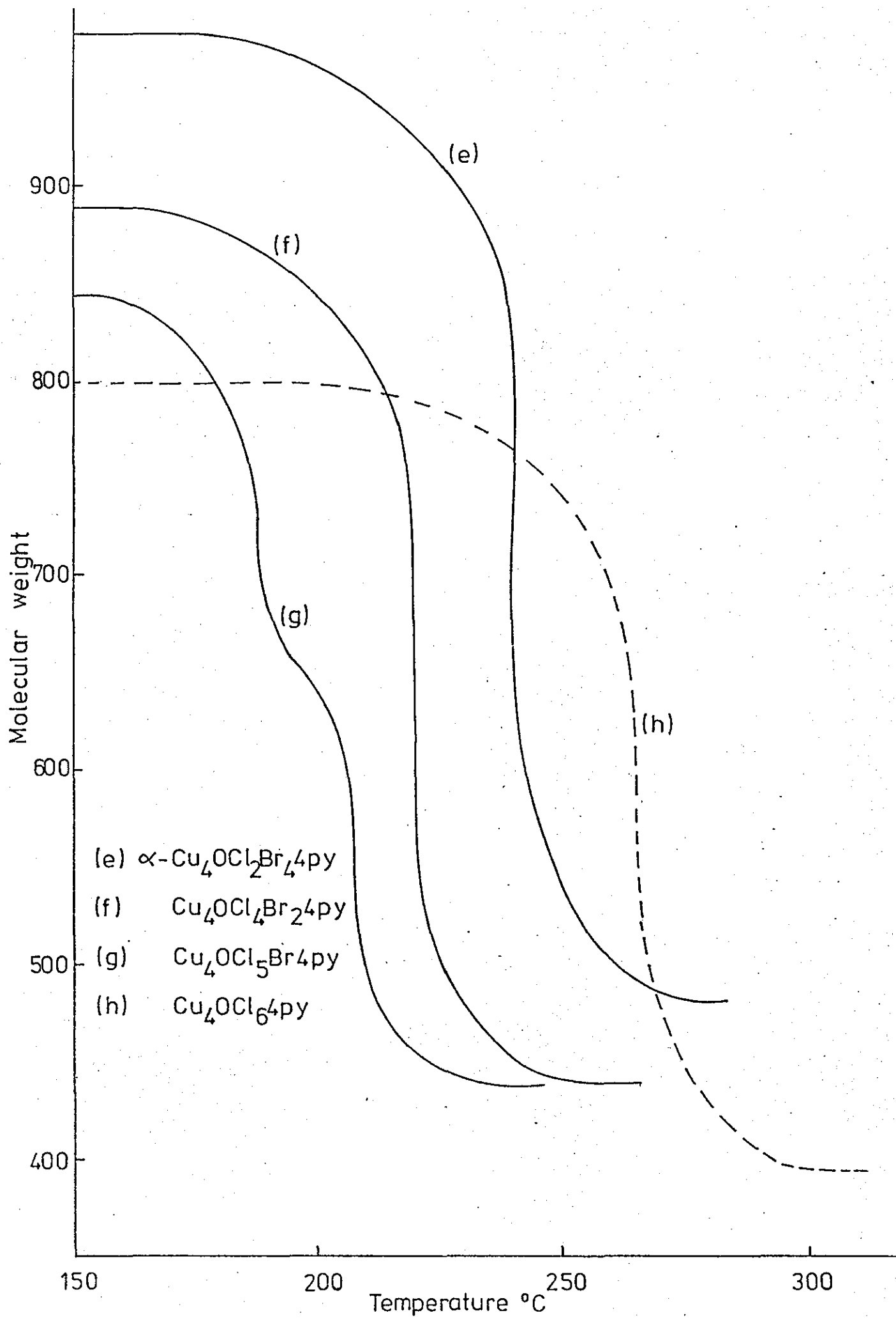
FIGURE 4.3. Thermogravimetric decomposition curves for
tetranuclear complexes

The figure legend:

(e) $\alpha\text{-}Cu_4OCl_2Br_44py$

(f) $Cu_4OCl_4Br_24py$

(g) Cu_4OCl_5Br4py

(h) Cu_4OCl_64py

Axis labels: Molecular weight (vertical), Temperature °C (horizontal)
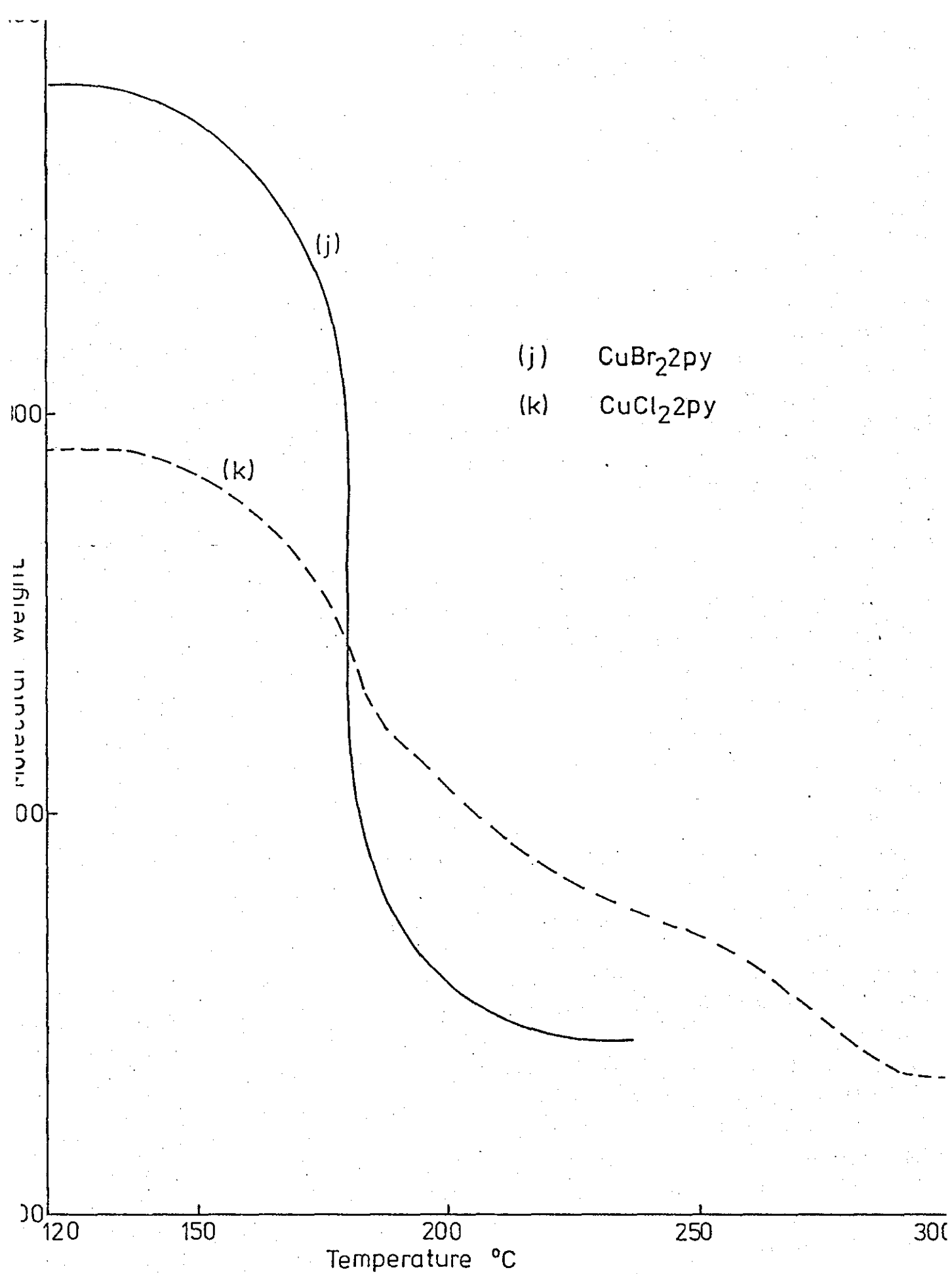
FIGURE 4. 4.   Thermogravimetric decomposition curves for bispyridine dihalo copper(II) complexes

Copper analyses, infrared spectra, x-ray powder diffraction data,

electronic reflectance spectra and thermogravimetric data were obtained

as previously described. Mixed halide analyses were determined

potentiometrically by a standard method (104), using silver wire

and calomel electodes and a potassium nitrate salt bridge. Potentials

were recorded on a high impedance digital voltmeter. This method

produced excellent results on standard samples (mixtures of

$CuCl_2 2py$ and $CuBr_2 2py$). However, when either halide was in very

low concentration, coprecipitation produced some inaccuracies, and

in these cases total halide values are included in the analytical data

(table 4.1). Mass spectral data was obtained using an A.E.I. MS.12

spectrometer.

4.2 Discussion

Mixed halide complexes of copper are not well known. Apart from

Copper (II) bromide chloride mentioned above, the preparation (105)

and crystal structure (106) of the five co-ordinate mixed halide

copper complex $[Cr(NH_3)_6]^{3+} [CuBr_3Cl_2]^{3-}$ has been reported. In

addition Rosenstock et al. (34) have shown by mass spectrometric

methods, that when two copper (I) halides are volatilised together,

the vapour contains mixed polymeric ions such as $Cu_4Br_3Cl^+$ and

$Cu_3Br_2Cl^+$. The complexes described in this chapter as well as

extending the number of known mixed halide complexes of copper, represent

the first reported tetranuclear complexes with the structural unit M_4O,

containing mixed halide bridges. The characterisation and properties

of these compounds will be discussed under the appropriate physiochemical

techniques.

4.2.1 X-ray data

From the x-ray powder diffraction data (table 4.2) it can be
seen that:-

(i)   the mixed halide complexes are true compounds and not mixtures

   of the hexachloride, and hexabromide complexes,

(ii) the complexes Cu_4OCl_5Br4py, $Cu_4OCl_4Br_24py$, $Cu_4OCl_3Br_34py$ and

   $\alpha\text{-}Cu_4OCl_2Br_44py$ are isomorphous with the hexachloride complex.

(iii) there appear to be two forms of the hexabromide complex, one

   of which is isomorphous with the hexachloride compound.

(iv) the α- and β- forms of $Cu_4OCl_2Br_44py$ have different powder

   patterns,

(v)   the complexes $\beta\text{-}Cu_4OCl_2Br_44py$ and Cu_4OClBr_54py have badly defined

   powder patterns, containing one intense line, with only a few

   other lines of low intensity present.   They appear, however, to be

   isomorphous.

The crystal structure of the hexachloride complex is well

established (57).   Kilbourn and Dunitz reported unit cell dimensions for

the hexabromide complex in 1967 (57), but it was not until very recently

that a complete refinement of the structure was reported by Swank et al.

(63).   This latest paper reveals that these two hexahalide complexes

are not isomorphous, the difference between the two being only in the

packing of tetrameric units within the unit cell.   However the data

in table 4.2 indicate that there are two hexabromide complexes, one

of which is apparently isomorphous with the hexachloride complex, and

shows an increase in 'd' spacing as expected on going from a chloride

to the corresponding bromide complex.   During eight theoretically

identical preparations of the hexabromide species, seven resulted in

the complex isomorphous with the hexachloride compound, and only one

in the other complex (designated by an asterisk in table 4.2).

Analytical, infrared and reflectance spectra were identical for both forms. Apparently there are two crystalline forms for the hexabromide species, one isomorphous with the hexachloride complex and the other, the crystal structure of which has been resolved by Swank et al, differing only in the packing of the Cu_4OBr_64py units within the crystal. A similar type of isomorphous behaviour has been observed by Bailey et al. (107), who have prepared nine crystalline forms of the compound $CuL(NCS)_2$, (L = 1, 7-bis-(2-pyridyl)-2,6-diazoheptane). Crystal studies on two of these complexes indicated that they each contain five co-ordinate copper, but differ in the packing of molecules in the unit cell. The two crystalline forms of $Cu(NO_3)_2$ 2(2-mepy) described by Cameron et al. (108) provide another example of this phenomenon. A reproduceable preparative method for the non-isomorphous hexabromide complex has not been discovered.

It can be seen from table 4.2, that not only are the pentachloride, tetrachloride, trischloride and α-bischloride complexes isomorphous with the hexachloride complex, but the trischloride complex has an almost identical powder pattern to this latter compound, which indicates that these two species must have very similar unit cell dimensions. The unit cell constants of the trischloride complex have been determined in this department (109), and are contained along with the hexahalide species in table 4.5. From these data it does appear that the hexachloride and trichloride species are crystallographically very similar. The space groups $P2_{1/n}$ and $P2_{1/c}$ are closely related and the two unit cells can be correlated since the c dimension of the mixed halide is the same length as the diagonal of the (010) face of the hexachloride cell. A complete structural refinement for the mixed halide complex is underway.

TABLE 4.5

X-RAY SINGLE CRYSTAL DATA FOR TETRANUCLEAR PYRIDINE COMPLEXES

COMPLEX	SPACE GROUP	UNIT CELL CONSTANTS			
		$a\text{Å}$	$b\text{Å}$	$c\text{Å}$	$\beta°$
Cu_4OCl_64py (57)	$P2_{1/n}$	11.3	21.4	12.0	92
$Cu_4OCl_3Br_34py$ (109)	$P2_{1/c}$	11.9	21.53	16.32	45
Cu_4OBr_64py (63)	$C_{2/c}$	30.64	12.43	20.17	129.6

One might expect to be able to prepare structural isomers of some of the tetranuclear mixed halide complexes. $Cu_4OCl_3Br_34py$ will have three structural isomers, whilst $Cu_4OCl_4Br_24py$ and $Cu_4OCl_2Br_44py$ will have two each. These isomers are shown in figures 4.5 and 4.6. From the x-ray powder diffraction data, it seems likely that the α- and β- forms of $Cu_4OCl_2Br_44py$ correspond to the two isomers of this complex. Although x-ray powder data will not reveal the type of structural differences between such isomers, these differences may result in different packing arrangements within the crystals, which will then show up in the powder patterns. This seems to be the case with $Cu_4OCl_2Br_44py$. The anomolous powder pattern of the β-isomer of $Cu_4OCl_2Br_44py$, isomorphous with Cu_4OClBr_54py, may be due to a preferential orientation of the crystals in these complexes, which can occur, for example, when a complex crystallises as platelets. A microscopic examination of the crystals of these two complexes revealed that they were too small to determine crystal type. The presence of structural isomers should manifest itself in physical and physiochemical properties of the complexes in question, and the isomers of $Cu_4OCl_2Br_44py$ will be further discussed in relation to infrared and thermogravimetric studies.

4.2.2 Infrared data

The infrared spectra of the tetranuclear halide and mixed halide complexes of pyridine, between 1700 and 400 cm^{-1}, (table 4.3), reveal that the bands due to pyridine ring vibrations are almost unchanged in frequency from those in the bispyridinedihalo copper (II) complexes (table 2.2), although some band splitting can be observed in the former complexes, noticeably in the 749, 700, 605 and 405 cm^{-1} bands of the free amine. The assymmetric Cu-O stretching vibration provides further proof that the mixed halide complexes are true compounds and not
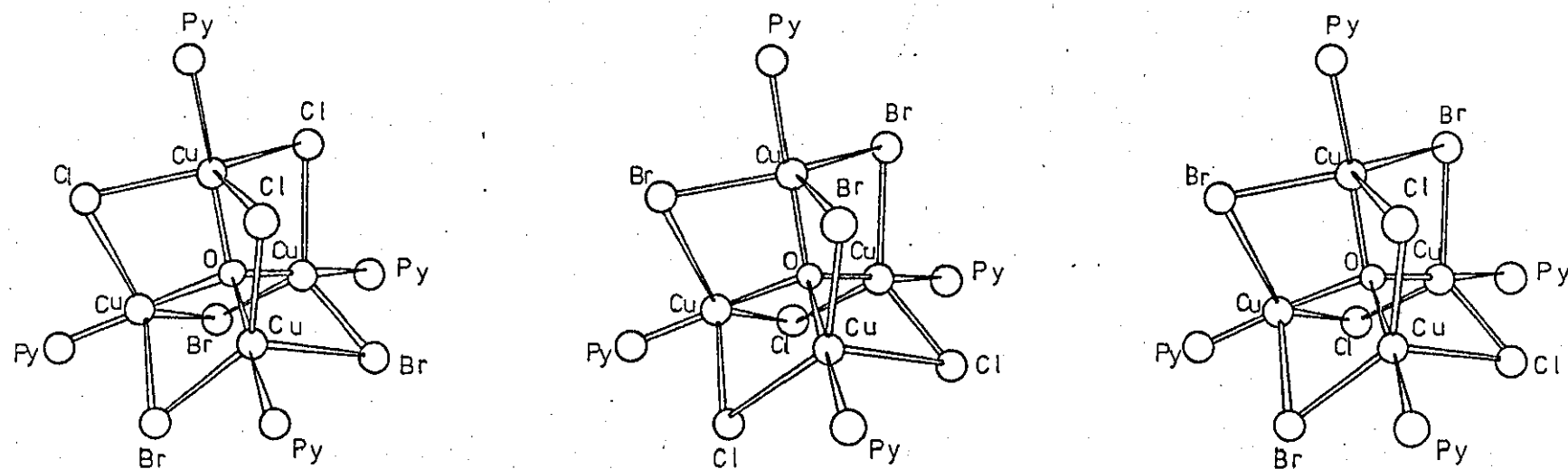
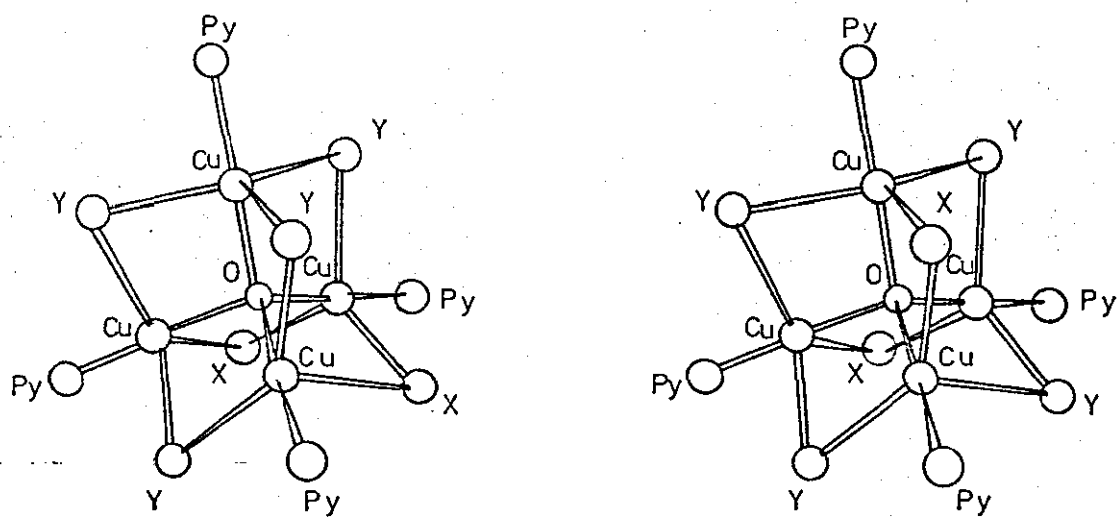FIGURE 4. 5. The three structural isomers of $Cu_4OCl_3Br_34py$

FIGURE 4.6.   The two structural isomers of Cu$_4$OCl$_2$Br$_4$4py
[x=Cl,y=Br] and Cu$_4$OCl$_4$Br$_2$4py [x=Br,y=Cl]

mixtures of Cu_4OCl_64py and Cu_4OBr_64py. They exhibit a single Cu-O band which lies between that of the hexachloride and hexabromide, decreasing in frequency from the pentachloride to the pentabromide complex as might be expected. Mechanical mixtures of the hexachloride complexes were made, and showed twin Cu-O bands at 576 and 536 cm^{-1} in the infrared spectra. The structural isomers mentioned in 4.2.1 above might be expected to exhibit slightly different frequencies for the Cu-O vibration, due to different arrangements of halide atoms around the central Cu_4O unit. The two complexes α- and β-$Cu_4OCl_2Br_44py$ show Cu-O bands at 544 and 541 cm^{-1} respectively and although this difference is close to the experimental limits of the apparatus ($\pm$ 1 cm^{-1}), it does indicate that the two complexes may well be different isomers. There are other differences between the infrared spectra of these two compounds. Several pyridine vibrations which occur as single bands in the β-complex, appear split in the spectrum of α-$Cu_4OCl_2Br_44py$. A similar situation can be observed with the trishalide complex (table 4.3). This compound prepared by the usual method shows some spectral differences to that obtained as single crystals from a dilute "$Cu_4OCl_3Br_3$"solution. These differences lie again in the frequency of the Cu-O vibration and in the splitting of pyridine vibrational bands, but are smaller in magnitude than in the $Cu_4OCl_2Br_44py$ complexes. Far infrared data for tetranuclear complexes will be discussed in Chapter Six.

4.2.3 Reflectance spectra

Electronic reflectance spectra in the region 600 to 1000 nm (figure 4.1) are similar to other tetranuclear copper (II) complexes. One broad band, sometimes with an associated shoulder, is observed in the spectra of the mixed halide complexes, which is typical for copper (II) ions in a distorted trigonal bipyramidal crystal field, as was discussed in Chapter Three.

4.2.4 Thermogravimetric data

The thermal decomposition of metal-amine and polyamine complexes has been studied extensively in recent years (93-96, 111-116). In general this work has been carried out in order to correlate thermal stability and ligand basicities, with bond energies evaluated by far infrared spectroscopy. It was mentioned in Chapter Three that the thermal decomposition of copper (II) complexes is sometimes complicated by redox reactions, and it is perhaps for this reason that the decomposition of copper-amine complexes has not been studied in any great detail. Redox decomposition reactions involving copper (II) compounds have been studied by Bowman and Rogers (96), Billing (101), Pappas et al. (117), Liptay et al. (112) and Smith and Wendlandt (119). Reduction of the metal has also been reported in the thermal decomposition of cobalt (III)-amine complexes (120) and in mercury (II) pyridine-N-oxide complexes (117). Little work has been done to characterise the products from the redox decomposition reactions of copper (II) complexes; the only reaction in which all the products have been positively identified, is that of copper (II)-ammonia complexes which have been shown to decompose in accordance with equations 4.1 to 4.4 below (119).

$$[Cu(NH_3)_6] X_2 \rightarrow Cu(NH_3)_2X_2 + 4NH_3 \tag{4.1}$$

$$6Cu(NH_3)_2X_2 \rightarrow 6CuX + 6NH_4X + N_2 + 4NH_3 \tag{4.2}$$

$$X = Cl \text{ or } Br$$

$$2[Cu(NH_3)_4]I_2 \rightarrow 2Cu(NH_3)_2I_2 + 2NH_3 \tag{4.3}$$

$$2Cu(NH_3)_2I_2 \rightarrow 2CuI + I_2 + 4NH_3 \tag{4.4}$$
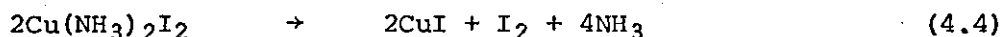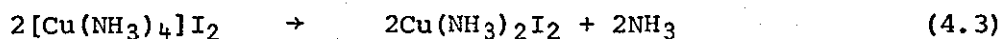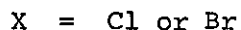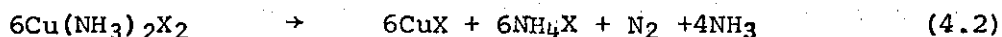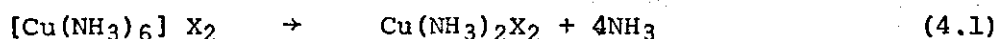
Billing (101) has suggested that haloamines are formed during the decomposition of copper (II) halide-quinoxaline complexes. Pappas et al. (117) have shown that the thermal decomposition of copper (II) halide-pyridine N-oxide complexes involves an oxidation of the pyridine ring. Furthermore, the work of Yoke et al. (121), Weiss et al. (122) and

Clifton and Yoke (123), on the reactions of primary, secondary and tertiary ethylamines with copper (II) chloride, indicated that complexes were formed which decomposed below room temperature, by means of a redox reaction involving dehydrogenation of the ligand and subsequent polymerisation of the resulting vinylamine. A similar system with triethylphosphine complexes of copper (II) chloride yielded triethylchlorophosphonium chloride, $(C_2H_5)_3 PCl_2$, and complex copper (I) cuprates amongst the redox decomposition products (124).

Thermogravimetric studies on the tetranuclear halide and mixed halide complexes (table 4.4, figures 4.2 and 4.3), indicate that redox decompositions are involved. The non volatile decomposition products were characterised by weight loss (table 4.4), colour (they were all white or cream as expected for copper (I) halides), and in the case of the hexachloride and hexabromide complexes, by x-ray powder diffraction data which corresponded to copper (I) chloride (Nantokite) and γ-copper (I) bromide respectively (78). The thermogravimetric curves (figures 4.2 and 4.3) show a similar decomposition mechanism for all the complexes; a loss of about one molecule of pyridine, followed by a rapid loss of the three remaining ligands, together with oxygen and the two halide atoms in a one step reaction. The exception to this was Cu_4OCl_5Br 4py, which lost two molecules of pyridine before the rapid final decomposition (figure 4.3(g)) Assuming the temperature of the maximum rate of weight change (Tm) corresponds to the point at which the redox reaction occurs, one can use this temperature as an indication of the relative stabilities of these complexes (table 4.4). It might be expected that the more bromine atoms there were in the cluster, the less stable would be the complex to a redox reaction, as it is normally found that the copper (I) state becomes more stable as the covalent character of the Cu-X bond

increases, that is, with more polarizable anions. This stability trend has been observed with copper (II)-ammonia complexes (119), as well as with amine complexes of cobalt (III) (120), and can clearly be observed on comparing the decomposition temperatures of the hexachloride (Tm ≐ 265°C) and hexabromide (Tm = 210°C) complexes.

However, a stability trend down the series from the hexachloride to hexabromide complex is not observed. Evidently the structure of the mixed halide complexes has a marked effect on their thermal stability. The trishalide complex, which has been shown by x-ray data to have similar structural dimensions to the hexachloride complex (4.2.1 above), has similar thermal stability (Tm = 255°C). The two isomers of $Cu_4OCl_2Br_4 4py$ undergo different redox decomposition reactions, the α-form losing two bromine atoms to give 2CuCl: 2CuBr, while the β-complex loses a chlorine and a bromine atom and forms CuCl:3CuBr, thus providing further proof that these two complexes are indeed structural isomers.

Identification of the volatile oxidation products from these decomposition reactions was difficult, due to the fact that decompositions carried out under nitrogen in a muffle furnace, using large amounts of sample, did not always produce a pure sample of copper (I) halide. Only the hexachloride and hexabromide complexes were investigated by this method, and in some instances black tarry residues were obtained from the decomposition reaction. This may be due to sample packing (a large bulk of sample preventing the volatile oxidation products escaping so that they then undergo further reactions), and heating rate (difficult to control in a muffle furnace). However, a sample of the hexachloride complex which did decompose to copper (I) chloride, gave a volatile liquid which was positively identified by its mass spectrum as a mixture of pyridine and chloropyridine (table 4.5). The decomposition reaction for this complex is shown in equation 4.5

$$Cu_4OCl_6 4py \rightarrow 4CuCl + 2py + 2(Clpy) + H_2O \qquad (4.5)$$
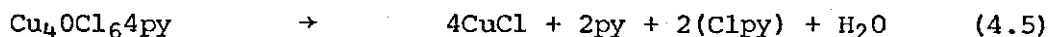
The decomposition of the hexabromide compound resulted in a volatile product which appeared to be a mixture of red and yellow solids at room temperature. A mass spectrum of the product showed no volatile copper compounds and revealed the presence of Br_2^+, Br^+ and probably py^+ (table 4.5). In addition there appeared to be several species present with molecular weights greater than 200, one of which clearly contained bromine. This indicates that pyridine condensation products were present.

Some confusion existed in the literature over the thermal decomposition of the species $CuX_2 2py$, where X = Cl or Br, which it had been hoped could be used for comparative purposes. The bromide complex had not been studied by this technique, whilst the chloride complex, according to Wendlandt and Ali (118), yielded $CuCl_2 py$ between 150 and 240°C, $3CuCl_2$: 2py between 240 and 270°C, and finally $CuCl_2$ at 340°C. Bowman and Rogers, who studied the decomposition by a D.T.A. method, reported that the complex underwent a redox reaction at 240°C to form a black tar. (96). The decomposition of both chloride and bromide complexes were studied in the present investigation. It was found that the decomposition curve of the chloride complex (figure 4.4) was similar to that obtained by Wendlandt and Ali, except that temperatures corresponding to individual stages were found to be about 30 - 40°C lower than reported by these workers. The product was copper (II) chloride (by weight loss). The analogous bromide complex (figure 4.4) underwent a redox decomposition reaction to yield copper (I) bromide which was characterised by x-ray powder diffraction data. This is another example of the relatively greater stability of copper (I) bromide with respect to the chloride, influencing the decomposition mechanism. A further example of a bromide complex which undergoes a redox reaction, whereas the corresponding chloride complex does not, can be found on consideration of the tetranuclear 3-methylpyridine complexes (tables 3.5 and 4.4).

4.3 Conclusions

The preparation and characterisation of tetranuclear copper (II) complexes containing mixed bridging halides represents an important development in the study of polynuclear cluster complexes. Not only has the number of possible complexes of the type been increased, but the effect of changes in the bromine to chlorine ratio on the physical and physiochemical properties of a series of complexes can now be studied. In theory several structural isomers of these mixed halide complexes should exist, and from x-ray, infrared, and thermogravimetric studies the two isomers of $Cu_4OCl_2Br_4 4py$ have been characterised. The isolation of the isomeric forms of $Cu_4OCl_4Br_2 4py$ and $Cu_4OCl_3Br_3 4py$ may be possible from preparations involving copper (II) bromochloride, when sufficiently pure samples of this compound are available. The tetranuclear pyridine complexes have been shown to undergo redox decomposition reactions, involving oxidation of the pyridine ring, and a corresponding reduction of the metal to copper (I). A redox reaction of this type probably involves the generation of free radicals, which in the case of hexachloride complex (equation 4.5) would lead to the production of $2Cl\cdot$ and $O\cdot$ by the reduction of copper (II) to copper (I). The chlorine radicals then attack the pyridine molecules to form chloropyridine with the abstraction of $H\cdot$. The presence of an oxygen atom in the tetranuclear complex is important in this type of reaction because the subsequent formation of an oxygen radical during the redox reaction facilitates the chlorination by reacting with the two hydrogen radicals to form water. By way of contrast, the thermal decomposition of bispyridinedichloro copper (II), which has no oxygen atoms to assist the hydrogen abstraction, does not proceed by a redox mechanism. The reason why tetranuclear pyridine complexes undergo redox decomposition reactions, whereas complexes with similar amine ligands (discussed in

chapter three) do not, is probably a result of the effect of the ligand on the redox potential of the particular complex. The redox potentials are not simply related to ligand pka values, but are altered by co-ordination number and steric effects, as well as the π-acceptor strength of the ligand (125-127). These effects are complex and not well understood, but could account for the differences between the decomposition mechanisms for various tetranuclear complexes.

CHAPTER FIVE

HALIDE EXCHANGE IN TETRANUCLEAR COPPER (II) COMPLEXES

5.1 Experimental and results

The preparation of the tetranuclear copper complex $[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$ had been reported by Bertrand and Kelley (55, 58) and Dieck and Brehm (68). In addition, the latter workers prepared the complex $[(CH_3)_4N]_4^+ Cu_4OCl_6Br_4^{4-}$, by the addition of an alcoholic tetramethyl-ammonium bromide solution to the tetranuclear compound $Cu_4OCl_6 4MeOH$ in ether. It was decided to attempt the preparation of the other two members of the series containing bridging bromine anions, $[(CH_3)_4N]_4^+ Cu_4OBr_{10}^{4-}$ and $[(CH_3)_4N]_4^+ Cu_4OBr_6Cl_4^{4-}$, in order to interpret the far infrared spectra of this type of molecule. The decabromide complex was successfully prepared from ethanolic solution by the method described in chapters three and four. However, the addition of a stoichiometric amount of tetramethylammonium chloride to a "Cu_4OBr_6" solution in ethanol, resulted in the isolation of a complex containing more than four chlorine atoms per Cu_4O unit. The results of this preparation indicated that halide exchange was occuring between the bridging bromide anions and chloride ions. This exchange was confirmed by using a greater than stoichiometric amount of tetramethylammonium chloride in the reaction, which in turn resulted in a complex with an even higher chlorine to bromine ratio. It was discovered that by altering the reaction temperature, the amount of halide exchange could be controlled to some extent. In general the greater the bromine content of the particular tetranuclear complex, the greater was its solubility in ethanol, so by reducing the temperature of reaction, the amount of halide exchange could be limited by reducing the time the complex spent in solution and vice versa. By varying the reactants and reaction conditions, it should be possible to prepare the complete series $[(CH_3)_4N]_4^+ Cu_4OCl_nBr_{10-n}^{4-}$ where $n = 1-9$; however many of these will have several isomers, each containing a

different number of chloride or bromide anions in the equatorial

and axial positions and, in addition, a number of structural isomers

of the type discussed in chapter four. There are in fact fifty four

possible complexes including the $Cu_4OX_{10}^{4-}$ species. Only six mixed

halide complexes have been characterised in this present investigation;

table 5.1 details the preparative reactions. The preparations were

based on the usual method of adding ligand to "$Cu_4OCl_nBr_{6-n}$" solutions

in ethanol or methanol. The precipitated products were washed with

anhydrous petroleum spirit (B.P.40-60°C), and dried in vacuo

(2 torr) at 20°C. The complexes were difficult to obtain in a pure

state, as working with alcohol or even diethyl ether to remove

unreacted "$Cu_4OCl_nBr_{6-n}$" solution or tetramethylammonium halide, resulted

in halide exchange. Table 5.2 contains analytical and infrared data

for these six complexes and the two $Cu_4OX_{10}^{4-}$ species. Also

contained in table 5.2 is the composition of the central structural

unit, $Cu_4OCl_nBr_{6-n}$. It was found that reacting these complexes with

pyridine vapour displaced the axial ligands, leaving the species

$Cu_4OCl_nBr_{6-n}4py$, which could then be identified from its infrared

spectrum by comparing this with the spectra of the mixed halide

complexes discussed in the previous chapter. X-ray powder

diffraction lines for the six mixed halide complexes and the $Cu_4OX_{10}^{4-}$

species are contained in tables 5.3 and 5.4.

The "$Cu_4OCl_nBr_{6-n}$" solutions, and the complexes $[(CH_3)_4N]_4^+$

$Cu_4OX_{10}^{4-}$, X = Cl, Br, and Cu_4OCl_64MeOH in alcohol solution, exhibited

an intense band in the ultraviolet region of the spectrum between

270 and 307 nm. The position of this band could be used to study

the halide exchange reactions. λ_{MAX} appeared at different wavelengths

depending on both the particular compound and on the solvent in which

it was dissolved. This shift in λ_{MAX} for the complex Cu_4OCl_64MeOH

TABLE 5.1

PREPARATIVE METHODS FOR DECAHALIDE COMPLEXES

COMPLEX	"$Cu_4OCl_nBr_{6-n}$" SOLUTION (A)	TETRAMETHYLAMMONIUM HALIDE (B)	MOLE RATIO A:B	TEMPERATURE °C
$[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$	Cu_4OCl_6 in EtOH	$(CH_3)_4NCl$	1:4	20
$[(CH_3)_4N]_4^+ Cu_4OBr_{10}^{4-}$	Cu_4OBr_6 in MeOH	$(CH3)_4NBr$	1:4	60
$[CH_3)_4N]_4^+ Cu_4OCl_9Br^{4-}$	Cu_4OCl_6 in EtOH	$(CH_3)_4NBr$	1:2	80
$[(CH_3)_4N]_4^+ Cu_4OCl_8Br_2^{4-}$	$Cu_4OCl_3Br_3$ in EtOH	$(CH_3)_4NCl$	1:4	20
$[(CH_3)_4N]_4^+ Cu_4OCl_7Br_3^{4-}$	$Cu_4OCl_3Br_3$ in MeOH	$(CH_3)_4NCl$	1:3	5
$[(CH_3)_4N]_4^+ Cu_4OCl_5Br_5^{4-}$	Cu_4OBr_6 in EtOH	$(CH_3)_4NCl$	1:5	20
$[(CH_3)_4N]_4^+ Cu_4OCl_4Br_6^{4-}$	$Cu_4OCl_3Br_3$ in EtOH/MeOH	$(CH_3)_4NBr$	1:5	70
$[(Ch_3)_4N]_4^+ Cu_4OCl_3Br_7^{4-}$	$Cu_4OCl_3Br_3$ in MeOH	$(CH_3)_4NBr$	1.4	50

TABLE 5.2

ANALYTICAL AND INFRARED DATA FOR TETRANUCLEAR TETRAMETHYLAMMONIUM COMPLEXES

COMPLEX $[(CH_3)_4N]_4^+$	% COPPER		% CHLORIDE		% BROMIDE		%TOTAL HALIDE		Cu:Cl:Br RATIOS	Cu-O$_{asym}$ Cm^{-1}	COMPOSITION OF $Cu_4OCl_nBr_{6-n}$ UNIT
	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.			
$Cu_4OCl_{10}^{4-}$	28.01	27.59	38.22	38.48	–	–	–	–	–	542	–
$Cu_4OBr_{10}^{4-}$	18.51	18.61	–	–	58.04	58.50	–	–	–	528(Sh) 512(Sh) 495	–
$Cu_4OCl_9Br^{4-}$	25.91	26.32	32.79	33.04	7.54	8.27	40.6	41.3	4:9.1:0.9	538	Cu_4OCl_6
$Cu_4OCl_8Br_2^{4-}$	25.01	25.16	27.41	28.07	15.34	15.82	–	–	4:7.9:2.0	537	$Cu_4OCl_4Br_2$
$Cu_4OCl_7Br_3^{4-}$	23.75	24.10	23.10	23.54	23.10	22.83	–	–	4:7.0:3.1	530	$Cu_4OCl_3Br_3$
$Cu_4OCl_5Br_5^{4-}$	22.31	22.22	15.23	15.50	34.74	34.94	–	–	4:4.9:5.0	522	$Cu_4OCl_4Br_2$
$Cu_4OCl_4Br_6^{4-}$	21.06	21.39	11.28	11.94	40.72	40.36	51.4	52.3	4:3.8:6.2	518	$Cu_4OCl_3Br_3$
$Cu_4OCl_3Br_7^{4-}$	20.41	20.62	8.24	8.63	45.39	45.38	53.3	54.0	4:2.9:7.1	510	$Cu_4OCl_3Br_3$

TABLE 5.3

X-RAY POWDER DIFFRACTION DATA FOR ISOMOROPHOUS TETRAMETHYLAMMONIUM COMPLEXES

$Cu_4OCl_{10}^{4-}$		$Cu_4OCl_7Br_3^{4-}$		$Cu_4OCl_4Br_6^{4-}$		$Cu_4OCl_3Br_7^{4-}$		$Cu_4OBr_{10}^{4-}$	
d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I
9.86	40	10.04	30	10.03	50	9.99	30	9.99	40
9.12	20	9.31	90	9.31	40	9.31	70	9.37	60
8.79	100	8.93	100	8.95	100	8.95	100	8.93	100
8.53	5	8.60	40	8.59	20	8.60	10	8.60	30
8.02	90	8.16	90	8.15	40	8.13	90	8.15	70
6.37	5	6.40	30	6.43	10	6.38	5	6.44	30
		5.72	10	5.78	20	5.76	20	5.78	30
5.42	40	5.50	20	5.54	20	5.51	10	5.54	10
5.23	10							5.42	10
4.89	5							5.00	10
4.60	10							4.80	5
4.26	20	4.72	15	4.68	10	4.69	5	4.72	5
4.18	10			4.34	20			4.36	10
3.98	10	4.15	10	4.24	20			4.27	20
3.83	20							4.21	20
3.62	30	3.88	5	3.90	20			3.92	10
3.45	10	3.67	20	3.69	40	3.69	20	3.72	40
3.34	15	3.49	10	3.51	40	3.51	20	3.53	30
2.90	15	3.38	10	3.41	15			3.44	10
2.81	15	3.17	15	3.31	10			3.43	10
		2.84	20	3.27	10			3.33	20
				3.20	10			3.29	20
				3.00	10			3.22	20
				2.96	10				
				2.87	10	2.87	30		

TABLE 5.4

X-RAY POWDER DIFFRACTION DATA FOR TETRAMETHYLAMMONIUM MIXED HALIDE COMPLEXES

$Cu_4OCl_5Br_5^{4-}$		$Cu_4OCl_8Br_2^{4-}$		$Cu_4OCl_9Br^{4-}$	
d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I
11.41	10	11.41	20	9.22	100
9.93	30	9.93	20	8.50	60
8.85	100	8.87	100	6.33	50
8.06	90	8.04	90	5.97	5
5.70	10	6.00	10	5.49	5
5.44	10	5.45	20	4.71	10
4.62	10	4.41	10	4.14	20
4.29	10	4.28	20	3.17	20
3.88	40	3.89	20	2.78	10
3.65	30	3.63	30	2.71	10
3.48	20	3.44	20		
3.31	10	3.35	20		
2.93	20	2.93	20		
2.84	20	2.82	20		

in various solvents is shown in figure 5.1. The "$Cu_4OCl_nBr_{6-n}$"

solutions in ethanol, discussed in chapter four, each exhibited a

single band between 270 nm ("Cu_4OCl_6" solution) and 307 nm

("Cu_4OBr_6" solution): these bands are shown in figure 5.2. A Beer's

plot of absorbance versus concentration for $[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$ in

ethanol is shown in figure 5.3. Molar extinction coefficients

calculated from these data are about 27,000. An extinction coefficient

calculated for the decabromide species on a single concentration value

was 30,000. Table 5.5 contains λ_{MAX} data for complexes with different

axial ligands in the same solvent. To obtain data on the halide

exchange process itself, a method based on that of Yoé and Jones (128)

was employed. A series of decabromide solutions were made up in ethanol,

each containing a different amount of tetramethylammonium chloride, but

keeping the total analytical concentration of copper constant. One

hour after preparation, the position of λ_{MAX} was determined. The results

are shown graphically in figure 5.4, as a plot of λ_{MAX} versus moles of

halide added per mole of decabromide complex. A qualitative study of the

effect of adding hydroxide ions, in the form of a 20% aqueous solution

of tetraethylammonium hydroxide, to an ethanolic solution of the

decabromide was made. The changes in the wavelength of λ_{max} on the

addition of successive amounts of hydroxide, are shown in figure 5.5.

After each determination of λ_{MAX}, excess tetramethylammonium bromide

was added to ascertain whether a tetranuclear species was still

present. If it was, λ_{MAX} reverted to its original wavelength of 307 nm.

The presence of pyridine in the hexahalide – pyridine complexes gave

rise to large intensity ligand bands, which obscured the bands due to

the tetranuclear species, and prevented similar measurements being

TABLE 5.5

λ_{MAX} FOR TETRANUCLEAR COPPER COMPLEXES IN ALCOHOL SOLUTIONS

COMPLEX	SOLVENT	λ_{MAX} (nm)
$Cu_4OCl_6 4MeOH$	ethanol	270
$[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$	ethanol	270
"Cu_4OCl_6" solution	ethanol	270
"Cu_4OBr_6" solution	ethanol	307
$[(CH_3)_4N]_4^+ Cu_4OBr_{10}^{4-}$	ethanol	307
$Cu_4OCl_6 4MeOH$	methanol	250
$[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$	methanol	250
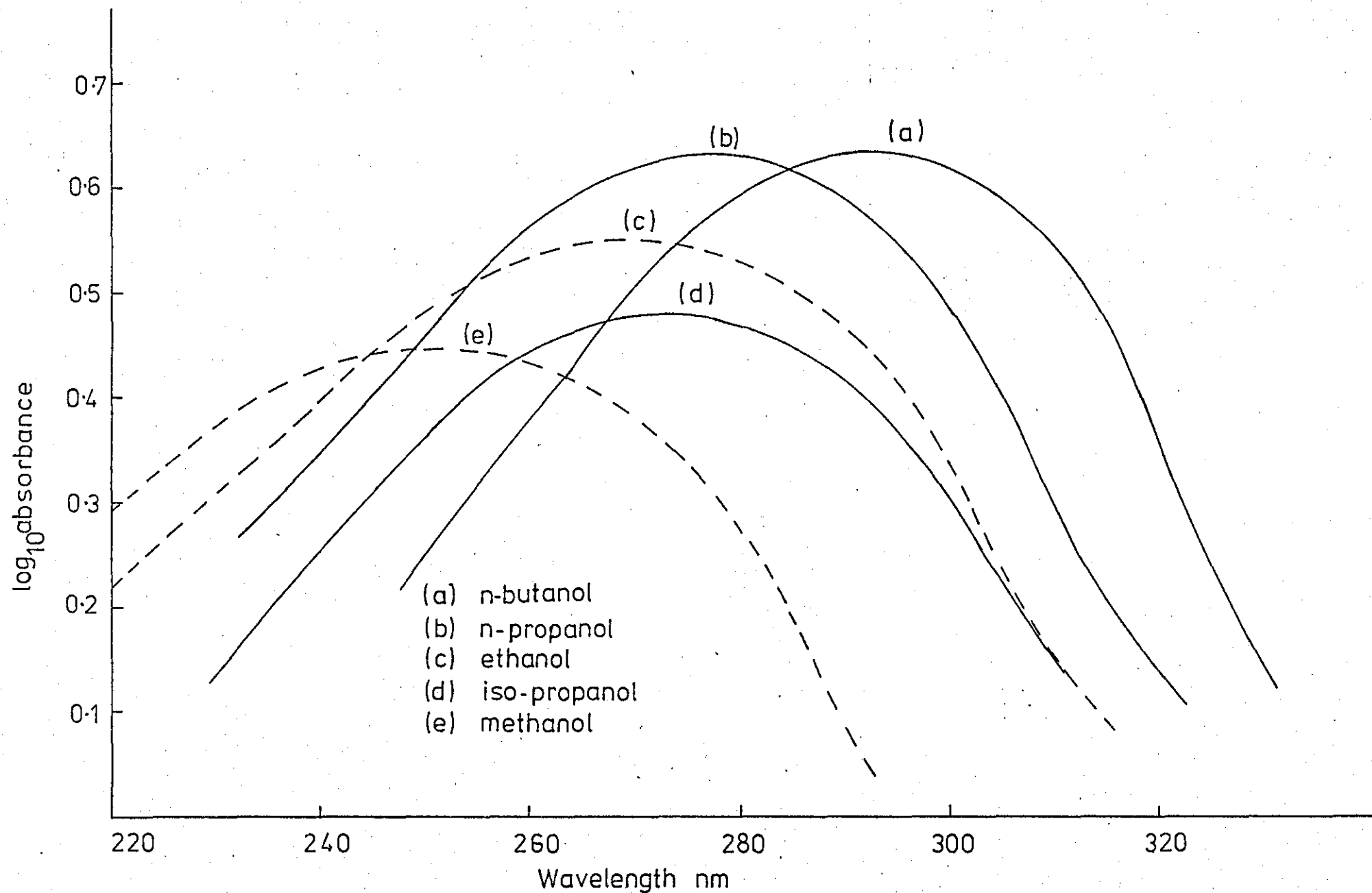
FIGURE 5.1. λ max for Cu_4OCl_64MeOH in various solvents

(a)   n-butanol
(b)   n-propanol
(c)   ethanol
(d)   iso-propanol
(e)   methanol
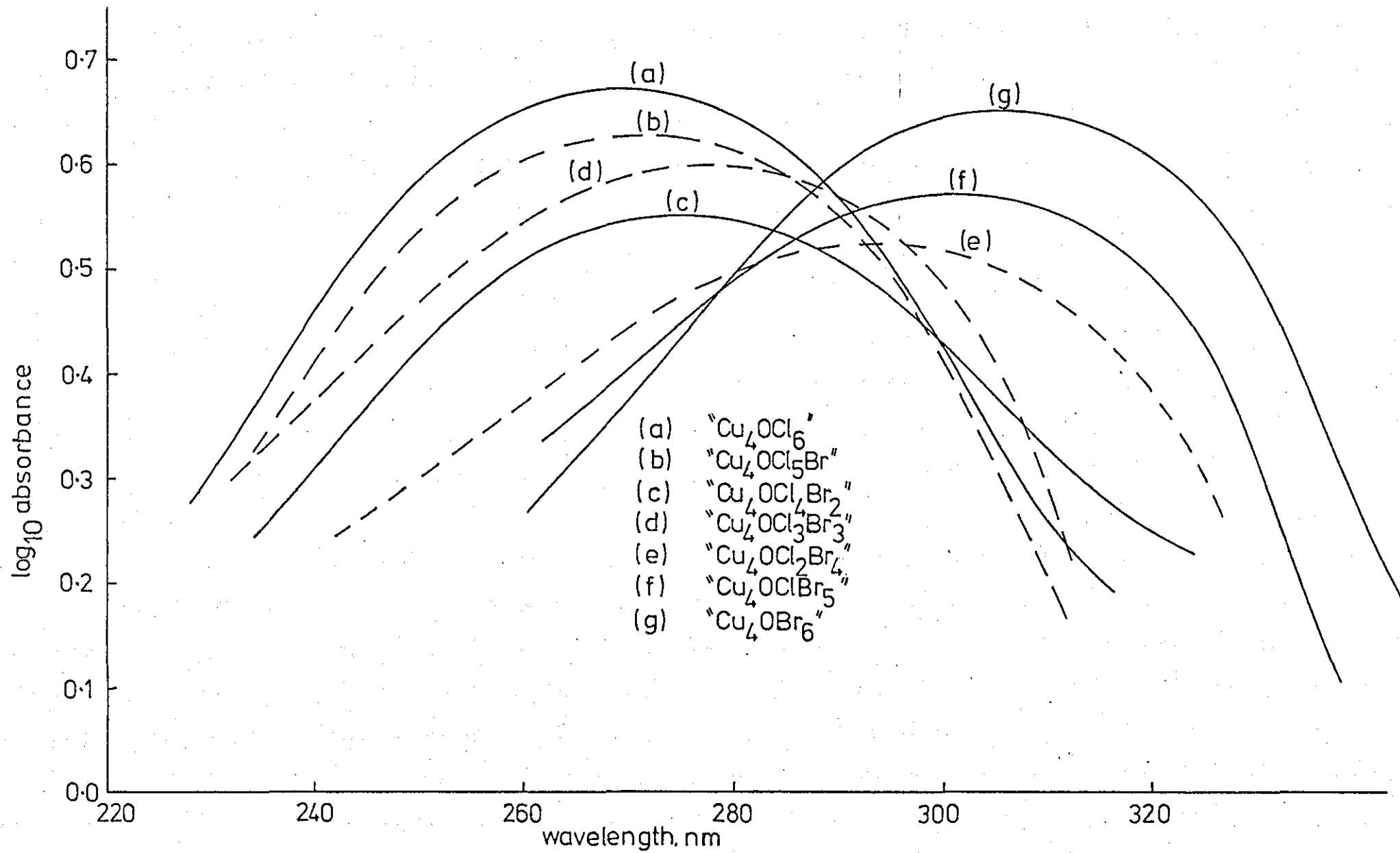
FIGURE 5. 2.   UV spectra for "$Cu_4OCl_nBr_{6-n}$" solutions in ethanol.
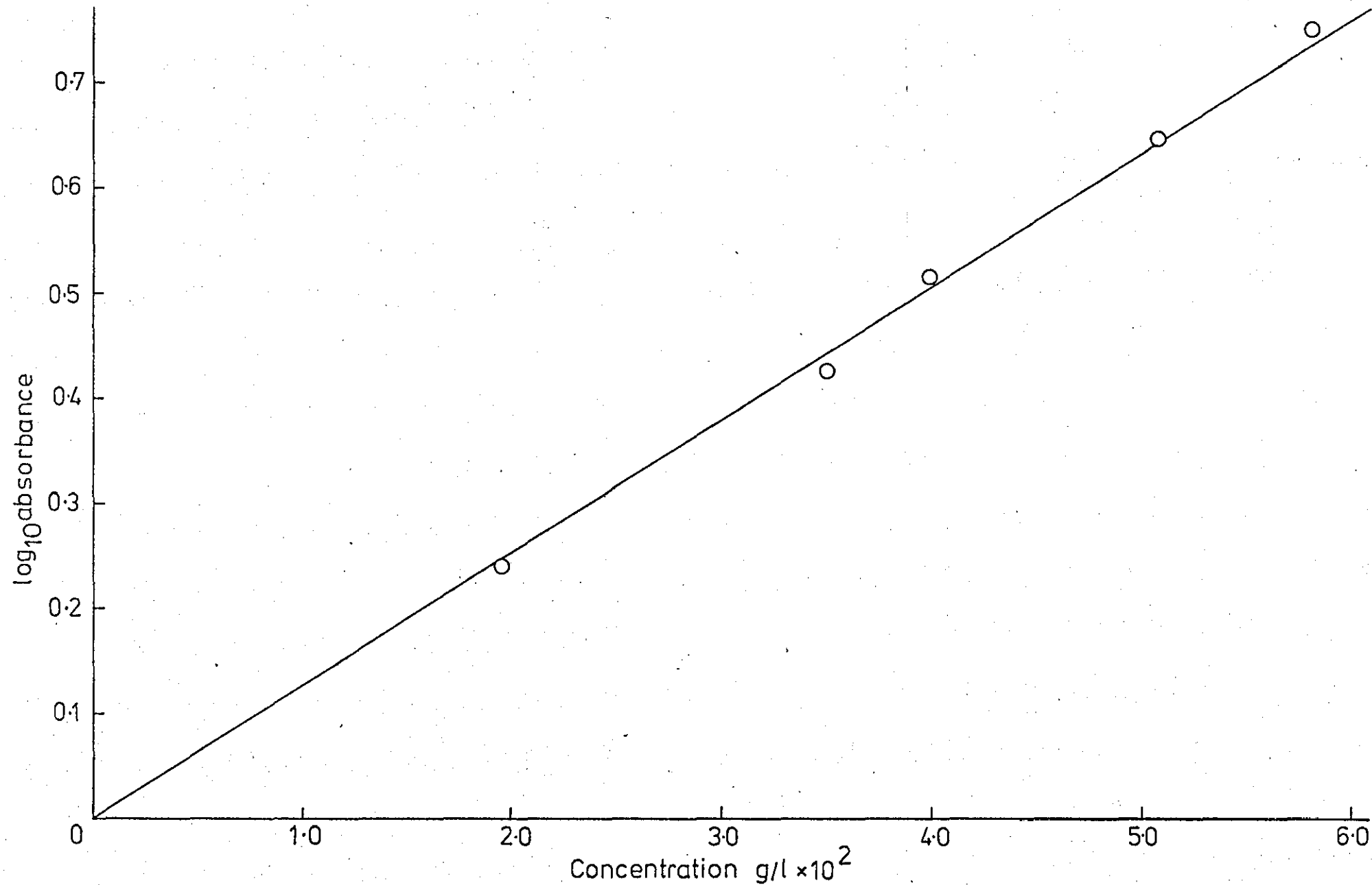
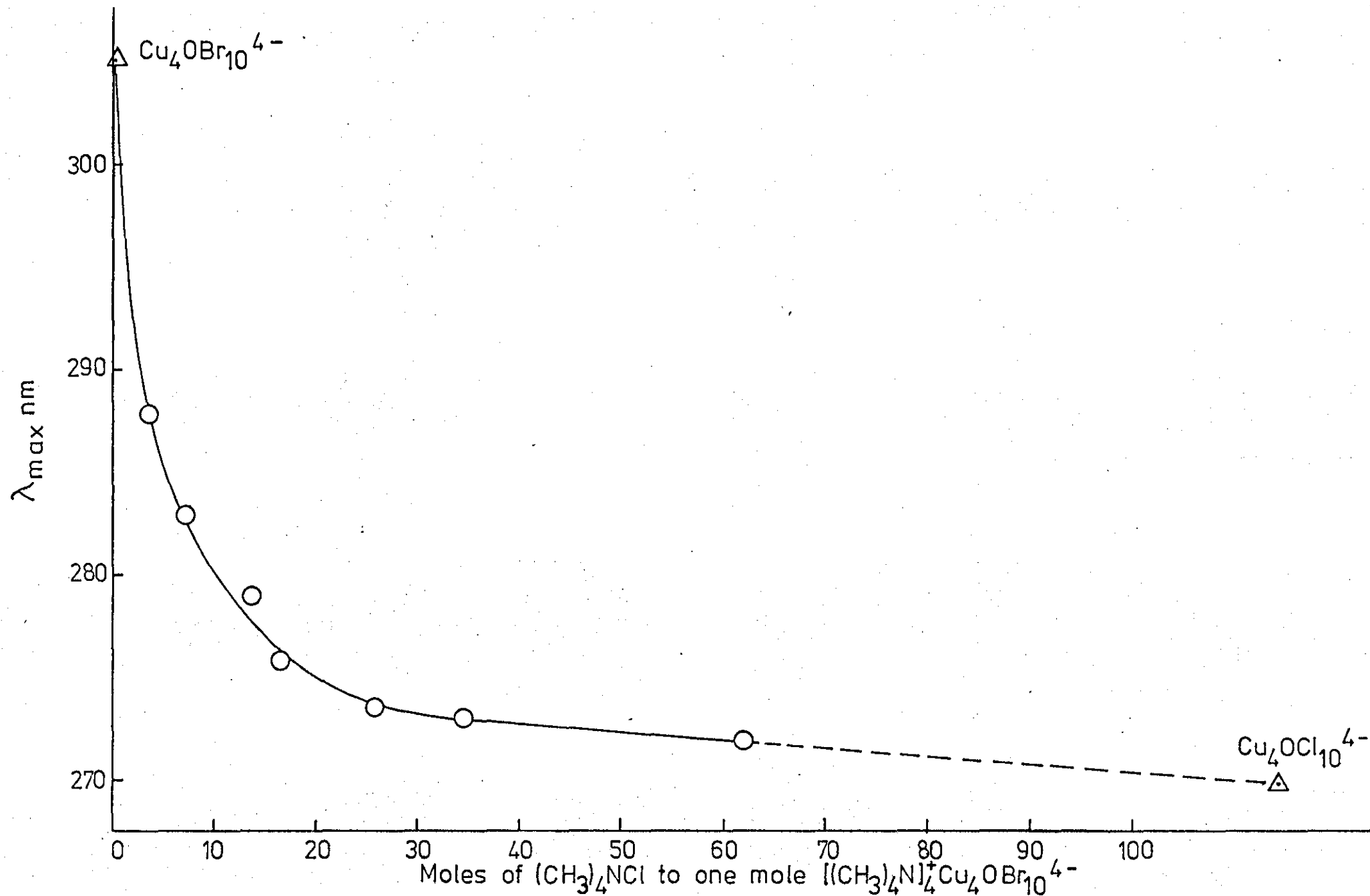FIGURE 5.3. Beer's law plot for $[(CH_3)_4N]_4^+ \quad Cu_4OCl_{10}^{4-}$ in ethanol, at 270n.m.

FIGURE 5.4. Change in λ_{max} on the addition of $(CH_3)_4NCl$ to $[(CH_3)_4N]_4^+ Cu_4OBr_{10}^{4-}$ in ethanol
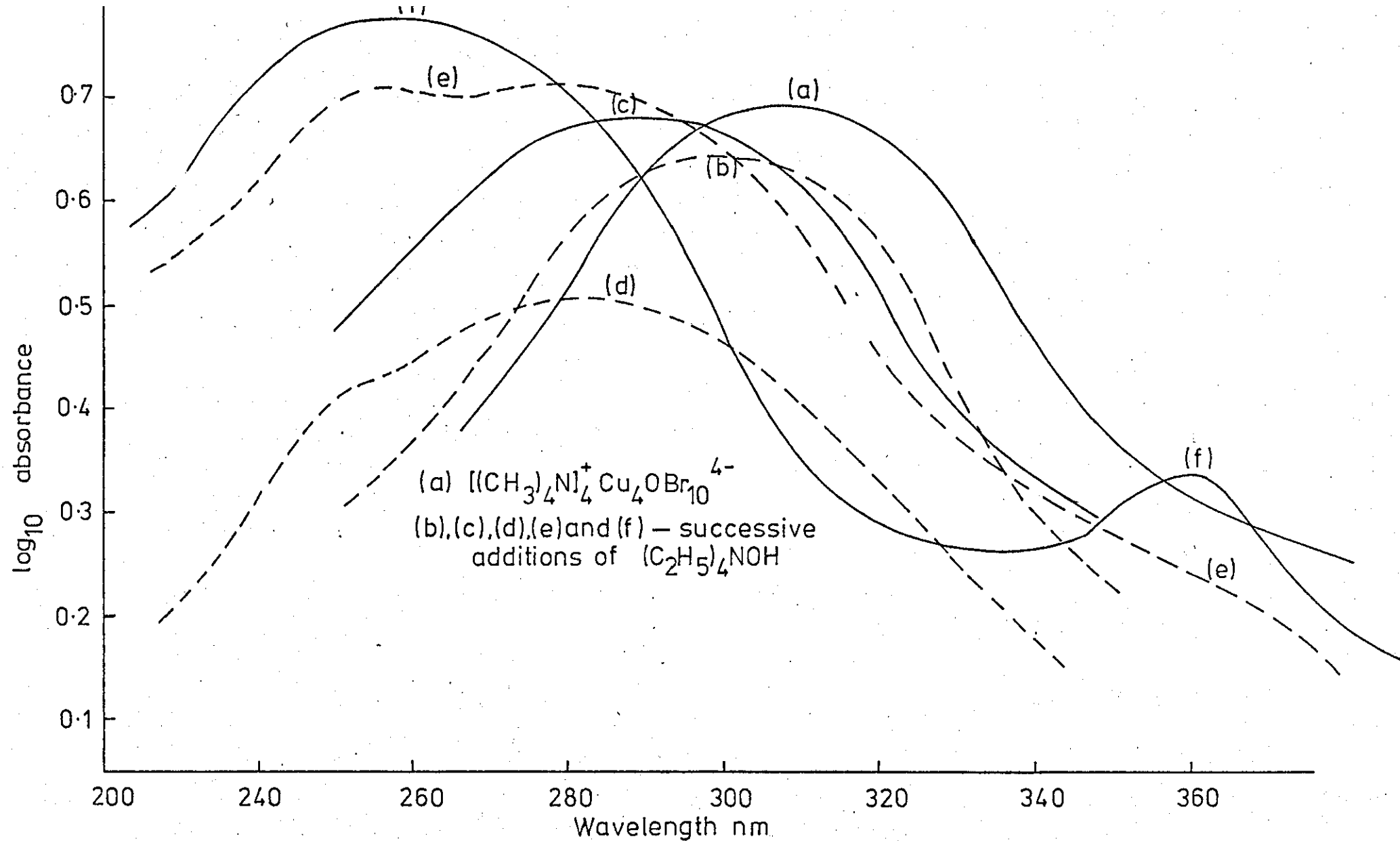
FIGURE 5. 5. The effect on λ_{max} of adding a solution of $(C_2H_5)_4NOH$ to $[(CH_3)_4N]_4^+ Cu_4OBr_{10}^{4-}$ in ethanol.

Within the figure:

(a) $[(CH_3)_4N]_4^+ Cu_4OBr_{10}^{4-}$

(b),(c),(d),(e) and (f) — successive additions of $(C_2H_5)_4NOH$

made on these compounds. Spectral studies were made in nitromethane also, but no bands in the region of 200 - 450 nm were observed for tetranuclear complexes in this solvent.

The lability of the bridging halide anions in tetranuclear complexes led to the speculation that these compounds might be dissociated to some extent in solution. This theory was investigated by determining the conductivity of the hexachloride and hexabromide-pyridine complexes in nitromethane. These complexes were chosen as they would appear to be non-electrolytes in solution were they undissociated, whereas complexes such as $[(CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$ could, according to solution spectral data, undergo dissociation of the axial ligand and so complicate conductivity data. Initial measurements indicated that charged species were present in nitromethane solutions of $Cu_4OCl_6 4py$ and $Cu_4OBr_6 4py$, and so the method of Feltham and Hayter (47) was used to determine electrolyte type, by conductivity measurements made over a range of concentrations. This method uses the Onsager equation in the form:-

$$\Lambda_o - \Lambda_e = B\sqrt{C}$$

Λ_o is determined from a plot of Λ_e versus $\sqrt{C}$, by extrapolating to zero concentration, and then $\Lambda_o - \Lambda_e$ is plotted against $\sqrt{C}$. The slope of this latter graph varies with electrolyte type, and can be compared with standard values (47) to determine the nature of the charged species present. Nitromethane was chosen for these studies as it is regarded as one of the best solvents for conductivity measurements in nonaqueous media (48). Apart from which, the tetranuclear pyridine complexes were not sufficiently soluble in other solvents to permit such an investigation. Although the conductivity of solutions of the hexabromide complex remained stable over periods of up to 24 hours, the hexachloride solutions increased in conductance over a period of 16 hours,

whereupon they remained stable. The results of the conductivity

measurements are shown graphically in figures 5.6 to 5.9. The data

for the hexachloride complex (figures 5.6 and 5.7) were taken after

16 hours. Measurements of Λ_o and $\frac{\Lambda_o - \Lambda e}{\sqrt{C}}$ after one hour, gave values

of 151.6 ohm^{-1} and 4,714 respectively for Cu_4OCl_64py.

Tetranuclear complexes and "$Cu_4OCl_nBr_{6-n}$" solutions were

prepared as described in the preceding chapters. Tetramethylammonium

halides were B.D.H. reagents and were reprecipitated from ethanol

(chloride) or methanol (bromide) by the addition of diethyl ether. The

products were stored under vacuum. The tetraethylammonium hydroxide solution

(20%w/w in water) was a Hopkin and Williams product. Alcohols were

purified and dried by standard techniques (45). The nitromethane used

for conductivity studies, a Fisons product, was refluxed with anhydrous

magnesium sulphate for twelve hours and distilled. The solvent was

then refluxed with 4A molecular sieve for 2 days, and distilled under

an atmosphere of dry nitrogen, the fraction boiling between 101 and

101.5°C being collected. The purified, dry solvent was stored under

nitrogen away from the light.

Copper, mixed halide analyses, infrared spectra and X-ray

diffraction data, were obtained as previously described. Solution spectra wer

recorded at ambient temperature using an S.P.8000spectrophometer and

1 cm matched silica cells. Solutions of the tetranuclear methanol

complexes were made up in a dry-box. Conductivity measurements

were made using standard cells and electrodes, and a Wayne Kerr

conductivity bridge. During the measurements a slow stream of dry

nitrogen was directed over the top of the cell, to prevent the

ingression of oxygen or water vapour. Measurements were made at

25°C by means of a thermostatically controlled water bath. The cell

constant was determined before and after each series of measurements

using a M/1000 potassium chloride solution. It was found to be
0.076. The specific conductivity of the nitromethane was 0.8×10^{-6} $ohm^{-1}cm^{-2}$.

5.2 Discussion.

5.2.1 Analytical, infrared and x-ray data

Analytical data (table 5.2) indicate that seven new tetranuclear
copper (II) complexes, containing axial halide atoms, have been
prepared. These complexes were difficult to obtain in a pure state,
due to the halide exchange that occured when the samples were washed
with solvents such as ethanol or diethyl ether. In addition, for
preparations involving tetramethylammonium bromide, the low solubility
of this compound in alcohols resulted in small amounts precipitating
with the tetranuclear product. The infrared spectra of these complexes
all contained the C-N band at 954 cm^{-1} characteristic of the
tetramethylammonium cation. The bands assigned to the Cu-O assymmetric
stretching vibration (table 5.2), show a decrease in frequency
corresponding to an increase in the bromine to chlorine ratio, similar
to the mixed halide-pyridine complexes of chapter four. However, the
position of this band is affected by axial as well as equatorial halides,
in these latest complexes. If potassium halide discs were used to
obtain infrared spectra, the Cu-O band appeared considerably broadened
and in some cases split into two, presumably due to halide exchange.
X-ray powder diffraction data indicate that the decachloride and
decabromide complexes are isomorphous, the "d" spacing increasing as
expected from a chloride complex to the isomorphous bromide complex
(table 5.3), in a similar manner to that observed for the pyridine
complexes. These two decahalide complexes also appear to be isomorphous
with the three complexes which were shown to have the central structural
unit $Cu_4OCl_3Br_3$, by the reaction with pyridine vapour. The two
complexes with the $Cu_4OCl_4Br_2$ central units, $[(CH_3)_4N]_4^+ Cu_4OCl_5Br_5^{4-}$ and
$[(CH_3)_4N]_4^+ Cu_4OCl_6Br_2^{4-}$, appear to be isomorphous from x-ray data (table 5.4).

The complex $[(CH_3)_4N]^+_4 Cu_4OCl_9Br^{4-}$, however, has a diffraction pattern

dissimilar to those of the other complexes (table 5.4).

5.2.2 Solution spectra

Solution studies reveal that a band in the ultraviolet region

of the spectrum can be used to study the various tetranuclear

mixed halide complexes, with respect to halide exchange phenomena.

The Beer's law plot for the decachloride complex (figure 5.3) shows a

linear relationship between absorbance and concentration, and implies

that only one species is present in ethanol solution. The position

and extinction coefficient of this band for the decachloride (270 nm:

27,000) and bromide (307 nm:30,000) complex, indicates that it is

change transfer in origin. Studies on the complex $Cu_4OCl_6 4MeOH$ in

various solvents (figure 5.1) reveal that the value of λ_{MAX} for this

band is apparently very sensitive to the nature of the solvent.

However the band appears to be constant for complexes with different

axial ligands, but similar central structural units (table 5.5) in one

solvent. These data indicate that in alcohol solution the axial ligands

of the tetranuclear complex are replaced by solvent molecules, so that

the species $Cu_4OX_6 4EtOH$ is present in ethanol. From figure 5.2 it is

clear that each "$Cu_4OCl_nBr_{6-n}$" species in solution exhibits an absorption

band in a position characteristic of the number of chloride and bromide

atoms in the central structural unit of the cluster. Data such as

these can be used to follow the halide exchange reaction when

tetramethylammonium chloride is added to a solution of the decabromide

complex in ethanol (figure 5.4). The results of this experiment indicate

that over 100 moles of chloride, per mole of Cu_4O unit, must be added

to $Cu_4OBr_{10}^{4-}$ before exchange is complete (indicated by a shift in

λ_{MAX} from 307 to 270 nm). Although one hour was allowed for these

solutions to reach equilibrium before λ_{MAX} was determined, it is not

clear at present how fast equilibrium conditions are set up, or whether
this varies with concentration of added halide. Preliminary
investigations of the analogous system (tetramethylammonium bromide
added to a decachloride solution) indicated that exchange of chloride
for bromide was very much slower.

The results of a similar exchange reaction involving tetraethylammonium
hydroxide and the decabromide complex in ethanol (shown in figure 5.5),
suggest that exchange of hydroxyl for bromide ion may be taking place,
(a shift in λ_{MAX} from 307 to 280 nm - (a) to (d)). Up to the position
of λ_{MAX} corresponding to (d) in figure 5.5, the exchange reaction could
be reversed by adding excess bromide ions, which caused λ_{MAX} to revert
to 307 nm. However, after (d) the addition the bromide ions had no
effect, indicating that the tetranuclear structure of the species in
solution may have been destroyed, perhaps by a hydrolysis reaction, as
the hydroxide was added as a 20% solution in water. These solution
studies were of a preliminary nature only, and it is clear that further
work is needed to fully investigate the nature of halide exchange
reactions in tetranuclear complexes.

5.2.3 Conductivity studies

Prior to this investigation, the only conductivity study of tetranuclear
copper (II) complexes had been made by Dieck and Brehm (68) on the
hexahalide complexes with di-isopropylcarbodiimide ligands, which were
reported to be non-electrolytes in nitrobenzene. However the results
of the present investigation indicate that the two hexahalide-pyridine
complexes are dissociated to some extent in nitromethane (figure 5.6
to 5.9). According to Feltham and Hayter (47), the average value of
the $\frac{\Lambda_0 - \Lambda e}{\sqrt{C}}$ slopes for 1:1, 2:1 and 3:1 electrolytes in nitromethane
is 200, 450 and 1000. These slopes for the tetranuclear pyridine
complexes are around 11,000 (figures 5.7 and 5.9). This implies a considerable
degree of dissociation. The $\frac{\Lambda_0 - \Lambda e}{\sqrt{C}}$ slopes reported by Feltham and Hayter
can be numerically extrapolated to give a value of around 10, 000 for 6:1
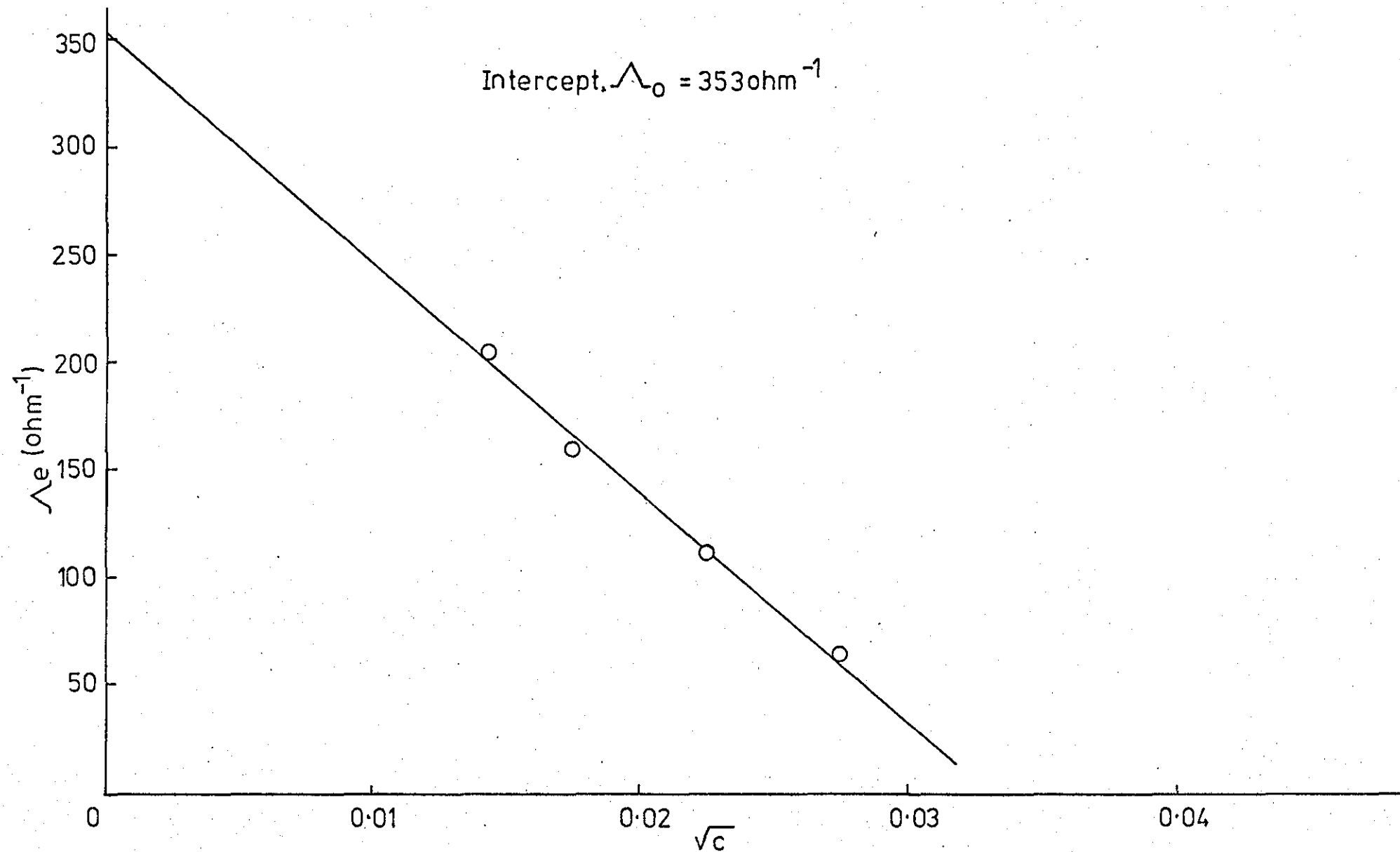electrolytes (lack of information concerning ionic conductances in

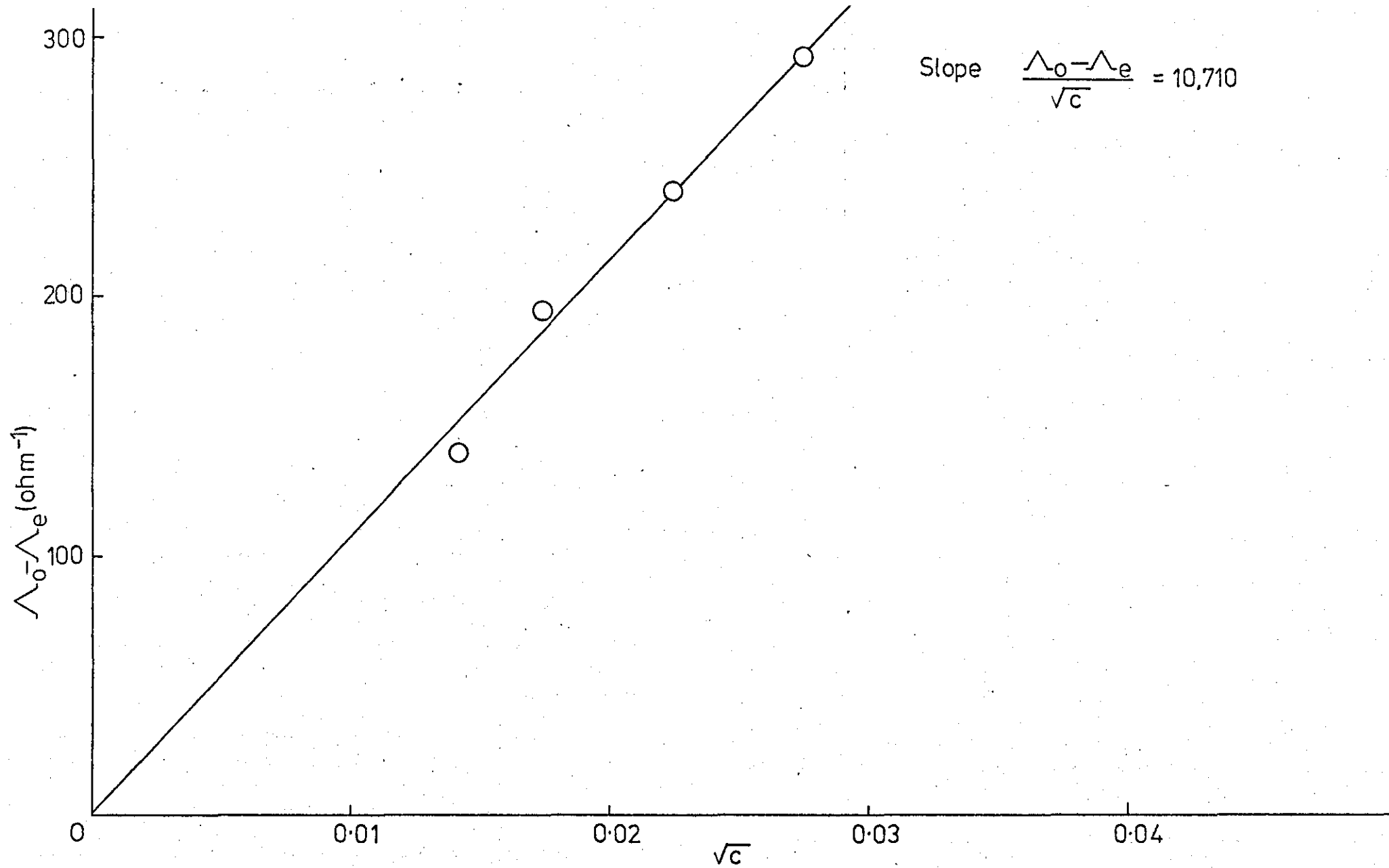FIGURE 5.6. Λe vs $\sqrt{c}$ for Cu_4OCl_64py in nitromethane.

FIGURE 5.7. $\Lambda_o - \Lambda_e$ vs $\sqrt{c}$ for Cu_4OCl_64py in nitromethane
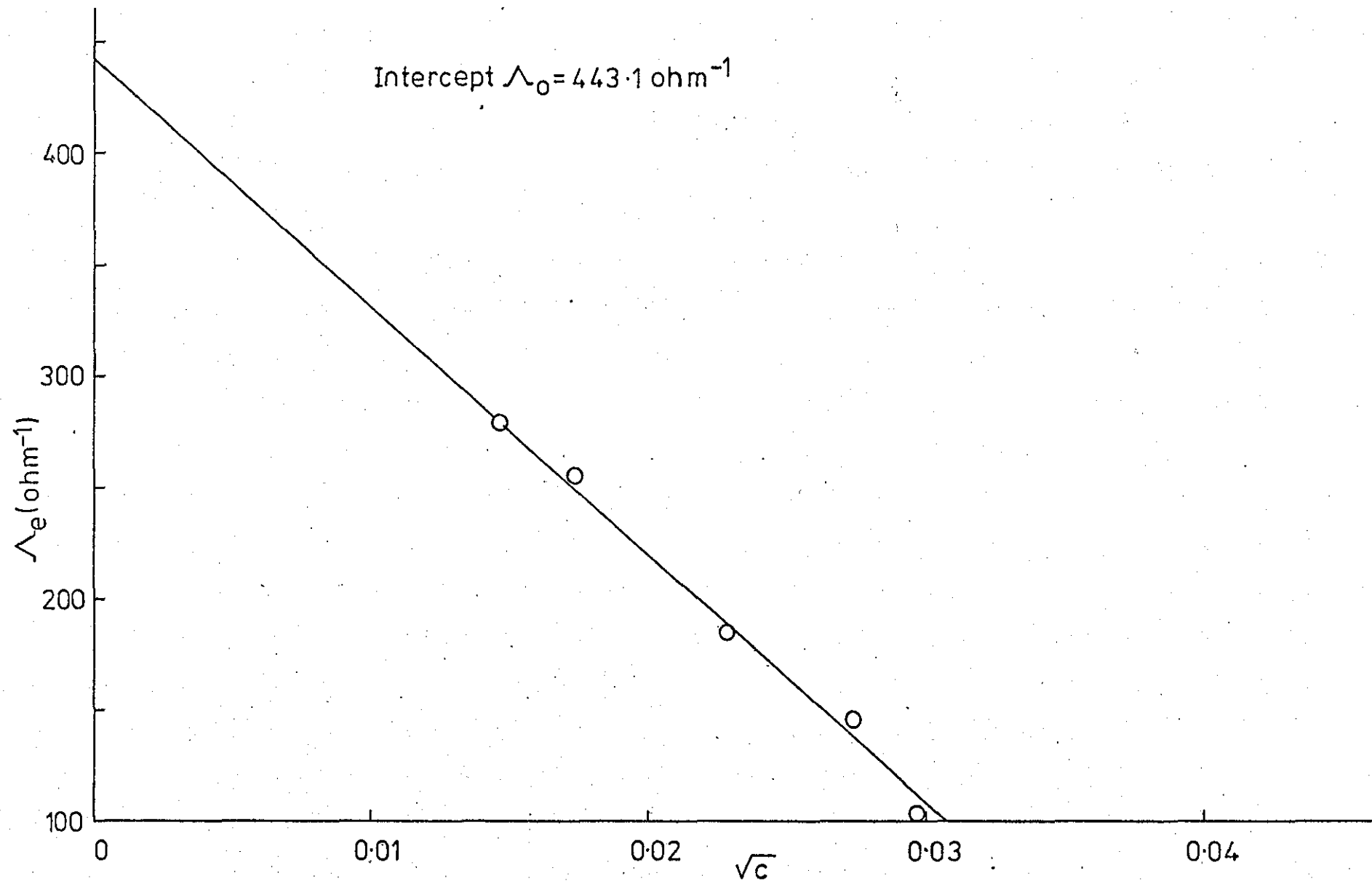
FIGURE   5.8 $\triangle_e$ vs $\sqrt{c}$ for $Cu_4OBr_6 4py$ in nitromethane.

Slope. $\dfrac{\Lambda_o - \Lambda_e}{\sqrt{c}} = 11,005$
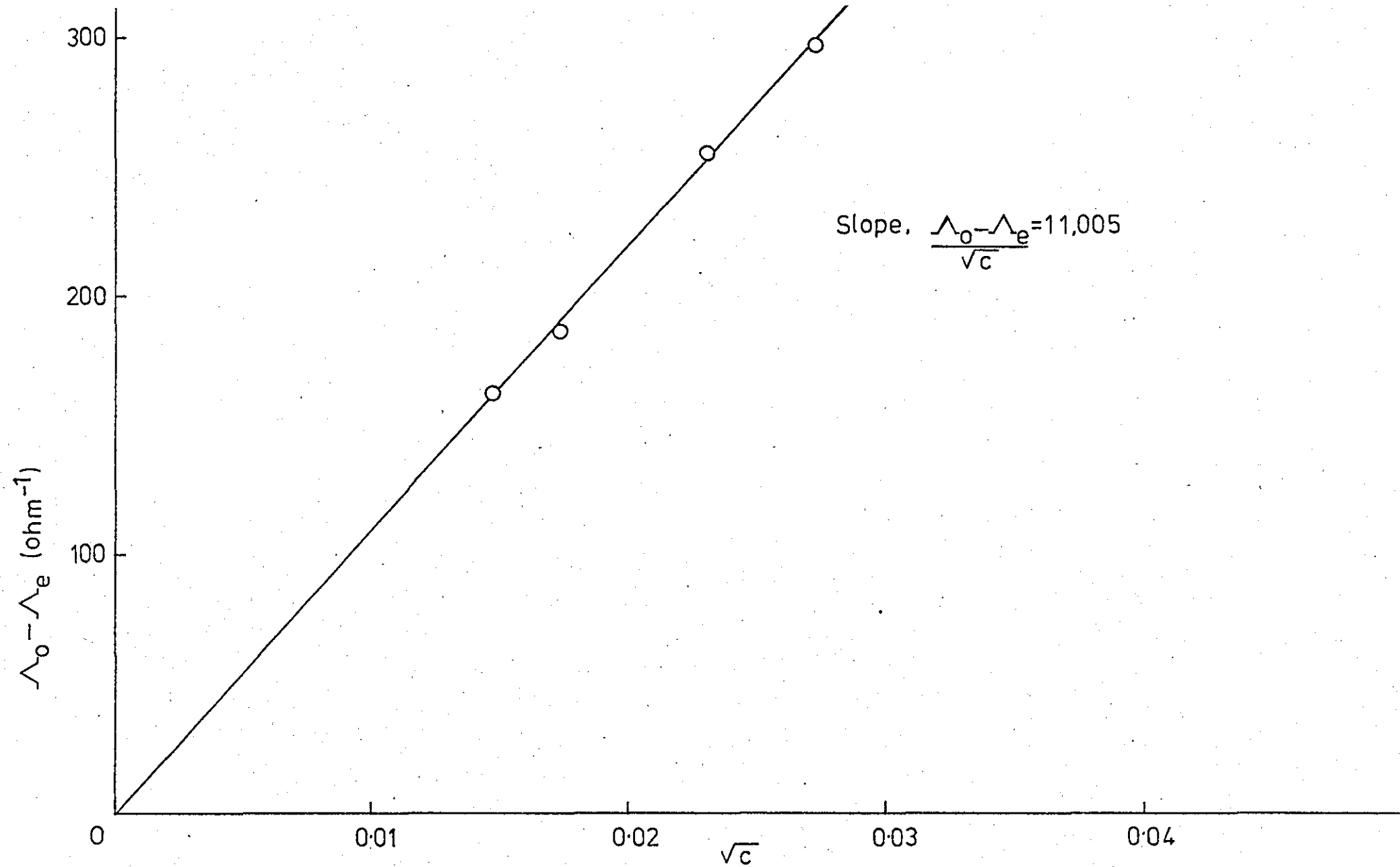
FIGURE 5.9. $\quad \underline{\Lambda_o - \Lambda_e \text{ vs } \sqrt{c} \text{ for } Cu_4OBr_64py \text{ in nitromethane.}}$

nitromethane preclude a theoretical approach

to the value of these slopes and the corresponding electrolyte.

types). However the value of Λe for a M/1000 solution (Λ_{1000})

of the tetranuclear complexes is very much lower than might have

been expected for the degree of dissociation implied by the $\frac{\Lambda_o - \Lambda e}{\sqrt{c}}$

slopes. Geary (48) has reported typical Λ_{1000} values for 4:1

electrolytes in nitromethane to be in the region of 300 ohm^{-1}; 5:1

and 6:1 electrolytes might be expected to have even higher values,

whereas Λ_{1000} for Cu_4OCl_64py and Cu_4OBr_64py is 35 and 100 ohm^{-1}

respectively. Nicholson and Sutton (129) reported similar anomalously

low Λ_{1000} values for some nickel (II) sulphate complexes. They found,

however, that a graph of Λe versus $\sqrt{c}$ was not linear, in a manner

that suggested that these complexes were behaving as weak electrolytes.

This does not seem to be the case of the present system, as Λe

versus $\sqrt{c}$ graphs do not appear to deviate significantly from linearity

(figures 5.6 and 5.8). Ion pairing, which might be expected with

highly charged anions, would cause similar non linear plots (47) and

so can probably be ruled out in this system. It has been observed

that complexes containing large ions such as $(C_6H_5)_4B^-$ and $(i-C_5H_{11})_4B^-$

exhibit very small Λ_{1000} values, due to the low ionic mobilities of

these species. (130). An analogous situation may well exist with

the tetranuclear pyridine complexes. The variation in the conductivity

of the hexachloride complex with time, and the variation of the $\frac{\Lambda_o - \Lambda e}{\sqrt{c}}$

slope from 4,700 to 11,000, indicates that some dissociative process

is taking place, but whether further dissociation occurs on

dilution after 16 hours is a matter of speculation at present.

Assuming the tetranuclear Cu_4O unit is still present in nitromethane

solutions (there was no evidence for the formation of insoluble

copper (II) oxide during these experiments, that would have

indicated a reaction such as $Cu_4OCl_8 \rightarrow 3CuCl_2 + CuO$ taking place),

the bridging halide atoms must have been replaced by solvent

molecules, bridging the copper atoms by means of one of the oxygens

of the nitro-group. The replacement of an anionic species by a neutral

solvent molecule is fairly usual in solvents with strong donor properties

like DMF. (131), but has only been observed in a few cases with

nitromethane (132, 133). The presence of a charge transfer band in

the ultraviolet solution spectra of tetranuclear copper (II) complexes,

was discussed in 5.2.2 above. This band does not appear in the spectra

of these complexes in nitromethane solutions, which may strengthen

the speculation that dissociation of the bridging halide atoms has

taken place in this solvent. Further conductivity studies will be

needed to elucidate the nature of the species present in nitromethane

solution.

5.3   Conclusions

The number of tetranuclear copper (II) complexes containing

mixed bridging halide atoms has been extended with the preparation

of several tetramethylammonium complexes. The bridging

halide anions have been shown to be labile, and exchange of chloride

for bromide and vice versa demonstrated. This exchange may occur

through dissociation of the halide octahedron, with the formation

of charged tetranuclear anions. Evidence for this dissociation comes

from the discovery that the tetranuclear pyridine complexes behave

as electrolytes in nitromethane. There is, in addition, some evidence

to show that exchange of bromide for hydroxide occurs in these

complexes, and that a certain proportion of OH^- ions can be tolerated

in the structure before its collapse.

CHAPTER SIX

THE FAR INFRARED SPECTRA OF TETRANUCLEAR COPPER (II) COMPLEXES

6.1 Introduction

Little work has been reported on the measurement of the far infrared spectra of tetranuclear copper (II) complexes (the term "far infrared" is used in this chapter to describe the region of the spectrum between 650 and 40 cm^{-1}), and only one vibrational band has been assigned. For the complex anion $Cu_4OCl_{10}^{-4}$ which has T_d symmetry, thirty nine vibrations may be expected. Dieck and Brehm (68) calculated that these were of the form $3A_1, 3E, 3T_1$ and $7T_2$ and of these, seven only were expected to be infrared active (all the T_2 vibrations). By analogy with the CH_4 molecule (134), there will be four stretching and six bending vibrations in the Cu_4O unit, and each type of vibration will contain one T_2 species. A similar argument will apply for the stretching and bending vibrations of the four axial Cu-Cl bonds. For the six Cu-Cl stretching vibrations associated with the bridging chloride octahedron, by analogy with molecules such as SF_6 (134), one T_2 mode will be present in this case as well. The bending vibrations of this bridging system however, are complex and no easy comparisons can be made, but at least one T_2 mode might be expected.

On consideration of the mass of the atoms involved and the strength of metal-oxygen bonds, Dieck and Brehm (68) assigned the strong band that appeared in the infrared spectrum of $[CH_3)_4N]_4^+ Cu_4OCl_{10}^{4-}$ at 540 cm^{-1} to the assymmetric Cu-O stretching vibration, and similarly assigned the strong bands which appeared between 500 and 600 cm^{-1} in other tetranuclear copper complexes, to the same vibration. Bock et al. arrived at a similar conclusion for the tetranuclear copper-pyridine complexes (67). This band is now widely used to characterise

complexes of this type. Dieck and Brehm (68) suggested that the far infrared spectra of these complexes may be complicated by the presence of unsymmetrical ligands in the axial position, which would lower the symmetry of the molecule, and cause many more bands to appear. In addition to the work mentioned above, Carr and Harrod (74) reported the far infrared spectra of six tetranuclear copper (II) complexes, but made no attempt to assign any of the bands.

In the present investigation, an attempt has been made to assign individual bands to copper-halogen or copper-nitrogen vibrations, by reference to reported data concerning these vibrations in other copper (II) complexes, and by comparing similar tetranuclear complexes. It is assumed that coupling between the copper-nitrogen, copper-halogen and copper-oxygen vibrations is at a minimum and hence trends and correlations that have been reported by other workers with regard to these vibrations, can also be applied to this system. Lattice vibrations, which also tend to complicate the far infrared spectra of solid complexes, are usually of low energy and are assumed to lie below 100 cm^{-1} (135).

6.2 Experimental and Results

Spectra in the region 650 to 400 cm^{-1} were recorded as previously described using a paraffin oil mull. In addition, measurements between 400 and 40 cm^{-1} were made by the P.C.M.U. at Harwell, using a wax disc with polythene optics. The spectra of many of the complexes containing pyridine and related amines, showed very broad bands between 400 and 40 cm^{-1}: lowering the temperature of the sample to that of liquid nitrogen failed to sharpen these bands to any extent. It was hoped that the Raman spectra of these complexes might be measured, but the excitation radiation was absorbed (the complexes being yellow, brown and red) with subsequent

decomposition, and so these data are not available at present.

The infrared spectra, 400 to 40 cm^{-1} for the tetranuclear

complexes $[(CH_3)_4N]_4^+ Cu_4OX_{10}^{4-}$ X = Cl, Br, are shown in figure 6.1;

similar spectra for the complexes with pyridine and related amines

are contained in figures 6.2 to 6.6. This last figure also shows

the background spectrum for all the complexes. These figures

represent the spectra observed in the 40-400 cm^{-1} region of the

spectrum, the only bands that were observed between 400 and 650 cm^{-1}

were due to amine ligand vibrations, cation vibrations and the νCu-O

assym., which are not listed. Table 6.1 contains the band maxima

for the mixed halide complexes.

6.3 Discussion

6.3.1 Copper-oxygen vibrations

The metal-oxygen stretching vibration is usually intense and

broad in nature and found between 200 and 1100 cm^{-1} for all types of

complexes (135). For copper (II) compounds, the assymmetric

stretching vibration (νCu-O assym.) occurs between 300 and 600 cm^{-1}

(28, 29, 84, 136, 137). For tetranuclear copper complexes of the

type Cu_4OX_64L, this band is well characterised, lying between 500 and

600 cm^{-1}. It is sensitive both to the nature of the bridging halide

atoms, as well as the axial ligand. This band for the structurally

similar complexes $Be_4O(CH_3COO)_6$ and $Be_4O(NO_3)_6$, occurs at 803 and

850 cm^{-1} respectively (138). The symmetrical Cu-O stretching

vibration is infrared inactive in T_d symmetry.

The assymmetric Cu-O stretching vibration in tetranuclear copper

complexes belongs to the symmetry species T_2, and it would be expected

to split when the symmetry of the complexes is lowered by the presence

of unsymmetrical ligands. This splitting has been reported in the

2-methylpyridine complexes (59, 68), where two bands have been

TABLE 6.1

FAR INFRARED SPECTRA OF SOME TETRANUCLEAR MIXED HALIDE COPPER(II)COMPLEXES

COMPLEX	BAND MAXIMA cm^{-1}
Cu_4OCl_5Br 4py	254, (S,br), 240(S,sh),200(S,br), 124(w)
$Cu_4OCl_4Br_2$4py	254, (S,br), 240(S,sh),192(S,sh), 142(w,br)
$Cu_4OCl_3Br_3$4py	250, (S,br), 236(m,sh),204(S,sh),156(m,sh),144(m)
$Cu_4OCl_2Br_4$4py	244, (S,br), 222(S,br),200(S,br)
$Cu_4OClBr_5$4py	244, (S,sh), 224(S,br),200(S,br),160(S,br)
$[(CH_3)_4N]_4^+ Cu_4OCl_8Br_2^{4-}$	286(s), 233, (S,Br), 183(m,sh),140(m,sh),110(m,br)
$[(CH_3)_4N]_4^+Cu_4OCl_7Br_3^{4-}$	310(m), 282, (S), 252(S,br), 196(m,sh),140(m,sh), 114(m,br)
$[(CH_3)_4N]_4^+ Cu_4OCl_5Br_5^{4-}$	284, (s), 230, (S,br), 190(m,br), 176,(m,w), 104(S,br)
$[(CH_3)_4N]_4^+ Cu_4OCl_4Br_6^{4-}$	300(m,br), 274(w), 225(S,br), 192(m,br)172(m,sh), 104(m)
$[(CH_3)_4N]_4^+ Cu_4OCl_3Br_7^{4-}$	290(w,br), 274(w,sh), 224(S,br), 182(S,br)100(s)

S = strong   br = broad

m = medium   sh = shoulder

w = weak

FIGURE 6. 1.   Far infrared spectra of tetranuclear copper (II) complexes.

FIGURE 6.2. Far infrared spectra of tetranuclear copper(II) complexes

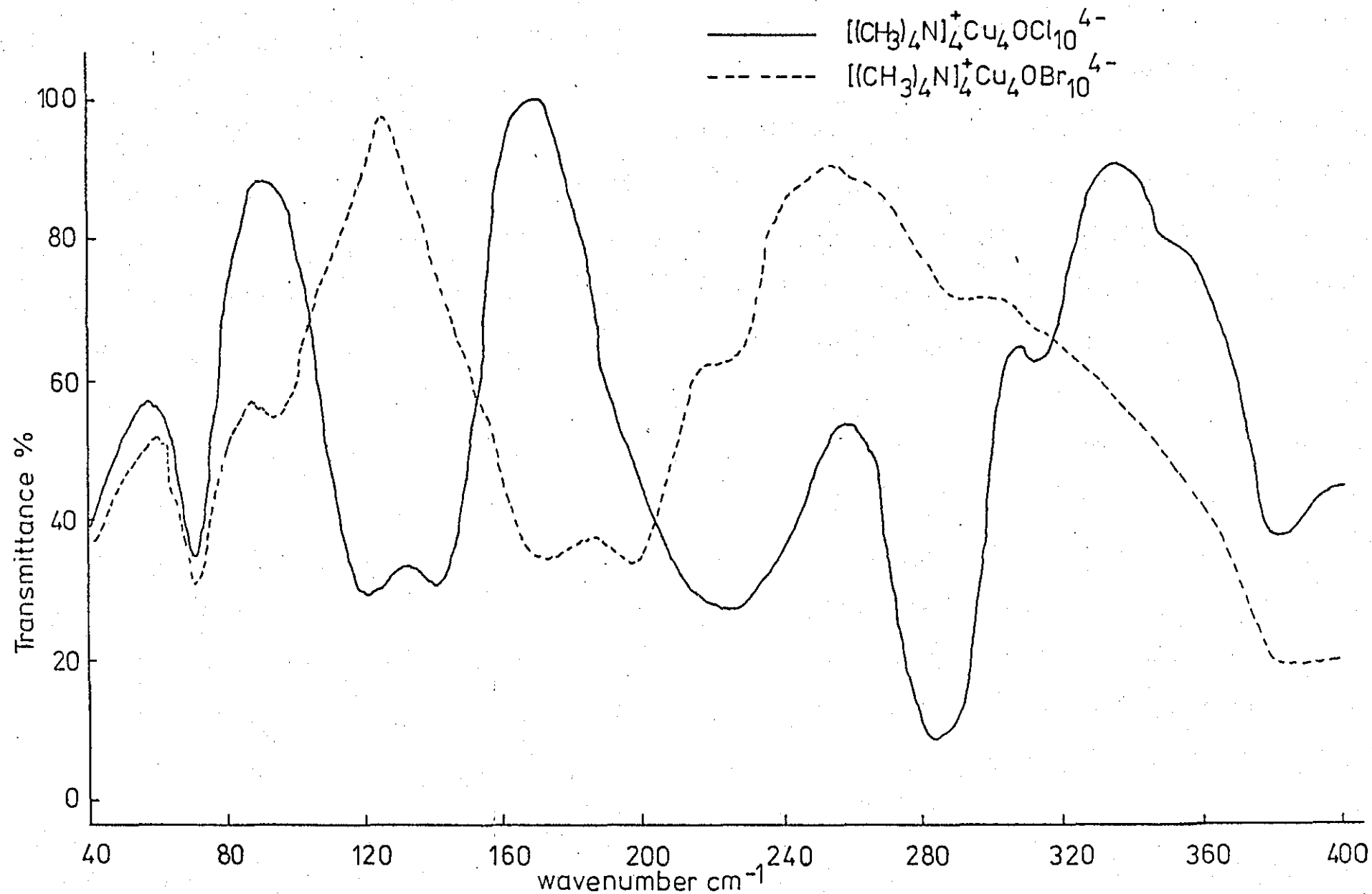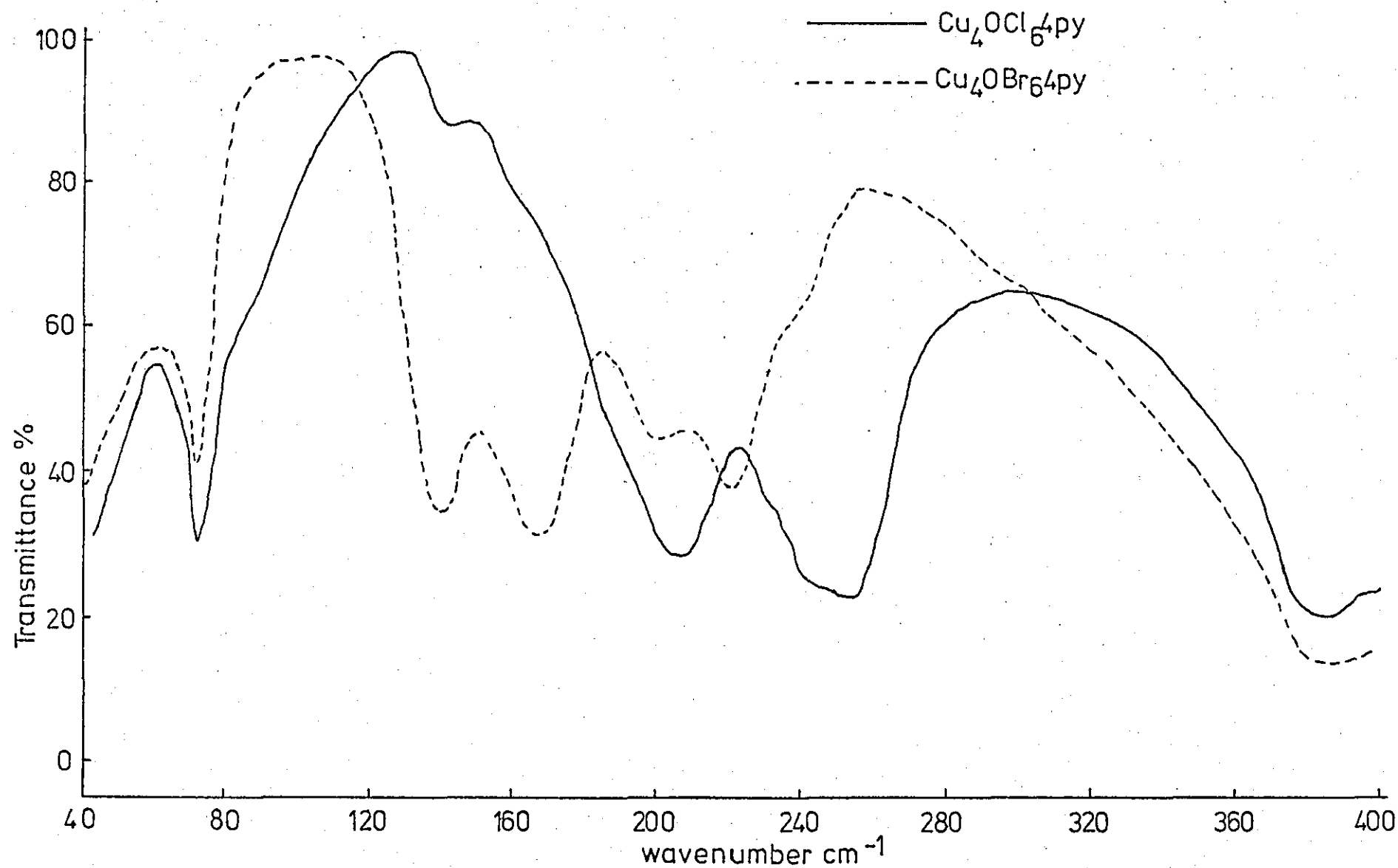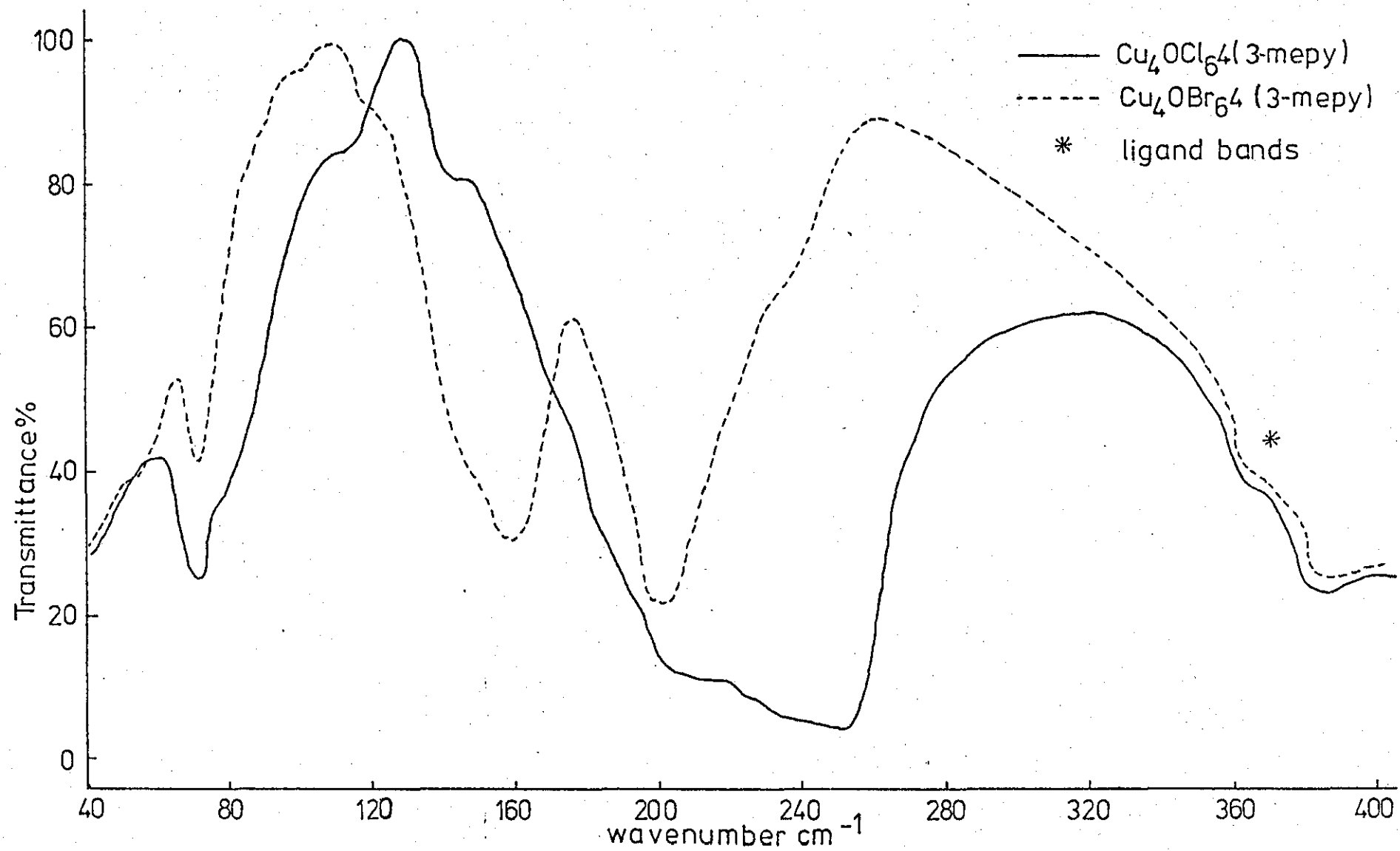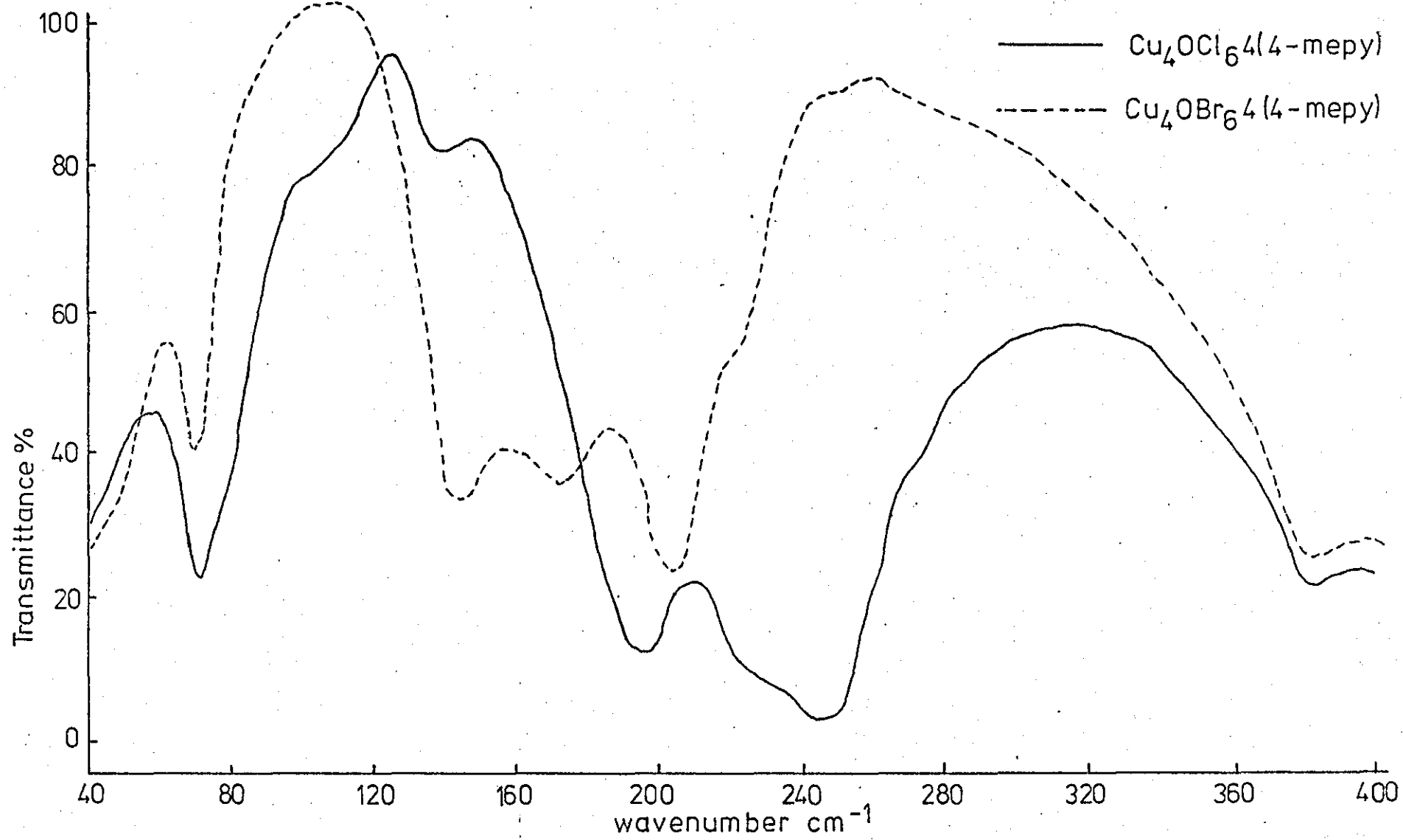FIGURE 6.3.   Far infrared spectra of tetranuclear copper(II) complexes

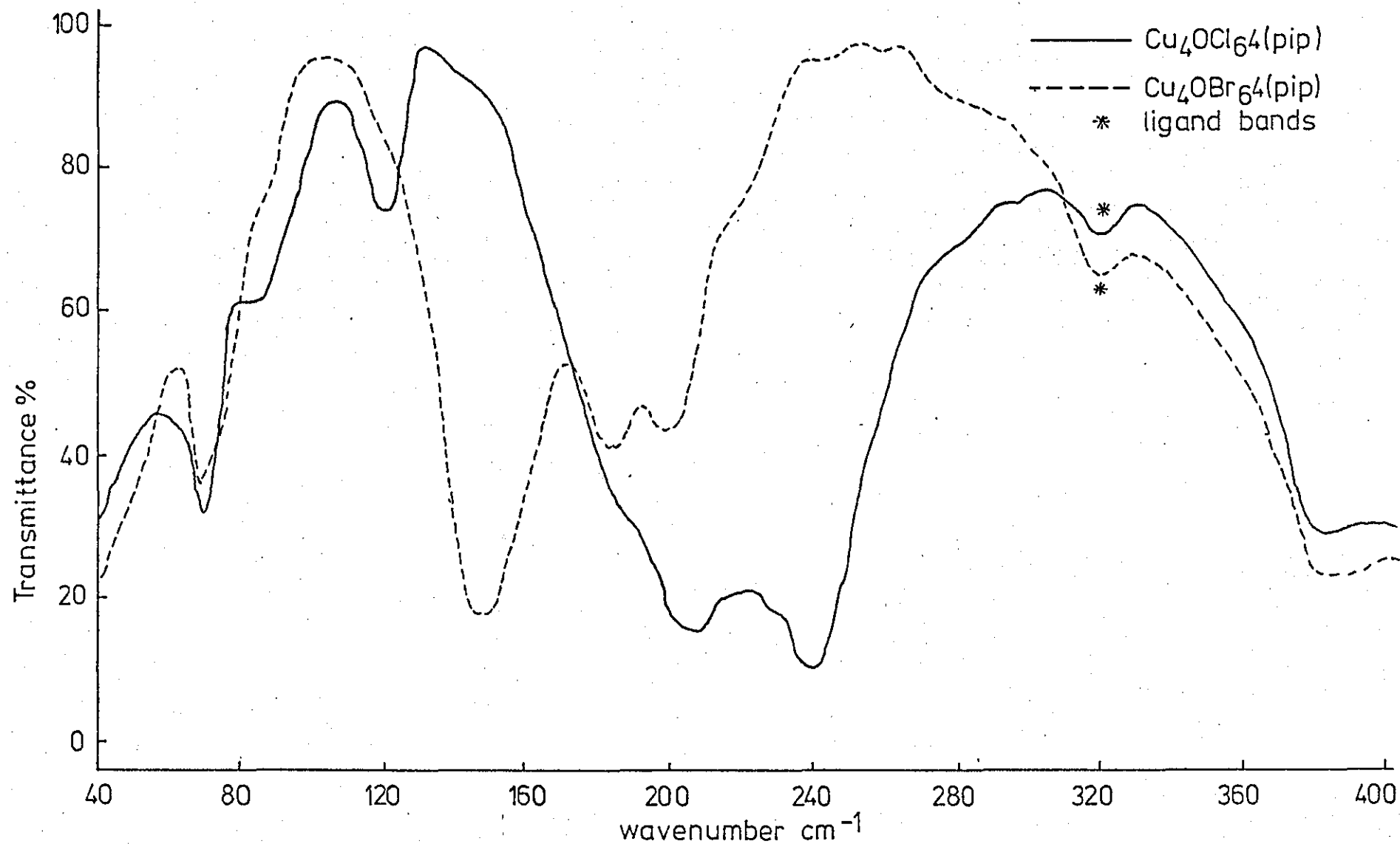FIGURE 6. 4. Far infrared spectra of tetranuclear copper (II) complexes.

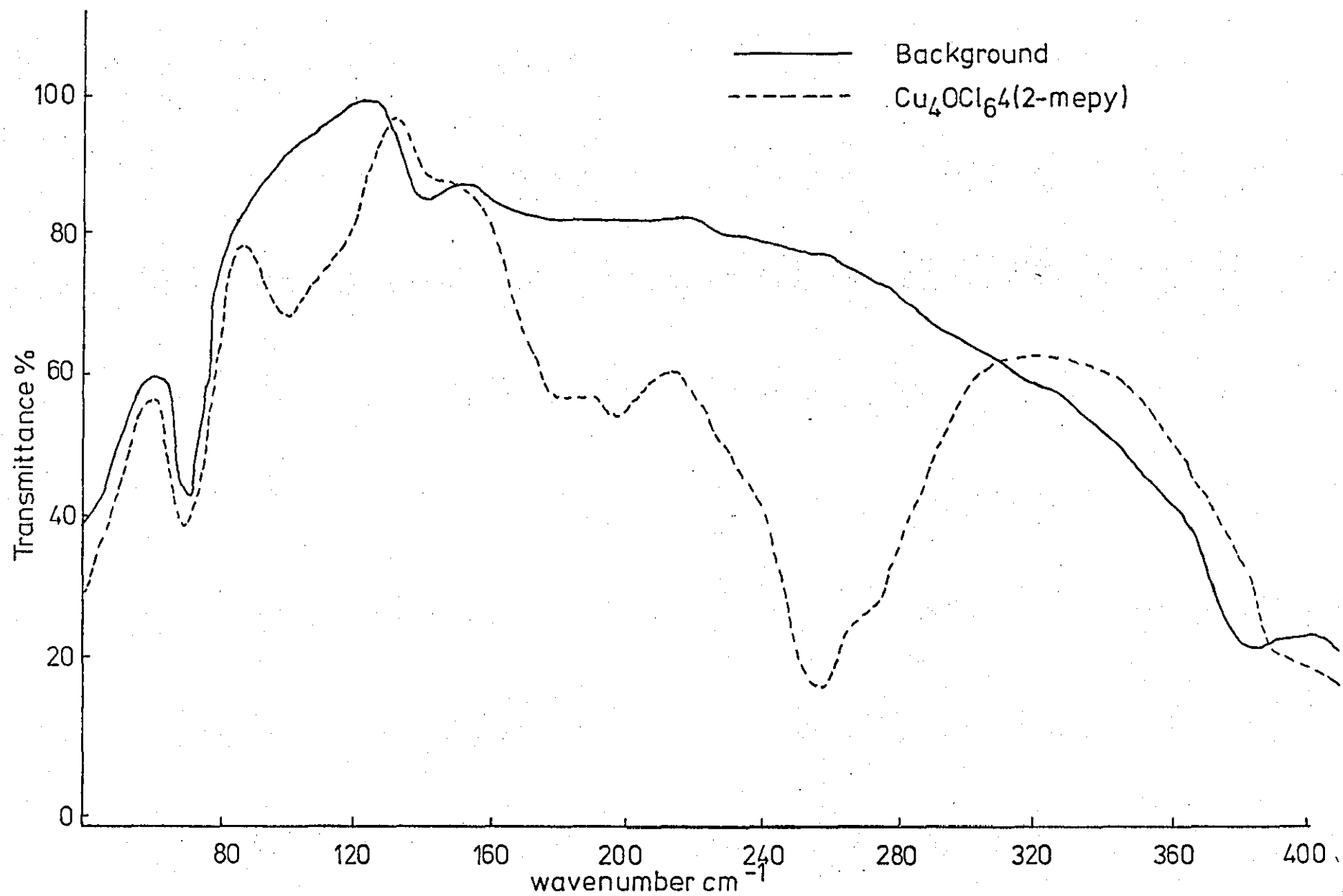FIGURE 6.5. Far infrared spectra of tetranuclear copper (II) complexes.

FIGURE 6.6.   Far infrared spectra of tetranuclear copper(II) complexes.

assigned to νCu-O asym. between 500 and 600 cm^{-1}. However, assignments in this region are difficult for 2-methylpyridine complexes, due to the 6a ligand vibration. This vibration is present at 559 cm^{-1} in $CuCl_2 2(2\text{-mepy})$ (50), and may be causing some confusion over band assignments in the tetranuclear copper compounds. Table 6.2 contains the frequencies of bands assigned to νCu-O asym. for the 2-methyl pyridine complex and several other tetranuclear compounds. Band splitting is not observed in other tetranuclear complexes containing unsymmetrical ligands such as 3-methylpyridine, although the Cu-O band appears considerably broadened and unsymmetrical in these complexes. νCu-O asym. in the complex $K_4^+ Cu_4 OCl_{10}^{4-}$ appears as a doublet and as three bands in $[(CH_3)_4 N]_4^+ Cu_4 OBr_{10}^{4-}$ (table 6.2). This apparent splitting of a T_2 vibration in a molecule with T_d symmetry may be due to site symmetry. The mixed halide complexes, described in Chapters Four and Five, might also be expected to exhibit multiple Cu-O bands due to their lower symmetry. However, the νCu-O asym. vibration, which appears between 500 and 600 cm^{-1} in these complexes, is present as a single symmetrical band, although somewhat broadened with respect to the hexachloride, decachloride, hexabromide and decabromide species. Typical Cu-O bandwidths for complexes such as $Cu_4 OX_6 4py$ X = Cl, Br, are in the region of 50 to 70 cm^{-1}, whilst for the mixed halide-pyridine complexes they are 75 – 125 cm^{-1}.

It may be expected that the presence of mixed halide atoms in the central sturctural unit of these complexes, results in smaller deviations from T_d symmetry than the replacement of a symmetrical for an unsymmetrical axial ligand. However, as no appreciable splitting of the other T_2 vibration present in the spectra seems to occur between compounds with apparently different symmetry (i.e. the total number of bands does not appear to increase from a $Cu_4 OX_{10}^{4-}$ species to a $Cu_4 OX_6 4(\text{amine})$ or $Cu_4 OCl_n Br_{6-n} 4py$ species), it can be argued that all these complexes may be considered to have T_d symmetry to a first approximation.

TABLE 6.2

νCu-O asym. for some tetranuclear complexes

COMPLEX	νCu-O Asym.(CM^{-1})
Cu_4OCl_64py (67, 68)	576
Cu_4OBr_64py (67, 68)	536
$Cu_4OCl_64(2\text{-mepy})$ (59, 68)	595, 571 (591, 564)
$K_4^+Cu_4OCl_{10}^{4-}$ (68)	562, 546
$[(CH_3)_4N]_4^+Cu_4OCl_{10}^{4-}$ (68)	540
$[(CH_3)_4N]_4^+Cu_4OBr_{10}^{4-}$	528(sh), 512(sh) 495
$Cu_4OCl_64(3\text{-mepy})$	574 (br)
$Cu_4OBr_64(3\text{-mepy})$	537 (br)

sh = shoulder

br = broad

One of the other copper-oxygen vibrations which is expected to be infrared active, is the Cu-O bending vibration (δCu-O). There is little information available concerning the expected frequency of this vibrational band, although Ferraro has suggested that it may lie below 200 cm^{-1} (135). However, on consideration of the position of νCu-O asym. in tetranuclear complexes (500 - 600 cm^{-1}), it might be expected that the bending vibration will be somewhat higher than 200 cm^{-1}, by analogy to the vibrations of copper-nitrogen bonds (νCu-N asym., Ca. 260 cm^{-1}: δCu-N, Ca.190 cm^{-1}; 6.3.3 below). The frequency of copper-oxygen stretching vibrations is usually unaffected by the nature of the halide atom in the complex (28, 29, 136), and the bending vibration might be expected to behave in a similar manner. Under these circumstances it would be possible to assign δCu-O vibrations by observing bands which did not alter in frequency between chloride and bromide complexes. Unfortunately, in the tetranuclear complexes under discussion, νCu-O asym. appears to shift about 40 cm^{-1} between chloride and bromide complexes containing identical axial ligands (table 6.2 and chapter three). This may be due to coupling between Cu-O and bridging Cu-X vibrations, and means that the Cu-O bending vibration may well be similarly affected. No attempt will be made to assign individual bands to the δCu-O vibration, because of the uncertainty of the group frequency of this band and the possible movement between chloride and bromide complexes. However, it may well lie between 200 and 250 cm^{-1} in tetranuclear complexes, as absorptions in this region are very broad (figures 6.1 - 6.6) and may contain several unresolved bands.

6.3.2 Copper-halogen vibrations

The assignments of copper-halogen stretching vibrations have been well established. The frequencies of vibration of the Cu-X bonds will

decrease as the mass of the halogen increases and hence, by observing

the disappearance of the copper-chlorine band and the appearance of a

new band on going from a chloride to a bromide complex, accurate

assignments can usually be made for these vibrations. The ratio $\frac{\nu Cu-Br}{\nu Cu-Cl}$

is often used to assist in making these assignments. This ratio has

not been calculated for copper complexes in particular, but in general

it has been reported as Ca.0.77 in tetrahedral anions of the type

MX_4^{2-} and Ca.0.74 for octahedral stereochemistry, in divalent first

row transition metals (90). Table 6.3 lists the copper (II) halogen

complexes for which unambiguous assignments have been made for the

$\nu Cu-X$ vibrations. $\frac{\nu Cu-Br}{\nu Cu-Cl}$ is shown for both terminal ($\nu tCu-X$) and

bridging ($\nu bCu-X$) copper-halide stretching vibrations. It was hoped

that these two ratios would be significantly different to be made

use of in the present investigation; the average value of $\frac{\nu tCu-Br}{\nu tCu-Cl}$

is 0.78 and the corresponding ratio for $\nu bCu-X$, 0.80. However, the

large variation in values for these ratios makes any differentiation

between terminal and bridging halides on this basis impossible.

There appears to be little correlation between the stereochemistry of

the copper complex and the $\frac{\nu Cu-Br}{\nu Cu-Cl}$ ratio, but an average value for this

ratio of 0.79 can be obtained, which serves as a guide for the assignment

of copper-halogen bands. It is unfortunate that data are not available

for complexes with similar stereochemistry to that of the tetranuclear

compounds (trigonal bipyramidal), as $\frac{\nu Cu-Br}{\nu Cu-Cl}$ could alter under these

conditions.

In general, a bridging halide vibration will be located at

lower frequencies than those found for terminal M-X vibrations as the

sharing of halogens between two metal atoms causes the bond to be

weaker than for the terminal M-X bond. Hence, assuming the expected

number of M-X bands are seen in a series of complexes of identical

TABLE 6.3

νCu-X BANDS FOR SEVERAL COPPER HALIDE COMPLEXES

COMPLEX	νCu-Cl (cm^{-1})	νCu-Br (cm^{-1})	TERMINAL(t) OR BRIDGING(b)	$\dfrac{\nu\text{Cu-Br}}{\nu\text{Cu-Cl}}$
CuX$_2$ (139)	328	250	b	0.76
	275	219	b	0.80
CsCuX$_3$ (139)	293	256	t	0.87
	287	251	t	0.88
	263	234	b	0.89
KCuX$_3$ (139)	301	237	t	0.79
	278	224	b	0.81
	236	168	b	0.71
[Ph$_3$MeAs]$_2$CuX$_4$ (90)	283	222	t	0.78
[MeNH$_3$]$_2$CuX$_4$ (139)	284	227	t	0.80
[EtNH$_3$]$_2$CuX$_4$ (139)	279	219	t	0.79
CuX$_2$2NH$_3$(α) (140)	267	218	b	0.82
CuX$_2$2py (76)	294	260	b	0.88
	237	204	b	0.86
CuX$_2$2(2-pic.) (91)	308	233	t	0.76
CuX$_2$2(3-pic.) (141)	291	238	b	0.82
CuX$_2$2(4-pic.) (141)	297	234	b	0.79
CuX$_2$2(2,6-lut.) (50)	314	230	t	0.73
CuX$_2$2(2,4,6-Coll.) (91)	296	228	t	0.77
CuX$_2$2(2-Etpy) (50)	320	251	t	0.78
CuX$_2$2(2-Brpy) (142)	333	244	t	0.73
CuX$_2$2(quin) (50)	330	266	t	0.81
CuX$_2$(quinox) (83)	324	255	b	0.79
CuX$_2$(2-mequinox) (83)	320	252	b	0.79
CuX$_2$(2,3-dimequinox) (83)	368	278	t	0.76
CuX$_2$(2,3-diphenquinox) (83)	337	269	t	0.80
CuX$_2$(pyN-oxide) (83)	315	237	t	0.75
CuX$_2$(thios) (143)	312	251	b	0.80
	234	184	b	0.79
[(CH$_3$)$_2$NH$_2$]CuX$_2$ (143)	312	224	t	0.72

coll.	=	collidine	quinox.	=	quinoxaline
lut.	=	lutidine	quin.	=	quinoline
pic.	=	picoline	thios.	=	thiosemicarbazide

stereochemistry, the bridging and terminal metal-halogen stretching vibrations can usually be identified. Adams and Lock (139) have reported the overall range for νCu-Cl as 368 cm^{-1} to 222 cm^{-1} and νCu-Br 278 to 168 cm^{-1}, but stated that the terminal and bridging vibrational frequencies are so overlapped, as to be of little diagnostic value.

Identification of Cu-X vibrations in the spectra of tetranuclear copper (II) complexes is difficult due to the diffuse nature of the observed bands. Although several bands are clearly distinguished in the spectra of the decachloride and decabromide complexes (figure 6.1), the pyridine and substituted pyridine compounds (figures 6.2 to 6.6) show two or three very broad bands. The decahalide complexes (figure 6.1, table 6.1) may be expected to contain vibrational bands due to terminal as well as bridging halides. The bands at 312 and 286 cm^{-1} in the spectrum of the decachloride compound, do not appear in the spectra of the pyridine complexes (figures 6.2 - 6.6), and are probably of too high a frequency to be associated with bridging Cu-Cl vibrations. Consequently they must be connected with terminal Cu-Cl stretching vibrations, and can be associated with bands at 224 and 199 cm^{-1} in the spectrum of the decabromide complex. This results in low $\frac{\nu\text{Cu-Br}}{\nu\text{Cu-Cl}}$ ratios (0.72 and 0.70), but is in agreement with relative band intensities. νCu-X for many copper complexes are also found at similar frequencies (139). As only one ν_tCu-X band is expected (6.1 above), the shoulders in the chloride and bromide complexes, at 312 and 224 cm^{-1}, may represent partial splitting of the main T_2 band at 286 and 199 cm^{-1} respectively or activation of an infrared inactive mode (A_1), due to site symmetry or coupling effects. The bands at 224 and 173 cm^{-1} in the spectra of the chloride and bromide complexes, can be assigned to the bridging νCu-X vibration, in agreement with the lower frequency expected for this type of vibration. Two other bands are present in these spectra,

at 142 and 120 cm^{-1} in the chloride and at 96 and 82 cm^{-1} in the bromide

complex.   These bands could be asigned to lattice vibrations, however,

changing the nature of the halogen is not expected to give shifts in

lattice modes of the order of 40 cm^{-1}, and so both bands can be

tentatively assigned to bending or deformation modes associated with

the terminal or bridging halides.   Bands at similar frequencies have

been observed in the spectra of copper (II) halide-pyridine complexes and

similarly assigned (50).   The data in the paper of Goldstein et al. (50)

suggest that these δCu-X modes have low $\frac{\delta\text{Cu-Br}}{\delta\text{Cu-Cl}}$ ratios, in the order of

0.66, which is also observed in the case of these two bands.   Table 6.4

summarises the assignments for the decachloride and decabromide complexes.

The weak band at 350 cm^{-1} in the chloride, and 290 cm^{-1} in the bromide

appear to be due to some vibration involving the halogen, but no reasonable

assignment for this can be made: it may be due to the activation of an

inactive species by lattice or coupling effects.

The spectra of the tetramethyl ammonium mixed halide complexes

(table 6.1), confirms the above assignments, especially those of the

terminal Cu-X.vibrations $[(CH_3)_4N]_4^+Cu_4OCl_7Br_3^{4-}$, which contains four

terminal chlorines, has bands at 310 and 282 cm^{-1}, due to vtCu-Cl and

$[(CH_3)_4N]_4^+Cu_4OCl_3Br_7^{4-}$ with four terminal bromines, has bands at 224 and

182 cm^{-1}, assigned to vt Cu-Br. Complexes containing mixed halides

in the axial position show vibrational bands attributable to both

vtCu-Cl and vtCu-Br.   The broad nature of the other bands present in

these mixed halides complexes makes other assignments difficult.   In

all these spectra, between 40 and 400 cm^{-1}, absorptions due to the

tetramethylammonium cation are absent, the lowest vibrational band due

to this species is at 456 cm^{-1} (68).

The tetranuclear complexes containing pyridine and substituted

pyridine (figures 6.2 to 6.6), may be expected to have vibrational

TABLE 6.4

VIBRATIONAL BAND ASSIGNMENTS FOR TETRANUCLEAR TETRAMETHYLAMMONIUM COMPLEXES

$Cu_4OCl_{10}^{4-}$ cm^{-1}	$Cu_4OBr_{10}^{4-}$ cm^{-1}	$\dfrac{Cu-Br}{Cu-Cl}$	Assignment	
350	290	0.83	?	
312	224	0.72	$(\nu_1 tCu-X)$	
286	199	0.70	$\nu_1 tCu-X$	
224	173	0.77	$\nu_1 bCu-X$	
142	96	0.68	$\delta Cu-X$	?
120	82	0.68	$\delta Cu-X$	?

bands due to stretching and bending and/or deformation modes of the copper-halogen bridges. The spectra of these complexes are very much alike: the chloride complexes showing a broad absorption between ca. 160 and 280 cm^{-1} which contains at least four bands, and perhaps five; the bromide complexes showing a similar broad absorption between 140 and 240 cm^{-1}, but with better resolution of the individual bands. On the basis of the assignment of $\nu bCu-X$ to ca. 224 cm^{-1} and 173 cm^{-1} for the decahalide complexes, this mode has been assigned to bands at 224 - 252 cm^{-1} and 160 - 182 cm^{-1} for the chloride and bromide-amine complexes, although due to the broad nature of the bands, these assignments are very tentative. These complexes also have low frequency vibrations, one of which, at ca. 180 cm^{-1} for the chloride and 145 cm^{-1} for bromide complexes, can be assigned to a copper-halogen bending or deformation mode. These assignments are summarised in table 6.5.

The possibility of the copper-oxygen vibrations being affected by coupling with copper-halogen modes was discussed in 6.3.1 above. If coupling effects are greater in tetranuclear copper (II) complexes than in other copper (II) species, this may well explain the poor $\frac{Cu-Br}{Cu-Cl}$ ratios which are found for several of the bands assigned in this section to copper-halogen vibrations.

6.3.3 Copper-nitrogen vibrations

A considerable amount of data have been published concerning the metal-nitrogen stretching vibration $\nu(M-N)$ in complexes containing pyridine and related ligands. For copper-(II) complexes, this vibration is located between 230 and 280 cm^{-1} (135) and is generally of weak to medium intensity. Little work has been reported on the assignment of the bending or deformation vibration of the copper-nitrogen bond in these complexes, due in part to the low frequency of this type of

TABLE 6.5

ASSIGNMENT OF THE VIBRATIONAL BANDS OF TETRANUCLEAR COPPER(II) COMPLEXES
CONTAINING PYRIDINE TYPE LIGANDS

Cu_4OX_64py			$Cu_4OCl_64(2\text{-mepy})$	$Cu_4OX_64(3\text{-mepy})$			$Cu_4OX_64(4\text{mepy})$			$Cu_4OX_64(Pip)$			Assignment
X=Cl	X=Br	$\frac{Cu\text{-}Br}{Cu\text{-}Cl}$		X=Cl	X=Br	$\frac{Cu\text{-}Br}{Cu\text{-}Cl}$	X=Cl	X=Br	$\frac{Cu\text{-}Br}{Cu\text{-}Cl}$	X=Cl	X=Br	$\frac{Cu\text{-}Br}{Cu\text{-}Cl}$	
256	242	-	268	252	240	-	246	228	-	240	224	-	νCu-N
242	169	0.70	252	224	160	0.71	232	176	0.76	232	182	0.79	vbCu-X
204	200	-	194	206	200	-	196	204	-	206	200	-	δCu-N
	222	-											
188 ?	140	0.75	174	184?	146	0.79	?	146	-	188	150	0.80	δCu-X ?
			118	116		-	118 ?		-	122	88	0.72	δCu-X ?
100		-	100	84		-	80		-	84		-	

Pip. = piperidine

vibration, which complicates the assignment as lattice and copper-halogen vibrations also appear in this region (<200 cm^{-1}). However, from the available data, the copper-nitrogen bending vibration appears to lie between 180 and 200 cm^{-1} for pyridine type ligands (50, 144, 145). Metal-nitrogen vibrations in general, are characterised by the fact that they are not affected to any great extent by the nature of the halide atom in the complex, and so can be identified by their constant position in chloride and bromide complexes with identical ligands and stereochemistry. Table 6.6 lists copper-nitrogen stretching and bending modes that have been assigned for copper complexes containing pyridine and methylpyridine ligands.

The assignment of νCu-N for tetranuclear copper (II) complexes is difficult due to the broad nature of the bands in the spectra of these complexes. This band is expected to lie in the region of 250 - 270 cm^{-1} from the data in table 6.6 In the majority of the bromide complexes (figures 6.2 to 6.6), the only band present above 200 cm^{-1} is a weak to medium shoulder on the strong 200 cm^{-1} band. This shoulder lies between 242 and 224 cm^{-1} in these complexes and probably corresponds to the highest frequency band (between 240 and 268 cm^{-1}) in the spectra of the chloride complexes. This assignment is made on the assumption that the Cu-N bond strengths are of a similar order in tetranuclear and $CuX_2 2L$ complexes, and hence νCu-N vibrations will appear at similar frequencies. Certainly the Cu-N bond length in these two types of complex is approximately the same (1.99 - 2.01Å), and the pyridine ring vibrations at 405 and 605 cm^{-1} in the free amine appear at very similar frequencies in both $Cu_4 OX_6 4py$ and $CuX_2 2py$ (the magnitude of the frequency shift of these ligand bands on co-ordination, can be used as an indication of relative Cu-N bond strengths (90)). However, the overall range of frequencies for this vibration is far greater than in the

TABLE 6.6

νCu-N AND δCu-N VIBRATIONS FOR CuX$_2$2L COMPLEXES

COMPLEX		νCu-N	δCu-N
CuCl$_2$2py	(50)	266	200
CuBr$_2$2py	(50)	268	196
CuCl$_2$2(2-pic)	(50)	259	191
CuBr$_2$2(2-pic)	(50)	259, 268	194
CuCl$_2$2(3-pic)	(141)	265	—
CuBr$_2$2(3-pic)	(141)	269	—
CuCl$_2$2(4-pic)	(50)	260	—
CuBr$_2$2(4-pic)	(50)	256	—

corresponding $CuX_2 2L$ species (table 6.6) Here again the coupling of

vibrations in these tetranuclear complexes may be responsible for such

effects, an analogous situation exists with the unusually large

frequency range for νCu-Oasym. discussed above. The strong band

that appears at ca. 200 cm^{-1} in these tetranuclear complexes, is

tentatively assigned to a δCu-N mode, in agreement with the frequency

of this band in $CuX_2 2L$ compounds (table 6.6), and its constant position

in chloride and bromide complexes, although this latter factor may not

be so relevant in tetranuclear complexes. These assignments are

summarised in table 6.5 with the copper-halogen vibrations. The spectra

of the tetranuclear mixed halide complexes with pyridine offer no

assistance to the identification of these vibrational modes, due to the

very broad absorptions present, which extend over the relevant frequency

range.

6.4   Conclusions

Assignments have been made for νCu-Cl, νCu-N δCu-Cl and δCu-N

vibrations, but because of the presence of broad bands in the spectra

of some of the complexes, these assignments are of a tentative nature

only. There appears to be little splitting of the T_2 vibrations in

these complexes, even where species with apparently different symmetry

are concerned. The usual method of assignment of metal-oxygen and

metal-nitrogen bands may not be relevant to this system, where coupling

effects may result in large frequency ranges for these vibrations.

CHAPTER SEVEN

THE REACTION BETWEEN TETRANUCLEAR COPPER (II) COMPLEXES AND WATER

7.1 Introduction

A study of the reaction between tetranuclear copper (II) complexes and water was considered important, not only to provide additional data concerning the properties of these complexes, but as information which ·might be relevant to the study of the oxidative copper catalyst and its reactions. The majority of the tetranuclear cluster complexes appear to be unreactive in the presence of water; complexes such as Cu_4OCl_64py are stable to large amounts of water vapour, and only appear to undergo some reaction in solution. The only complexes to be affected by small amounts of water are the tetranuclear methanol compounds, Cu_4OX_64MeOH , $X=Cl$, Br (described in chapter three) and $Cu_4OCl_3Br_34MeOH$ (described in chapter four). Consequently, a study was made on the reactions of these three complexes with water, in order to ascertain the nature of the hydrolysis product and determine the way the Cu_4O structure breaks down under these conditions.

7.2 Experimental and Results

During the preparation of $Cu_4 OCl_64MeOH$ (chapter three), it was observed that if the product was exposed to traces of moisture it underwent a rapid colour change from golden-yellow to bright green, with a correspondingly drastic change in the infrared spectrum. A similar (but much faster) reaction was observed for the other two tetranuclear methanol complexes, $Cu_4OCl_3Br_34MeOH$ and Cu_4OBr_64MeOH, but with a less noticable associated colour change (brown to dark brown, and dark red to black respectively). In the examination of the effect of water on these complexes, it was decided to concentrate more on the reaction of the hexachloride compound than on the other two complexes for two reasons. Firstly, the large colour change of the hexachloride species could be used to determine the point at which the cluster structure broke down; and secondly, there are many basic copper (II) chloride

TABLE 7.1

ANALYTICAL DATA FOR HYDROLYSIS PRODUCTS OF TETRANUCLEAR METHANOL COMPLEXES

COMPLEX	% COPPER		% CHLORIDE		% BROMIDE		%HYDROXIDE		% WATER (BY DIFFERENCE)	
	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.
$Cu_4(OH)_2Cl_6 4H_2O$ (green)	44.62	44.36	37.40	37.12	–	–	5.69	5.94	12.33	12.58
$Cu_4(OH)_2Cl_6$ (Yellow)	50.55	50.74	42.33	42.47	–	–	–	6.79	–	–
$Cu_4(OH)_2Cl_3Br_3 2H_2O$ (dark brown)	38.10	37.92	15.71	15.87	36.20	35.77	5.07	5.08	4.92	5.38
$Cu_4(OH)_2Cl_3Br_3$ (dark brown)	39.91	40.07	16.43	16.77	37.25	37.80	–	5.36	–	–
$Cu_4(OH)_2Br_6$ (black)	33.30	33.11	–	–	61.99	62.46	4.32	4.43	–	–

compounds available (such as $Cu(OH)Cl$ and $Cu_2(OH)_3Cl$) which could be used to characterise the product of the hydrolysis reaction, whereas only a few basic copper (II) bromide compounds exist, and fewer still have been characterised by x-ray and infrared data.

The products from the reaction of all these tetranuclear complexes with water were obtained as follows.

The tetranuclear methanol complex (ca. 5g) was placed on a watchglass in the open laboratory for one hour. The product was then placed in an oven at 105°C for 5 hours, and then transferred to a dry-box for analysis. In this way the anhydrous products were obtained. The hexachloride and mixed halide complexes were found to exist in a hydrated, as well as anhydrous form. These products were allowed to absorb water by standing overnight in the laboratory. Analytical and infrared data are contained in tables 7.1 and 7.2 respectively. This latter table also contains the spectra of copper (II) chloride and copper hydroxychloride, which are used for comparative purposes below. Both the hexachloride and mixed halide complexes were found to absorb different amounts of water depending on the partial pressure of water surrounding them, to the extent that they would eventually pass into solution. The tetra- and bishydrates in table 7.1, refer to complexes formed on exposure to the laboratory atmosphere. The complex $Cu_4(OH)_2Cl_64H_2O$ lost two molecules of water on evacuation to 2 torr for 2 hours and could be completely dehydrated by heating at 105°C for 5 hours. Rehydration of the anhydrous compound occured under normal laboratory conditions with about 15% weight increase (equivalent to the gain of four molecules of water per $Cu_4(OH)_2Cl_6$). Dehydration and rehydration experiments could be carried out many times with the formation of the same two products. Exposure of the tetranuclear complex Cu_4OCl_64MeOH to moisture without dehydration of

TABLE 7.2

INFRARED DATA, $4000 - 40$ cm^{-1}, FOR HYDROLYSIS PRODUCTS AND REFERENCE COMPOUNDS

Cu$_4$(OH)$_2$Cl$_6$		Cu$_4$(OH)$_2$Cl$_3$Br$_3$		Cu$_4$(OH)$_2$Br$_6$	CuCl$_2$(139)		Cu(OH)Cl
4H$_2$O	ANHYDROUS	2H$_2$O*	ANHYDROUS		2H$_2$O	ANHYDROUS	
3400 (S,br)	3420 (S)	3400 (S,W)	3420 (m)	3398 (m)	3400 (S, br)		3620 (m)
1588 (S)	3395 (S)	1585 (S)	3380 (S, Br)	3365 (m)	1580 (S)		3400 (S)
965 (m)		960 (m)	940 (m)	935 (m)			905 (m)
935 (m)	938 (m)	935 (m)	890 (m)	892 (m)			852 (S)
892 (m)	892 (m)	880 (w)	835 (m)	832 (m)			808 (S)
838 (m)	838 (m) 795 (S)	840 (m)	790 (S)	780 (S)			440 (S)
515 (w)	518 (m)	788 (w)	515 (m)	505 (m)			405 (m)
450 (m)	452 (S)	510 (m)	450 (S)	450 (m, sh)			350 (S)
310 (m, sh)	430 (S)	450 (m)	428 (S)	435 (m)	299 (S)		244 (m)
302 (S)	328 (S)	298 (S)	320 (m)	415 (m, sh)		328 (S)	206 (w)
265 (w)	292 (S, sh)	280 (S, sh)	298 (m)				170 (S)
248 (w)	285 (S)		280 (m, sh)			275 (m)	150 (m)
228 (w)					236 (M)		133 (m)
186 (m)							82 (w)
164 (w)							
116 (w)							
110 (m)							

s = strong, m = medium, w = weak, br, = broad, sh = shoulder,   *data only available 4000-250 cm due to hygroscopic samples

the resultant product, led to a species containing traces of methanol (identified by the presence of the CH_3 symmetrical deformation band at 1480 cm^{-1} in the infrared spectrum).

Table 7.3 lists X-ray powder diffraction lines for the two hydrated complexes and $Cu_4(OH)_2Br_6$, whilst table 7.4 contains similar data for some copper halide reference compounds. Table 7.5 lists the near infrared spectra of the tetranuclear methanol complexes. The reflectance spectra of the hexachloride complexes are shown in fig.7.1.

The reaction of the tetranuclear complex $Cu_4OCl_6 4MeOH$ with water was studied in more detail using the apparatus shown in figure 7.2. A sample of the complex (about 20 mg) was placed in a platinum pan which was suspended by means of a glass whisker to the arm of a Cahn electrobalance, connected to an A.E.I. chart recorder. Dry nitrogen was used to avoid exposure of the sample to any moisture prior to the start of the experiment. The sample pan was enclosed in a container through which wet or dry nitrogen could be passed. Wet nitrogen was obtained by passing the gas through a vessel containing a saturated sodium chloride solution, maintained at 25° by means of a thermostated water bath. This gave a partial pressure of water of 18 mm.Hg. The sample itself was held at 25°C by means of a water bath. Changes in sample weight were observed on the chart recorder.

A stream of dry nitrogen was first directed over the sample, until no further weight change was observed. Then wet nitrogen was passed over the sample until, after a period of about one day, it dissolved. The changes in weight on reaction are shown as a graph of molecular weights versus time in figure 7.3. At point (C) on the graph, the sample began to change colour, and was completely green between (C) and (D). At this point during a subsequent experiment, an

TABLE 7.3

X-RAY POWDER DIFFRACTION LINES FOR HYDROLYSIS PRODUCTS

$Cu_4(OH)_2Cl_64H_2O$		$Cu_4(OH)_2Cl_3Br_32H_2O$		$Cu_4(OH)_2Br_6$	
$d\overset{\circ}{A}$	I	$d\overset{\circ}{A}$	I	$d\overset{\circ}{A}$	I
7.04	40	7.13	40	8.32	20
6.78	60	6.84	50	6.13	100*
5.64	80	6.14	80*	5.54	20
5.49	100	5.72	70	4.06	10
4.05	60	5.51	20	3.60	50*
3.51	25	3.88	20	3.41	10
3.35	10	3.59	30*	3.28	20
3.10	25	3.55	20	3.13	40*
2.90	25	3.35	10	3.08	100*
2.82	20	3.07	100*	3.02	40*
2.73	20	3.02	20*	2.78	20
2.71	20	2.96	20	2.71	20
2.64	50	2.85	20	2.50	80*
2.61	20	2.75	60		
2.58	20	2.63	50		
2.55	10	2.57	20		
2.40	15	2.49	70*		
2.22	10	2.46	20		
2.13	5				
2.02	5				

* lines attributable to $CuBr_2$ (table 7.4)

TABLE 7.4

X-RAY POWDER DIFFRACTION DATA FOR REFERENCE COMPOUNDS

Cu(OH)Cl		$CuCl_2 2H_2O$		$Cu_2(OH)_3Cl$ (Botallackite)		$Cu(OH)_2$		$Cu_2(OH)_3Cl$ (Atacamite)		$Cu_2(OH)_3Cl$ (Paratacamite)		$CuBr_2$	
d Å	I	d Å	I	d Å	I	d Å	I	d Å	I	d Å	I	d Å	I
6.13	1	5.44	100	5.66	100	5.30	90	5.40	100	5.45	100	6.11	100
5.54	100	4.02	14	4.14	5	3.73	100	5.00	100	4.70	60	3.59	35
2.77	3	3.07	4	3.26	5	2.63	70	2.82	100	4.55	20	3.13	16
2.77	3	2.64	10	2.84	40	2.50	16	2.75	100	3.41	50	3.07	100
2.76	6	2.54	6	2.68	30	2.35	16	2.62	20	3.01	10	3.02	35
2.52	2	2.37	4	2.57	70	2.26	35	2.52	40	2.90	60	2.49	85
2.24	2	2.21	4	2.46	10	1.72	35	2.26	100	2.77	80	2.42	2
				2.40	80			2.19	40	2.34	50		
				2.06	20			2.13	60	2.27	80		
				1.98	20					2.25	60		
				1.93	30					2.22	20		
										2.05	20		
										2.03	40		

N.B. Data collected from reference (78), except Cu(OH)Cl

TABLE 7.5

INFRARED SPECTRA 4000 – 250 cm^{-1} FOR TETRANUCLEAR METHANOL COMPLEXES

$Cu_4OCl_6 4MeOH$	$Cu_4OCl_3Br_3 4MeOH$	$Cu_4OBr_6 4MeOH$
3350 (s)	3350 (s)	3355 (s)
1142 (m)	1138 (m)	1130 (w)
1118 (m)	1110 (m)	1105 (w)
1090 (w, sh)	1080 (w, sh)	1080 (w, sh)
1018 (s)	1015 (s)	1010 (m)
1001 (s)	998 (s)	995 (m)
980 (s)	978 (s)	975 (m)
840 (w)		
598 (s)	570 (s)	558 (s)
570 (m, sh)		
455 (w, sh)	450 (s, wh)	440 (w, sh)
418 (w)	410 (w, br)	395 (w)
325 (w)	320 (w)	

s = strong   w = weak

m = medium   sh = shoulder

br = broad

TABLE 7.6

DATA RELATING TO THE HYDROLYSIS PRODUCTS IN ETHANOL SOLUTION

COMPLEX	COLOUR OF ETHANOL SOLUTION	λ_{MAX}, NM	PRODUCT OF REACTION WITH PYRIDINE
$Cu_4(OH)_2Cl_6 4H_2O$	Yellow	274	$Cu_4OCl_6 4py$, $Cu-0,576\ cm^{-1}$ (% Cl: Found 31.61, Calc. 31.80)
$Cu_4(OH)_2Cl_3Br_3 2H_2O$	Brown	280	$Cu_4OCl_3Br_3 4py$, $Cu-0,553\ cm^{-1}$ (%Cl: Found 11.59 Calc. 11.40) (%Br: Found 25.96 (calc. 25.71)
$Cu_4(OH)_2Br_6$	Brown	310	$Cu_4OBr_6 4py$, $Cu-0,536\ cm^{-1}$ (%Br: Found 44.80, Calc. 44·97)
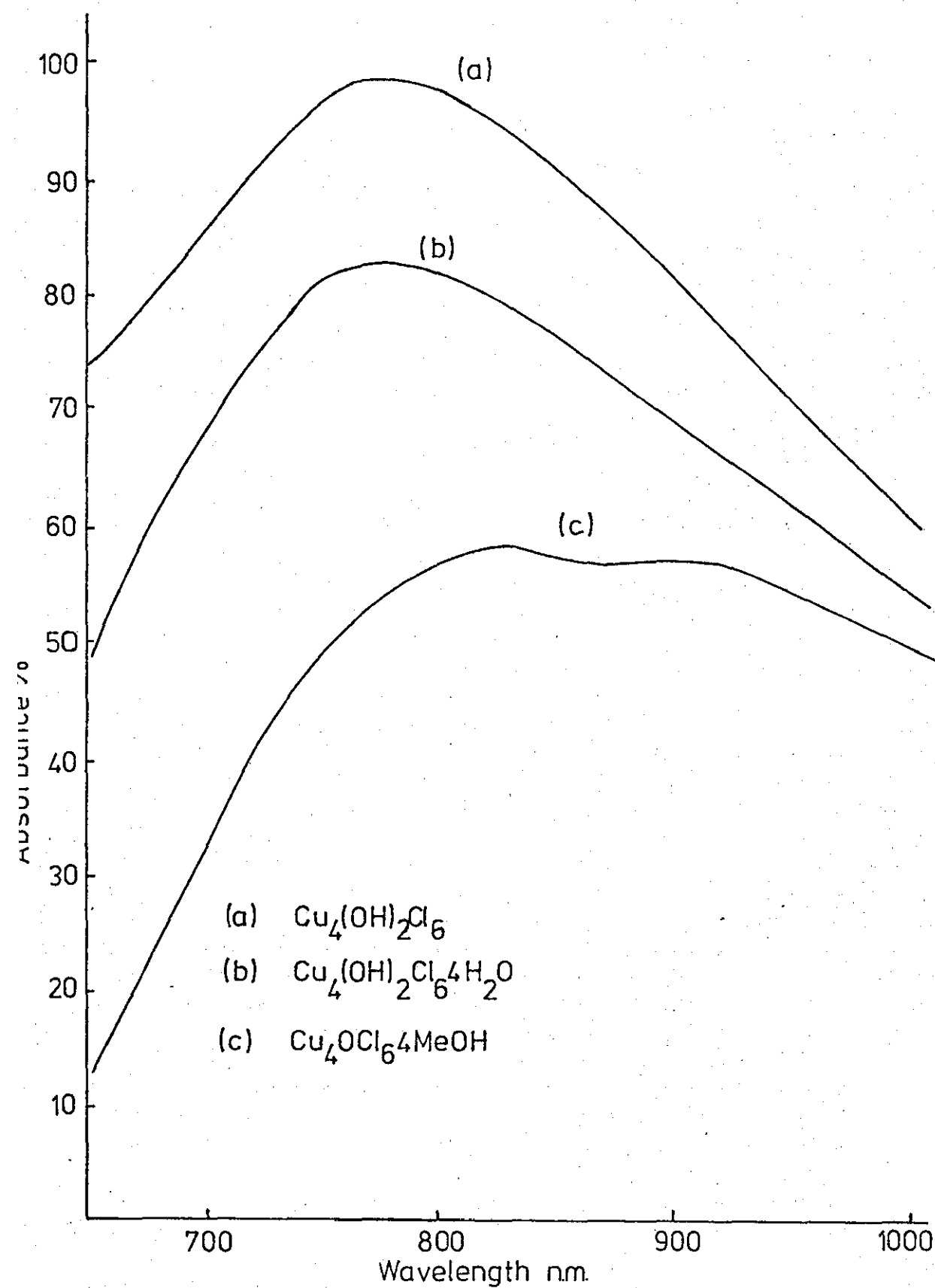
FIGURE 7.1 Reflectance spectra for hexachloride species.

dry nitrogen

to electro balance

saturated salt solution
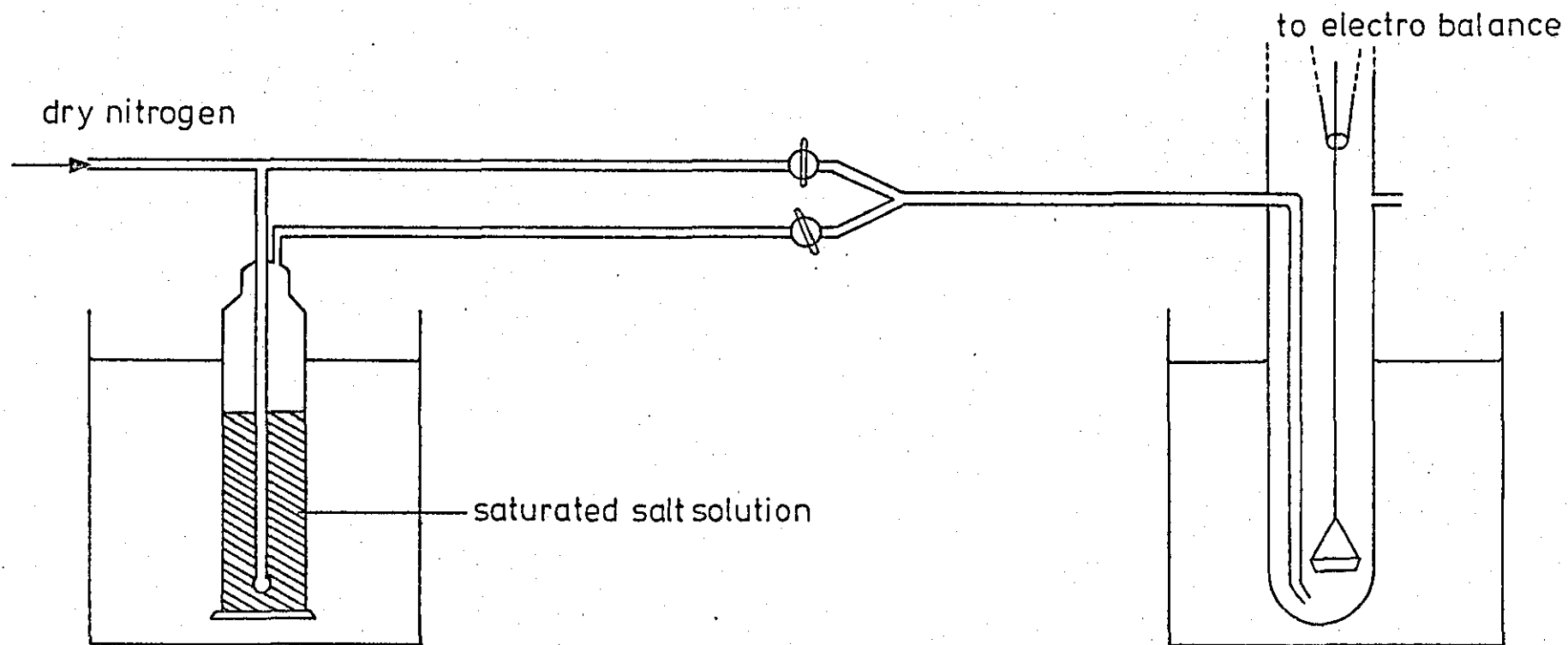
FIGURE 7.2. Apparatus for the investigation of the reaction between $Cu_4OCl_6 4MeOH$ and water vapour
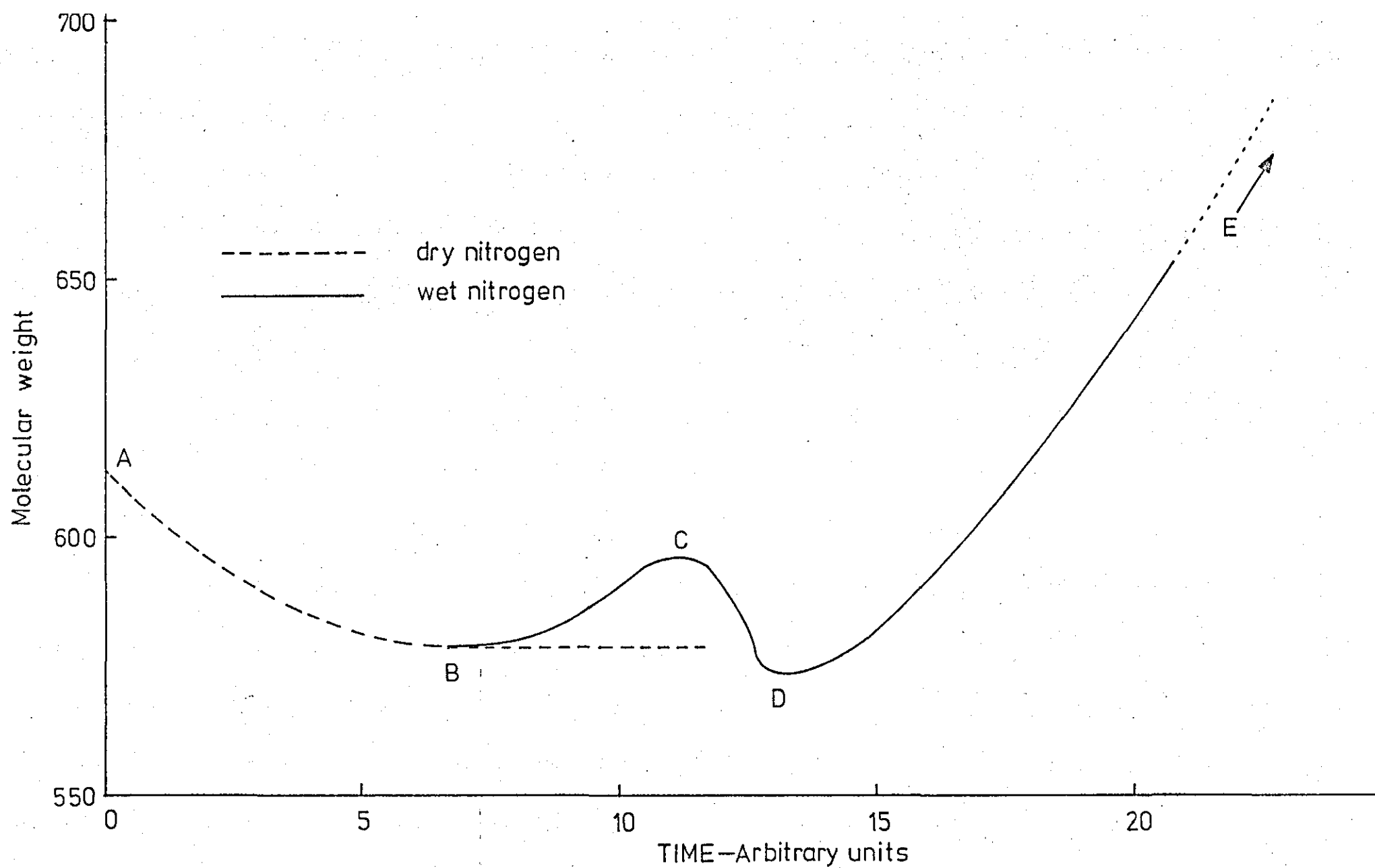
FIGURE 7. 3.   The reaction between $Cu_4OCl_6 \cdot 4MeOH$ and water vapour.

infrared spectrum of the product showed the absence of the Cu-O band

at 598 cm^{-1} in Cu_4OCl_64MeOH. The infrared spectrum of the product from

this hydrolysis reaction, taken before the sample passed into solution,

was identical to that of $Cu_4(OH)_2Cl_64H_2O$ (table 7.2) except that traces

of methanol (a band at 1450 cm^{-1}) were present.

The reaction of the complexes $Cu_4(OH)_2Cl_64H_2O$, $Cu_4(OH)_2Cl_3Br_32H_2O$ and

$Cu_4(OH)_2Br_6$ with pyridine in ethanol was studied. The complexes (ca. 5g)

were slurried in absolute ethanol (100 ml) and a pyridine- ethanol

solution (4g in 20 ml) added. The mixture was stirred for ten

minutes and then filtered; the solid product was washed with absolute

ethanol, followed by diethyl ether and dried in vacuo (2 torr) at 20°C.

The products from these reactions, tetranuclear pyridine complexes,

were characterised by halide analysis and infrared data. The

results of these reactions are contained in table 7.6.

In order to determine whether the complex $Cu_4(OH)_2Cl_64H_2O$

was a mixture of copper (II) chloride dehydrate and a basic copper (II)

salt, it was dissolved in ethanol. The complex was not very soluble

in this solvent, but gave a clear yellow solution. The colour of

a copper (II) chloride-ethanol solution is green. The ultraviolet

spectrum of the solution showed an absorption band at 274 nm, the

mixed halide and hexabromide complexes exhibited similar absorptions

in ethanol solution at 280 and 310 nm respectively (table 7.6).

The reaction between the complex $Cu_4(OH)_2Cl_64H_2O$ and water

vapour at elevated temperatures was studied, as this was relevant

to work described in the following chapter. $Cu_4(OH)_2Cl_64H_2O$ (1g) was heat

to 60°C under a partial pressure of water vapour of 18 mm.Hg for

24 hours. The product, a blue solid, was dried in a vacuum

desiccator. X-ray powder diffraction data and an infrared spectrum was

obtained, which showed the blue complex to be a mixture of $CuCl_22H_2O$ and
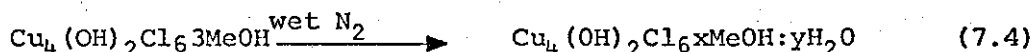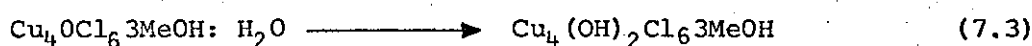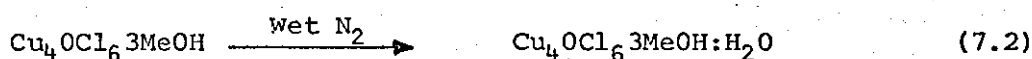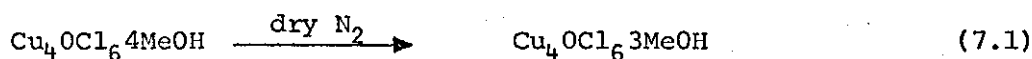
$Cu_2(OH)_3Cl$.

The tetranuclear methanol complexes were prepared as described in Chapters Three and Four. Copper hydroxychloride was prepared by the method of Iitaka (86). Copper, halide and mixed halide analyses, near infrared spectra, x-ray powder diffraction data, and reflectance and solution spectra were obtained as previously described. Hydroxide analyses were determined by dissolving the complex in a known volume of N/10 hydrochloric acid and back-titrating with N/10 sodium hydroxide solution, using screened methyl orange indicator. (pink to green).

Infrared spectra between 40 and 400 cm^{-1} were measured by the P.C.M.U..

7.3 Discussion

The reaction of the three tetranuclear methanol complexes with water, and subsequent removal of hydrated water and methanol, results in the formation of basic copper (II) complexes of stoichiometry $Cu_4(OH)_2Cl_6$, $Cu_4(OH)_2Cl_3Br_3$ and $Cu_4(OH)_2Br_6$ (table 7.1). In addition, the first two of these complexes appear to exist as tetra- and bishydrates respectively under normal laboratory conditions. The presence of hydroxide groups in these complexes is confirmed by the appearance of sharp bands between 3360 and 3420 cm^{-1} in the infrared spectra of the anhydrous salts (table 7.2). Metal hydroxides are known to exhibit similar bands due to the O-H stretching vibrations in this region of the spectrum (146). The infrared spectra of the hydrated complexes $Cu_4(OH)_2Cl_6 \cdot 4H_2O$ and $Cu_4(OH)_2Cl_3Br_3 \cdot 2H_2O$ (table 7,2), contain a broad band between 3300 and 3500 cm^{-1}, characteristic of aquo-complexes, and in addition, a band at 1585 - 1588 cm^{-1} which can be assigned to the H-O-H bending mode in coordinated or lattice water (146). This latter band appears with equal intensity at 1580 cm^{-1} in the spectrum of copper (II) chloride dihydrate.

A study of the hydrolysis reaction of the tetranuclear hexachloride complex under controlled conditions (figure 7.3), reveals that the

compound loses one molecule of axial ligand [(A) → (B) in figure 7.3]

under a stream of dry nitrogen. If wet nitrogen is then passed over

the complex, it gains approximately one molecule of water [(B) → (C)].

At this point, the complex remains yellow indicating that the

tetranuclear structure, Cu_4O, is still present. The sample then

begins to lose weight and turns from yellow to green. The absence of

the $Cu-O$ assymmetric stretching vibration in the infrared spectrum of

the complex at this stage, indicates that this colour change corresponds

to a breakdown of the Cu_4O structure. The weight loss at this stage is

presumably due to loss of methanol, probably accompanied by gain of water.

The loss of methanol ceases at about point (D) in figure 7.3, and water

continues to be absorbed until the sample passes into solution [(D) → (E)]

The infrared spectrum of the complex at a point between (D) and (E)

showed the presence of methanol, as did a similar spectrum of the product

of the hydrolysis reaction carried out in the open laboratory prior to

heat treatment. The reaction scheme for the hydrolysis of $Cu_4OCl_6 4MeOH$

is shown in equations 7.1 to 7.4. below.

$$Cu_4OCl_6 4MeOH \xrightarrow{dry\ N_2} Cu_4OCl_6 3MeOH \qquad\qquad (7.1)$$

$$Cu_4OCl_6 3MeOH \xrightarrow{wet\ N_2} Cu_4OCl_6 3MeOH:H_2O \qquad\qquad (7.2)$$

$$Cu_4OCl_6 3MeOH: H_2O \xrightarrow{\hspace{1cm}} Cu_4(OH)_2Cl_6 3MeOH \qquad\qquad (7.3)$$

$$Cu_4(OH)_2Cl_6 3MeOH \xrightarrow{wet\ N_2} Cu_4(OH)_2Cl_6 xMeOH:yH_2O \qquad (7.4)$$

In the absence of dry nitrogen, the product of equation 7.2 may

occur through straightforward substitution of water for methanol. The

hydrolysis reactions of the other methanol complexes probably occur

by a similar reaction scheme. The anhydrous salts are simply prepared

by the removal of the methanol and water in equation 7.4 on heating.

The fact that the hexabromide complex $Cu_4(OH)_2Br_6$ does not form a hydrate,

is consistent with basic copper (II) bromides and copper (II) bromide

itself which exist only as anhydrous compounds.

The problem that remains is whether these complexes are new basic copper salts (as complexes of this stoichiometry have not been observed before) or mixtures of known copper (II) compounds. Unfortunately, the problem cannot be completely resolved from a study of the X-ray powder diffraction patterns of these complexes. A comparison of these powder patterns (table 7.3) with those of standard copper (II) compounds (table 7.4), reveals that the hexabromide and mixed halide complexes contain the main powder lines of copper (II) bromide (marked with an asterisk in table 7.3). In addition, the hexachloride complex appears to contain all the powder lines corresponding to copper (II) chloride dihydrate, although the line intensities are different from those in this latter complex. These facts indicate that the three complexes could be mixtures of copper (II) halides and basic copper (II) salts. However, all three complexes contain powder lines at low angles (high "d" spacing), which do not appear in the reported powder patterns of any basic copper salt. Comparative studies involving the mixed halide or hexabromide complexes are not possible, owing to the limited number of basic copper (II) bromide salts available. However, there are many basic copper (II) chloride complexes with reported x-ray powder patterns (78) and infrared data (77), which can be used to evaluate the nature of the complex $Cu_4(OH)_2Cl_64H_2O$.

Many of the basic copper (II) chloride salts are structurally similar, and show related x-ray powder patterns. Nearly all have the strongest powder line corresponding to a "d" spacing of 5.5 $\overset{o}{A}$ (table 7.4) which complicates any comparative study. However, these basic salts do not contain powder lines at a greater "d" spacing than 6$\overset{o}{A}$. The presence of strong lines at 7.04 and 6.78 $\overset{o}{A}$ in the powder pattern of $Cu_4(OH)_2Cl_64H_2O$ precludes the possibility of this compound being a simple mechanical mixture of copper (II) chloride dihydrate and a basic copper salt

$(3Cu_4(OH)_2Cl_64H_2O = 8CuCl_2(2H_2O) + 2Cu_2(OH)_3Cl$, for example).

Although the presence of copper (II) hydroxide, Atacamite and Paratacamite in the complex $Cu_4(OH)_2Cl_64H_2O$ can be ruled out from the x-ray data, it could still contain copper (II) chloride dihydrate and copper hydroxychloride and, in addition, the powder pattern is very similar to that of the mineral Botallackite, $Cu_2(OH)_3Cl$.

The infrared spectrum of $Cu_4(OH)_2Cl_64H_2O$ indicates that it does not contain copper hydroxychloride (table 7.2), the majority of the vibrational bands of this latter complex being absent in the spectrum of the former compound. However, there is a strong band at 302 cm^{-1} in $Cu_4(OH)_2Cl_64H_2O$ which could be related to the band at 299 cm^{-1} assigned to the νCu-Cl vibration in $CuCl_22H_2O$(139). The Cu-Cl band appears at 328 and 275 cm^{-1} in the spectrum of anhydrous copper (II) chloride (139), and similarly bands appear at 328 and 285 cm^{-1} in the spectrum of the anhydrous complex $Cu_4(OH)_2Cl_6$, which indicates that $Cu_4(OH)_2Cl_64H_2O$ either contains copper (II) chloride dihydrate or contains structural units similar to those in $CuCl_22H_2O$. The infrared spectrum of $Cu_4(OH)_2Cl_64H_2O$ and the anhydrous complex, can be used to obtain further information as to the structural units present. The spectra of copper hydroxide complexes have been studied by many workers and attempts have been made to correlate the frequency and number of observed O-H stretching vibrations, with the presence or absence of bridging hydroxyl groups, without much success. McWhinnie (27, 28) reported copper (II) complexes containing bridging hydroxide groups, with νO-H bands at about 3600 cm^{-1}, some singlet some doublet; whilst the same vibration appears on a doublet at 3400 and 3340 cm^{-1} in the bridging hydroxide complex [(phen.)Cu(OH)ClO$_4$]$_2$ (29), and as a singlet at 3410 cm^{-1} in [Cu$_2${(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$}$_2$(OH)$_2$]Br$_2$ (22). The "free" ν O-H band occurs between 3590 and 3650 cm^{-1} (147), but can be

lowered by the presence of hydrogen bonding. The extent of this

shift depends on the strength of the hydrogen bond formed. From the

data available on the complex $Cu_4(OH)_2Cl_6$ it appears, from the value

of νO-H, that strong hydrogen bonding is taking place. A similar

conclusion can be reached from the infrared spectra of $Cu_4(OH)_2Cl_3Br_3$

and $Cu_4(OH)_2Br_6$ (table 7.2). Information about the nature of the

hydroxide groups can be obtained more easily from a study of the Cu-O

bands in the infrared spectrum. Empirically it was found (29, 135,

148) that the spectra of hydroxy complexes of copper, chromium and

iron, with bridging units of the type

$$
\begin{array}{c}
\text{OH} \\
M \diamondsuit M \\
\text{OH}
\end{array}
$$
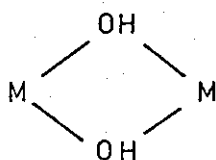
contained strong bands in the region $400 - 600$ cm^{-1} ($450 - 550$ cm^{-1} for

copper complexes), and these were assigned to M-O vibrations (29).

Many other complexes with similar bridging hydroxide groups also exhibit

absorptions in this region of the spectrum (77, 149-152). Consequently,

the two bands at ca. 450 and 510 cm^{-1} in the spectra of $Cu_4(OH)_2Cl_6$,

$Cu_4(OH)_2Cl_3Br_3$ and $Cu_4(OH)_2Br_6$ may be assigned to Cu-O vibrations of

this type, indicating that these complexes contain the structural unit:-

$$
\begin{array}{c}
\text{OH} \\
Cu \diamondsuit Cu \\
\text{OH}
\end{array}
$$
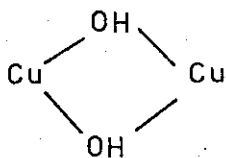
Any further assignments of infrared bands is difficult until the

complete structure of the complexes is known.

The reflectance spectrum of the tetranuclear methanol complex

(figure 7.1) is typical of this type of compound containing five

co-ordinate copper, with a broad band containing two absorptions at

820 and 925 nm. The reflectance spectra of the hydrolysis products,

$Cu_4(OH)_2Cl_6$ and $Cu_4(OH)_2Cl_64H_2O$, are almost identical, and similar to the spectra of basic copper (II) salts containing six coordinate copper (153).

The physiochemical properties are unable to resolve the problem unequivocably as to whether these hydrolysis products are true compounds or mixtures. However, the complexes could not be separated into any constituent compounds by solution in ethanol (which in theory would have separated the soluble copper (II) halide from a basic copper salt). The dehydration-rehydration reaction of the complex $Cu_4(OH)_2Cl_64H_2O$, although similar to the analogous $CuCl_22H_2O - CuCl_2$ reaction, occurred more readily in the former complex. In addition, the reaction of these complexes with pyridine in ethanol to yield the appropriate tetranuclear pyridine complex (table 7.6), is an indication that; (a) all three complexes are structurally similar, and (b) they are true complexes which may contain Cu_4 structural units. The presence of absorption bands at 270 - 310 nm in the ethanolic solution spectra of these complexes (table 7.6), suggests that they form tetranuclear structures when dissolved in this solvent (see Chapter Five). No other basic copper (II) compounds or mixtures of copper (II) halides and basic salts appear to undergo this type of reaction at room temperature. It was mentioned in Chapter Three, that mixtures of $CuCl_22H_2O$ and $Cu(OH)Cl$ when refluxed in ethanol, produced a "Cu_4OCl_6" solution. However, the yield was very small and long reaction times at elevated temperatures were required with these particular reactants.

7.4 Conclusions

Tetranuclear copper (II) complexes containing axial methanol groups undergo a reaction in the presence of water vapour, in which the central oxygen atom reacts with one molecule of water to form two hydroxide groups. The hydrolysis products, although structurally

similar to basic copper (II) salts, appear to be true complexes and not

mixtures of copper (II) halides and basic copper compounds, and thus

represent three new basic copper (II) salts. They probably contain

similar structural units to those in copper (II) halides and, in

addition, the bridging hydroxide unit shown below.

$$
\begin{array}{ccc}
 & OH & \\
Cu & & Cu \\
 & OH & \\
\end{array}
$$
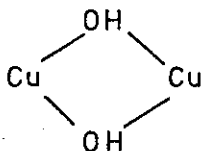
These complexes appear to form Cu_4O species in ethanol solutions, from

which tetranuclear complexes can be prepared. This supports the theory

proposed by Belford et al. (61) that such complexes are formed by the

dehydroxylation of copper (II) hydroxide species.

CHAPTER EIGHT

THE OXIDATION OF COPPER (I) HALIDES

8.1 Introduction

Of the copper (I) halides, only the oxidation of copper (I) chloride has been reported in any detail. This oxidation has been studied by many workers, using various oxidising agents and under varying reaction conditions (154 - 164). Berthelot (154) and Gröger (155) suggested that the aerial oxidation of an aqueous solution of copper (I) chloride resulted in the products shown in equation 8.1

$$6CuCl + 3/2O_2 + 3H_2O \longrightarrow CuCl_2: 3Cu(OH)_2 + 2CuCl_2 \qquad (8.1)$$
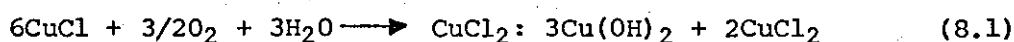
The oxidation of copper (I) chloride in neutral solution is of considerable interest, as the product from this reaction is used as a pesticide and fungacide in the fruit growing industry (165). This oxidation has been reported to yield "copper oxychloride", according to equation 8.2 (161, 162, 164).

$$6CuCl + 3/2O_2 \xrightarrow{\quad H_2O \quad} (3CuO: CuCl_2: 3H_2O) + 2CuCl_2 \qquad (8.2)$$
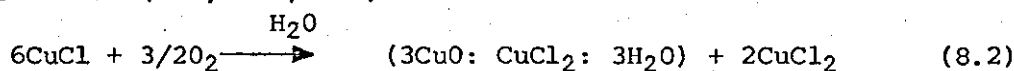
However, the product is more correctly formulated as $2Cu_2(OH)_3Cl$, a basic salt structurally related to the minerals Atacamite, Paratacamite and Botalackite (32) with the same formula, which were mentioned in earlier chapters. This basic salt is produced commercially by several methods involving the aerial oxidation of copper (I) chloride in the presence of sodium (166) and ammonium (167) chloride. The kinetics of this reaction have been studied by Jhaveri and Sharma (164), who found the rate of reaction second order with respect to copper (I) chloride and first order with respect to oxygen. A similar conclusion was reached by Ruthven and Kenney (36) for the oxidation of copper (I) chloride in melts (see Chapter One).

Very recently, the aerial oxidation of copper (I) chloride at various temperatures and partial pressures of water vapour has been studied in these laboratories (168). Preliminary results indicated that the reaction product at 20°C is a mixture of $Cu_4(OH)_2Cl_6xH_2O$ x = ca.4,

the basic salt described in Chapter Seven, and Paratacamite $Cu_2(OH)_3Cl$.
At temperatures of ca. 50-60°C, the oxidation product was found to be
a mixture of $CuCl_2 2H_2O$ and $Cu_2(OH)_3Cl$. It was mentioned in Chapter
Seven that the basic salt $Cu_4(OH)_2Cl_6 4H_2O$ reacted in the presence of
water at 60°C to give $CuCl_2 2H_2O$ and $Cu_2(OH)_3Cl$ and, bearing in mind
that this complex itself is also the hydrolysis product of a
tetranuclear copper compound, it is not unreasonable to envisage a
reaction scheme for the oxidation of copper (I) chloride similar to
that shown by equations 8.3 to 8.5 below, in which a tetranuclear
copper (II) complex is postulated as the initial oxidation product.

$$4CuCl + O_2 + H_2O \xrightarrow{\ 20°C\ } Cu_4O(OH)_2Cl_4 \tag{8.3}$$

$$2Cu_4O(OH)_2Cl_4 + (2 + x)H_2O \xrightarrow{20°C} Cu_4(OH)_2Cl_6 xH_2O + 2Cu_2(OH)_3Cl \tag{8.4}$$

$$3Cu_4(OH)_2Cl_6 xH_2O \xrightarrow{\ 60°C\ } 8CuCl_2 2H_2O + 2Cu_2(OH)_3Cl \tag{8.5}$$
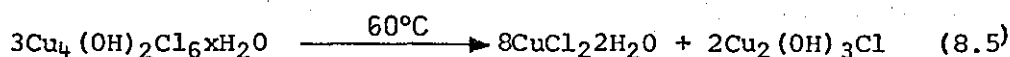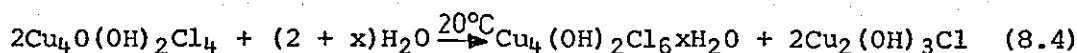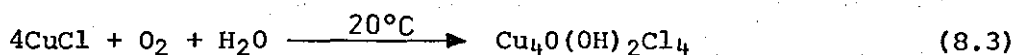
The results that have been obtained for this oxidation however,
are of a preliminary nature and further work will be needed to
ascertain the validity of this reaction scheme.

The oxidation of copper (I) chloride is very fast in neutral
solution, but much slower under acidic conditions (159, 164), where
the reaction product is copper (II) chloride (equation 8.6).

$$4CuCl + O_2 + 4HCl \longrightarrow 4CuCl_{2(aq)} + 2H_2O \tag{8.6}$$
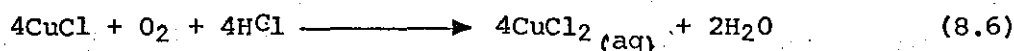
Henry (159) studied the oxidation in acetic acid solution, and found
it to be third order with respect to copper (I) chloride, with
regard to the mechanisms proposed for these oxidation reactions, both
Jhaveri and Sharma (164) and Ruthven and Kenney (36) favour the
formation of a peroxide intermediate of the type:-

$$(Cl_2Cu-O-O-CuCl_2)^{2-}$$
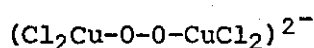
However, the existence of this species is based purely on a
comparison with the oxidation of other transition metal ions such as

Fe^{2+} and Pu^{3+} in aqueous solution, for which peroxide type intermediates have been proposed (169 - 171) [but only substantiated in the case of Pu^{3+} (171)]. No supporting evidence has been reported for the formation of this type of intermediate during the oxidation of copper (I) chloride.

The oxidation of copper (I) chloride in non-aqueous solvents has not been studied very extensively. Finkbeiner et al. (7) noted that in o-dichlorobenzene or benzene, copper (I) chloride is inert towards oxygen and that only in the presence of a co-ordinating ligand, such as pyridine, is an oxidation observed. The results reported by Finkbeiner et al. for the oxidation of copper (I) chloride in various solvents, were discussed in Chapter One. Oxidation in the presence of pyridine in an "inert solvent" leads to an ill-defined copper (II) complex, whilst oxidations in methanol and iso-propyl alcohol, result in the formation of Cu(OMe)Clpy and the tetranuclear complex Cu_4OCl_64py respectively. A tetranuclear complex, $K_4^+Cu_4OCl_{10}^{4-}$ has also been prepared by the oxidation of copper (I) chloride in melts containing K_2CuCl_4 as was mentioned in Chapter Three (62).

The possibility that tetranuclear copper (II) compounds were involved in the oxidation of the complex CuClpy (mentioned in Chapter One and discussed in detail in this chapter), and the occurrence of these polynuclear complexes in the products of oxidation reactions involving copper (I) chloride, lead to the work described in this chapter. The oxidation of copper (I) halide-pyridine complexes in the solid state, and copper (I) chloride in non-aqueous solvents is described, with a view to determining the nature of the amorphous oxidation product mentioned by Finkbeiner et al. and also the active catalyst complex which is produced by the oxidation of copper (I) chloride in an "inert solvent". In addition, the methoxide catalyst complex, Cu(OMe)Clpy, prepared by Finkbeiner et al. has been studied by several techniques and is discussed in detail. The oxidation of copper (I) chloride in

non-aqueous solutions containing halide ions has been studied, to ascertain the conditions under which tetranuclear copper (II) complexes are formed from copper (I) species and the results of these and some unsuccessful experiments are also reported.

8.2 Experimental and Results

8.2.1   The oxidation of copper (I) halide-pyridine complexes

The copper (I) halide-pyridine complex was analysed and a portion (ca. 1.5 g) accurately weighed and placed on a watch glass in a vessel containing, in addition to a normal oxygen-nitrogen atmosphere, a small quantity of water. The complex was allowed to react for up to 16 hours. During several experiments the complex was removed, at times ranging from 5 minutes to 16 hours after the beginning of the oxidation, placed in a vacuum desiccator for one hour and analysed. Spectral data were also obtained. It was found that for the complexes CuClpy, CuCl3py and CuBr3py the oxidation reaction was complete within 30 minutes, after which time the composition of the products remained unchanged for up to about 16 hours, under the particular conditions employed. In a further set of experiments, the copper (I) complexes were allowed to react for up to 100 hours, after which time the products were again placed in a vacuum desiccator for an hour and then analysed.

The oxidation of these copper (I) complexes with dry oxygen was studied in a similar manner, except that the copper (I) halide-pyridine complex was placed in a vacuum desiccator containing phosphorus pentoxide and immediately evacuated, after which dry oxygen was admitted to the vessel and the oxidation allowed to proceed for 16 hours. After this time the product was transferred to a dry-box for analysis. It was found that the products from the oxidation of CuClpy and CuCl3py with dry oxygen, would undergo a reaction with water vapour,

TABLE 8.1

ANALYTICAL DATA FOR THE OXIDATION PRODUCTS OF COPPER (I) HALIDE-PYRIDINE COMPLEXES

| COMPLEX | REACTION CONDITIONS | WEIGHT CHANGE % | PRODUCT | | | |
			COLOUR	% COPPER	% HALOGEN	% PYRIDINE
CuClpy	wet air 16 hours	+ 9.8	green	32.06	18.17	39.3
CuCl3py*	wet air 16 hours	−38.6	green	31.74	17.79	41.7
CuClpy	wet air 64 hours	− 4.3	blue	37.14	20.83	32.0
CuCl3py*	wet air 64 hours	−40.3	blue	37.01	20.72	31.0
CuClpy	dry oxygen 16 hours	− 1.9	dark green	−	−	−
CuCl3py*	dry oxygen 16 hours	−36.3	dark green	30.92	17.31	−
CuBr3py	wet air 16 hours	−37.2	bright green	26.63	33.71	−
CuBr3py	wet air 85 hours	−	pale green	28.94	36.07	−

* Analysed as CuCl (2.94 py)

TABLE 8.2

X-RAY POWDER DIFFRACTION DATA FOR OXIDATION PRODUCTS

CuCl3py Oxidation Products				CuClpy Oxidation products				CuBr3py Oxidation Products				CuCl$_2$2py		CuBr$_2$2py		Cu$_2$(OH)$_3$Cl (78)	
64 hours (blue)		16 hours (green)		64 hours (blue)		16 hours (green)		20 hours		85 hours							
d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I
8.43	60	8.45	70	8.42	40	8.43	50	8.82	100	8.81	100	8.45	80	8.80	100	5.45	100
7.60	100	7.61	100	7.58	100	7.60	100	7.54	50	7.55	60	7.60	100	7.54	80	4.70	60
5.99	30	6.01	5	6.00	20	5.98	40			5.83	20	6.07	10	6.05	2	4.55	20
5.22	5			5.21	10			4.79	20	4.80	10	4.74	30	4.80	10	3.41	50
5.43	50			5.43	20					4.42	10	4.14	10	4.44	2	3.01	10
4.69	70	4.71	20	4.69	60	4.70	10					3.82	15	4.17	2	2.90	60
4.54	5			4.54	10			4.05	10	4.05	10	3.80	15	4.06	5	2.77	80
4.15	10							3.90	10	3.89	20	3.46	.5	3.90	15	2.74	60
4.13	10	3.81	10	4.10	5							3.41	10	3.74	2	2.34	50
3.78	40	2.79	10	3.78	20	3.78	10	3.40	20	3.41	10	3.24	2	3.40	10	2.27	80
3.45	30	3.46	5	3.46	20			3.21	10	3.20	5	3.08	2	3.20	2	2.25	60
3.40	30	3.42	5	3.39	15	3.41	10			3.04	5	3.01	5	3.05	2	2.22	20
3.00	10											2.94	2	3.03	2		
2.85	20			2.85	10					2.98	5	2.87	2	2.97	2		
2.74	60			2.76	50							2.83	2	2.93	5		
2.65	10									2.85	20	2.75	5	2.75	2		
2.25	50			2.24	50			2.70	10	2.73	5	2.66	2	2.69	5		
								2.57	5	2.58	2			2.65	2		
										2.36	10			2.59	2		

TABLE 8.3

INFRARED SPECTRA ($4000-250\,cm^{-1}$) OF OXIDATION PRODUCTS (EXCLUDING PYRIDINE VIBRATIONS)

OXIDATION PRODUCT FROM CuClxpy x=1,3 IN WET AIR		OXIDATION PRODUCT FROM CuBr3py IN WET AIR		$Cu_2(OH)_3Cl$ (77)	$Cu_2(OH)_3$ (77)
16hrs (green)	64hrs (blue)	20 hrs	85 hrs		
3600 – 3200 (s,br)	3340 (s)	3600 – 3200 (s,br)	3510 (s)	3448	3516
	3350 (s,sh)		3418 (s,sh)	3360	3424
	3310 (s,sh)		3400 (s)	3317	3410
	985 (m)		870 (w)	990	3320
	920 (m)		842 (m)	925	880
800 (w,br)	830 (m)	800 (w,br)	810 (w)	910	860
	570 (w,br)		778 (m)	895	848
	510 (m)		528 (m)	866	814
	475 (m,sh)		502 (m)	832	787
450 (m,br)	452 (s)	450 (s,br)	420 (s)	579	684
	410 (m)		318 (m)		

s = strong   br = broad

m = medium   sh = shoulder

w = weak

TABLE 8.4

REFLECTANCE SPECTRA FOR OXIDATION PRODUCTS

COMPLEX	λ_{MAX} nm
CuCl3py in wet air	
16 hrs (green)	700 (V.br.)
64 hrs (blue)	700, 775 (sh)
CuCl3py in dry oxygen	780 (V.br.)
CuClpy in wet air	
16 hrs (green)	700 V.br.)
64 hrs (blue)	700, 780 (sh)
CuClpy in dry oxygen	790 (V.br.)
CuBr3py in wet air	
16 hrs.	710 (V.br.)
84 hrs	720, 810 (sh)
$CuCl_2 2py$	695
$CuBr_2 2py$	700

V.br. = very broad
sh = shoulder

under conditions similar to those described above, to produce identical products to those obtained from the oxidations in wet air.

Analytical data for the products of these experiments are detailed in table 8.1. X-ray powder diffraction lines for several of the oxidation products are listed in table 8.2, along with $CuCl_2 2py$, $CuBr_2 2py$ and $Cu_2(OH)_3Cl$ which are included for comparative purposes. Infrared spectra for the products of the wet air oxidation are contained in table 8.3. All these complexes were found to contain vibrational bands due to co-ordinated pyridine (discussed in Chapter Two). These bands were in an identical position to those in bispyridine-dihalo copper (II) complexes (table 2.2) and so are not listed. Reflectance spectra for all the oxidation products are contained in table 8.4. The products from the oxidation of CuBr3py in dry oxygen and CuBrpy in dry oxygen and wet air are not included in these tables for, even after several days reaction, traces of copper (I) complexes could still be seen (yellow or white) and the infrared spectra of the products showed the presence of copper (I) bromide-pyridine complexes with bands at 1596, 702 and 693 cm^{-1} (CuBrpy) and 1595, 699 and 693 cm^{-1} (CuBr3py).

In addition to these experiments, the oxidation of the monopyridine adduct of copper (I) chloride in wet air was studied using a gravimetric technique. A sample of the copper (I) complex was analysed and about 70 mg placed on a platinum pan which was suspended from a Cahn electrobalance (figure 8.1). Care was taken to protect the sample from atmospheric oxygen during this operation. The platinum pan was enclosed in a container which was continuously flushed out with dry nitrogen. The sample was held at 25°C by means of a thermostated water bath surrounding the apparatus. When the sample had reached thermal equilibrium and the balance and associated electronics adjusted to zero
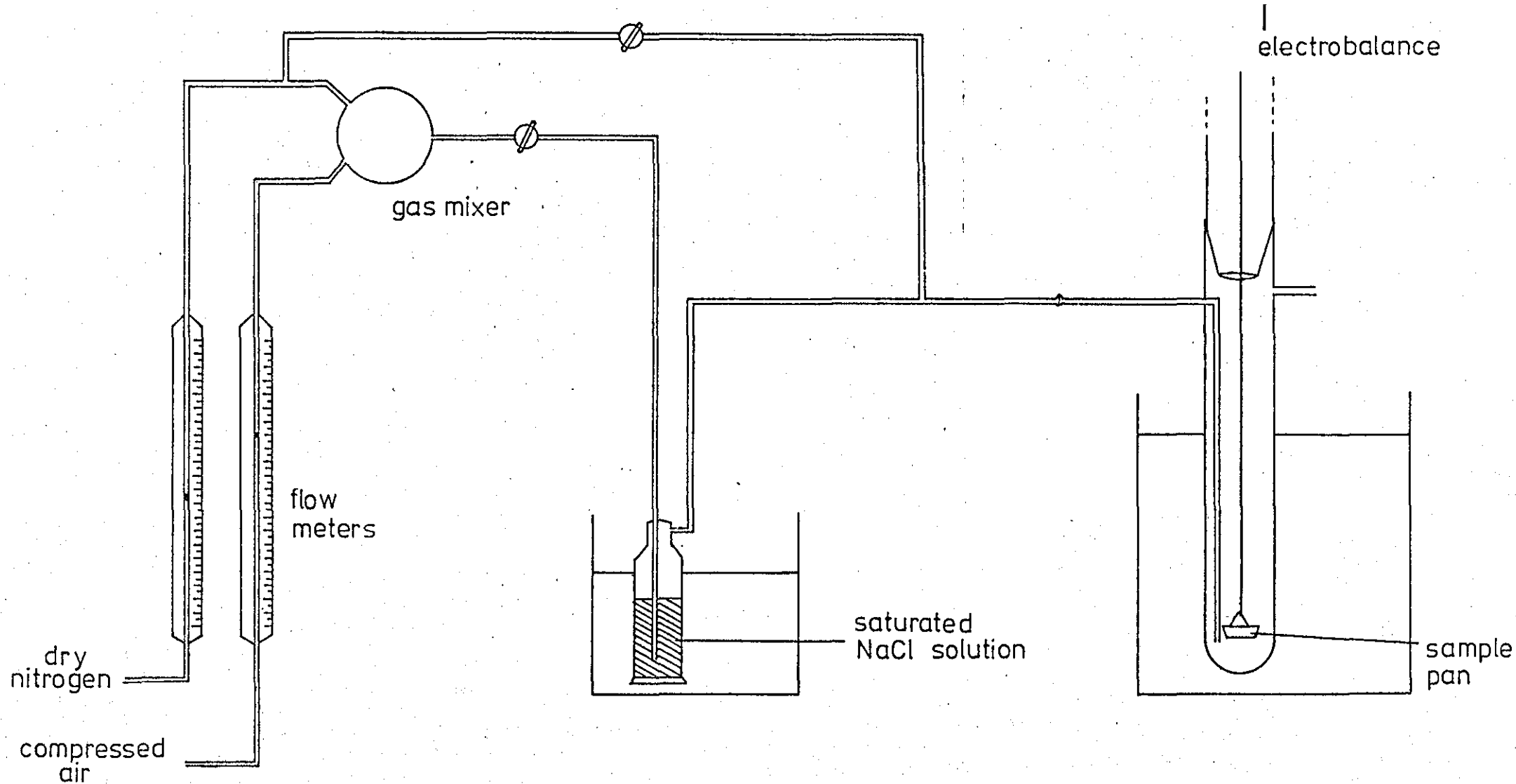
FIGURE 8.1. Apparatus for the study of the oxidation of CuClpy

the pen recorder, a wet air and nitrogen mixture was substituted for the
dry nitrogen by means of the two taps in figure 8.1. The wet gas was
obtained by passing compressed air and nitrogen through a gas mixer
and into a saturated sodium chloride solution held at 25°C by means of
a water bath. This gave a partial pressure of water vapour equal to
18 mm Hg. The gas flow rates could be adjusted and were monitored by
means of "Meterate" type A flow meters. The weight changes on oxidation
were followed on a chart recorder, using a chart speed of 40" per hour
and a full scale deflection equivalent to 10 mg. It was found that a
gas mixture containing 5% by volume of oxygen, at a flow rate of 20 ml's
per minute gave a reaction time of about 25 minutes for the oxidation.
After this time, the complex had turned green and gained weight.
There then followed a loss in weight resulting, after 1 - 2 hours, in
a blue complex. The results of this experiment are detailed in table 8.5.
The molecular weight changes are in terms of 4CuClpy, as they could only
be rationalised in terms of whole numbers of atoms or molecules, by
considering them on the basis of four copper atoms. The corresponding
experiment with the trispyridine adduct was not attempted, as this
oxidation is associated with the loss of a large amount of pyridine
(table 8.1), which would make weight changes due to the addition of
oxygen and/or water difficult to observe.

8.2.2 The oxidation of copper (I) chloride in solution

(a) oxygen absorption experiments

The apparatus shown in figure 8.2 was used to study the
quantity of oxygen absorbed during the oxidation of copper (I)
chloride-pyridine solutions in the presence of water and under
anhydrous conditions. The oxidation under these latter
conditions has not been studied previously.

TABLE 8.5

DATA OBTAINED DURING A GRAVIMETRIC STUDY OF THE OXIDATION OF CuClpy

STAGE	WEIGHT(mg.)	SAMPLE COLOUR	WEIGHT CHANGE	
			%	MOLECULAR WT. UNITS PER 4 COPPER ATOMS
0	77.0	v.pale yellow	–	–
1	82.9	green	+ 7.7	54.9
2	73.3	blue	– 12.5	89.1

dry oxygen

B

vacuum   C

3-way tap

dry nitrogen

A

reaction
vessel
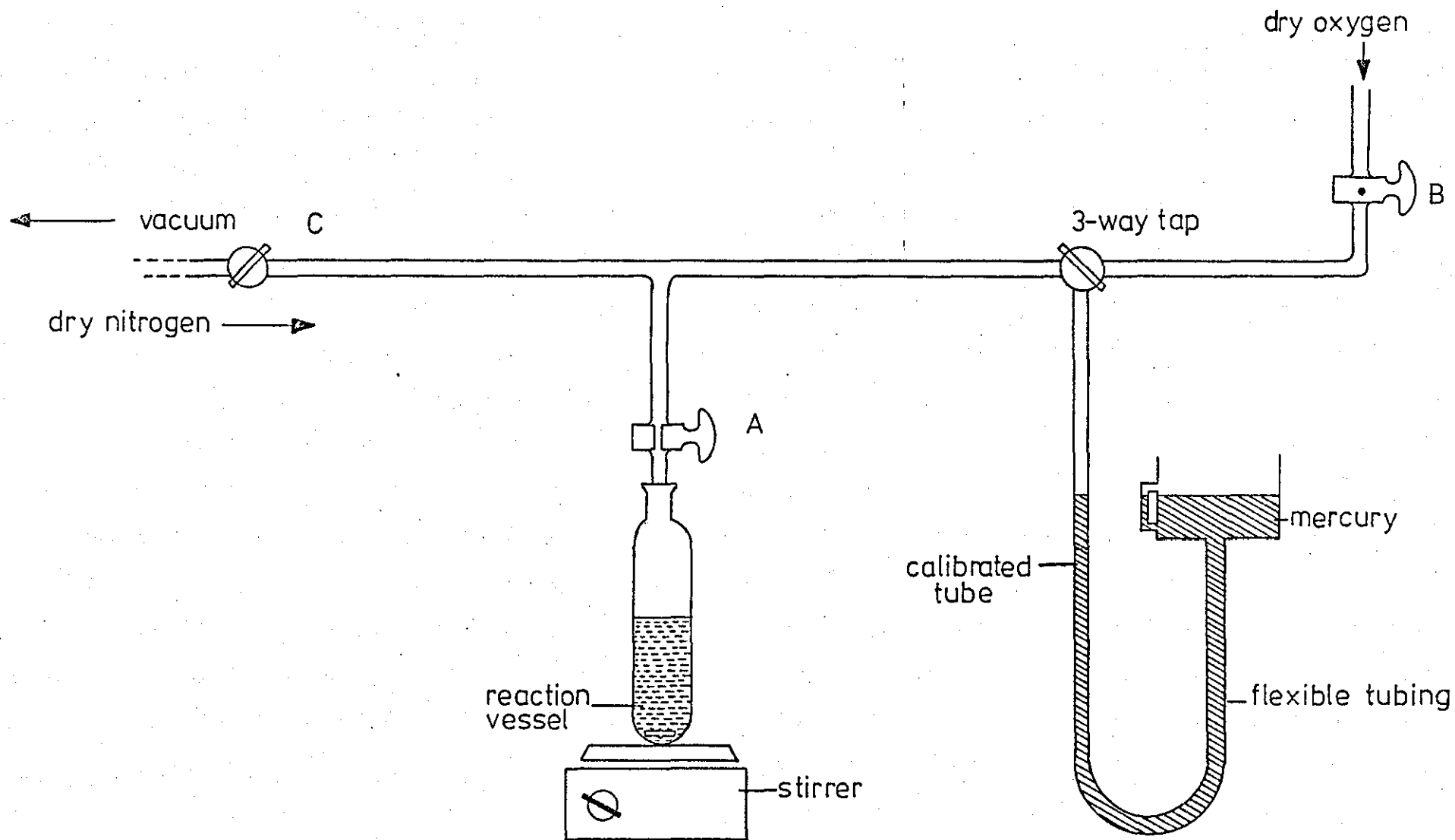
calibrated
tube

mercury

flexible tubing

stirrer

FIGURE 8.2.   Oxygen absorption apparatus

A quantity of anhydrous copper (I) chloride was weighed into
the reaction vessel, which contained a magnetic stirrer bar. The
vessel was attached to the vacuum frame and evacuated to < 0.1 torr.
Anhydrous, degassed pyridine (about 50 ml, containing ca. 20 ppm
water) was cold distilled onto the copper (I) halide from another
part of the vacuum frame. The copper (I) chloride-pyridine
mixture was allowed to reach room temperature, and magnetically
stirred until all the solid had dissolved. Dry nitrogen was
admitted to the apparatus until it was at atmospheric pressure
(as indicated by the mercury manometer). Tap A was then closed
and the frame evacuated. Then, with tap C closed, dry oxygen was
let into the apparatus at atmospheric pressure by means of tap B
which was then closed. Tap A was opened, and the manometer opened
to the frame by means of the three-way tap. The height of the
mercury in the calibrated manometer tube was recorded and the
oxidation allowed to take place over 15 hours. After this time,
the solution had turned from deep yellow to dark brown. The
pressure of gas in the apparatus was adjusted ʼto one atmosphere
by moving the flexible manometer and the height of mercury noted.
The difference in the height of mercury before and after the
oxidation was equal to the amount of oxygen absorbed during the
reaction, as the tube was calibrated directly in mls. The
experiment was repeated several times under anhydrous conditions
and twice using a pyridine water mixture (49 mls py: 1 ml water).
The results, presented as a graph of weight of CuCl versus mls of
absorbed oxygen at S.T.P., are shown in figure 8.3. The theoretical
line corresponding to the reaction of 1/4 mole oxygen per mole of
copper (I) chloride is also included. During these experiments
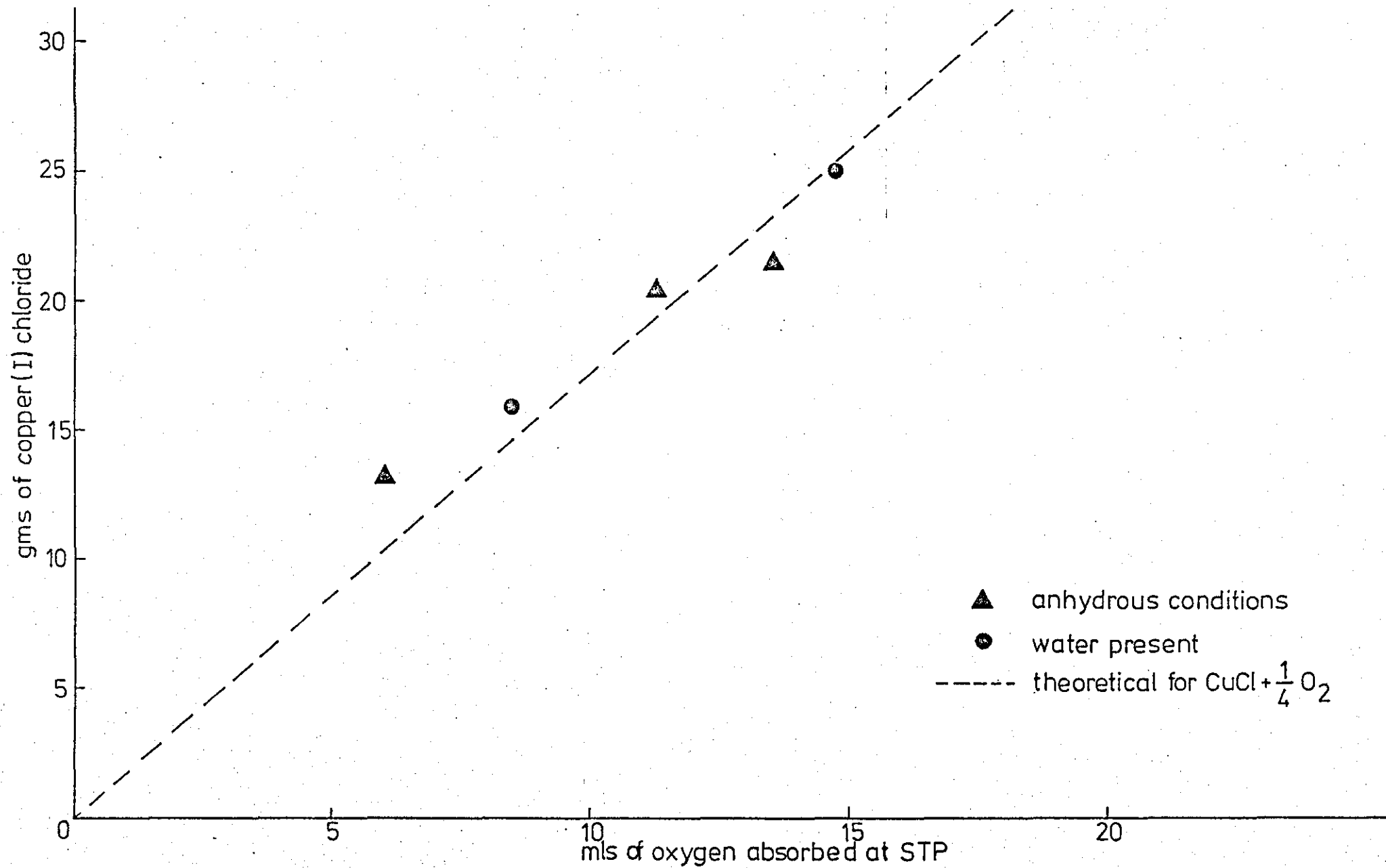it was observed that no oxidation reaction takes place between

FIGURE 8.3.   Results of oxygen absorption experiments.

copper (I) chloride-pyridine solutions and water, the
presence of oxygen is required for the reaction to occur.

(b)   isolation of a copper (II) complex from solution

Copper (I) chloride (0.015 mole) was stirred with pyridine
(250 ml) containing water (1 ml). Air was passed through the
solution for several hours. After this time the solution, which
had turned deep green, was poured into diethyl ether (500 ml) and
a green complex precipitated. The complex was filtered, washed
with absolute ethanol, followed by diethyl ether and dried in
vacuo (2 torr) at 20°C. This experiment was repeated using a
solvent system consisting of ethanol (250 ml) pyridine (5 ml)
and water (1 ml), with the precipitation of a similar product.
A further aerial oxidation was performed in o-dichlorobenzene
(250 ml) containing pyridine (5 ml) and water (1 ml). After
15 hours a green complex had formed, which was filtered, washed
and dried as above. These oxidation reactions are summarised in
table 8.6, which contains analytical data for the three complexes.
The infrared spectra, reflectance spectra and x-ray powder
diffraction lines for all three complexes, indicated that they
were identical to the green complex obtained by the reaction of
copper (I) chloride-pyridine complexes with wet air for up to
16 hours, data for which has been tabulated above. The infrared
spectrum between 700 and 250 cm^{-1}. of the oxidised copper (I)
chloride-pyridine solution described above showed the presence of
vibrational bands due to unco-ordinated pyridine only (605 and
405 cm^{-1}).

TABLE 8.6

RESULTS OF THE OXIDATION OF COPPER (I) CHLORIDE IN NON-AQUEOUS SOLVENTS

REACTION	PRODUCT		
	COLOUR	% COPPER	%CHLORIDE
$CuCl + O_2 + H_2O$ in pyridine	green	33.50	18.66
$CuCl + O_2 + H_2O + py$ in o-dichlorobenzene	green	33.21	18.46
$CuCl + O_2 + H_2O + py$ in ethanol	green	33.76	18.98

8.2.3   The preparation of the catalyst complex Cu(OMe)Clpy and related
species

The complexes Cu(OMe)Clpy, Cu(OMe)Brpy and [Cu(OMe)Cl2-mepy]$_2$

were prepared by the method described by Finkbeiner et al. (7) for

the preparation of Cu(OMe)Clpy, involving the oxidation of copper (I)

halide in a methanol solution containing the appropriate amine.

The complex [Cu(OMe)Cl2-mepy]$_2$ was also prepared by the method

of Gill and Sterns (59), which involves the reaction between

Cu$_4$OCl$_6$4(2-mepy) and 2-methylpyridine in methanol.

Analytical data for these complexes is presented in table 8.7.

X-ray powder diffraction lines are listed in table 8.8, whilst table 8.9

contains the infrared spectra (4000 - 600 cm^{-1}) for the pyridine

complexes. Table 8.10 contains the infrared spectra (600 - 40 cm^{-1})

for the pyridine complexes with band assignments, and similar data

for the 2-methylpyridine complex can be found in table 8.11. Figure

8.4 shows the reflectance spectra for the three complexes in the

region 500 - 900 nm. The magnetic moment of the pyridine complexes

was determined and found to be 0.66 B.M. for Cu(OMe)Clpy and 0.64 B.M.

for Cu(OMe)Brpy at 20°C. All three complexes described above underwent

a slow reaction with atmospheric water vapour, with the appearance of

hydroxyl bands in the infrared spectrum. Hence the compounds were

stored over silica gel.

Cu(OMe)Cl

This complex was prepared by the method of Brubaker and Wicholas

(23), involving the addition of a methanolic lithium methoxide solution

to excess anhydrous copper (II) chloride in methanol. The product, a

yellow-green solid, was found to be unstable in the presence of water

vapour.

Found % Cu, 49.32: % Cl, 27,39: Calc. for Cu(OMe)Cl, % Cu: 48.87:

% Cl, 27.26.

TABLE 8.7

ANALYTICAL DATA FOR THE METHOXIDE COMPLEXES

	Cu(OMe)Clpy		Cu(OMe)Brpy		[Cu(OMe)Cl2-mepy]$_2$		[Cu(OMe)Cl2-mepy]$_2$*	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
Copper %	30.51	30.38	24.91	25.06	28.36	28.47	28.21	28.47
Halogen %	16.99	16.95	31.16	31.51	16.12	15.89	15.78	15.89
Carbon %	33.5	34.5	28.0	28.4	-	37.7	-	37.7
Hydrogen %	3.3	3.9	3.0	3.2	-	4.5	-	4.5
Nitrogen %	6.6	6.7	5.4	5.5	-	6.3	-	6.3

TABLE 8.8

X-RAY POWDER DIFFRACTION DATA FOR THE METHOXIDE COMPLES

Cu(OMe)Clpy		Cu(OMe)Brpy		[Cu(OMe)Cl2-mepy]$_2$*		[Cu(OMe)Cl2-mepy]$_2$	
d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I	d$\overset{\circ}{A}$	I
7.81	30	8.04	100	8.42	100	8.43	100
7.43	100	7.61	70				
6.37	40	6.68	30	6.88	10	6.89	10
5.28	5	5.32	20	5.32	30	5.33	30
5.18	10	4.96	20	4.86	10	4.87	20
4.80	15	4.82	30	4.48	5	4.52	5
4.37	10	4.50	10	4.21	10	4.23	10
3.95	10	4.02	30	4.09	5	4.10	5
3.81	20	3.94	10	3.99	5	3.99	5
3.67	20	3.81	40	3.51	5	3.53	5
3.45	10	3.68	5	3.45	10	3.45	10
3.20	5	3.47	20	3.26	10	3.27	15
3.07	10	3.34	15	3.00	10	3.00	15
2.91	10	3.16	20	2.94	10	2.95	10
		3.03	25				

* prepared from Cu$_4$OCl$_6$4(2-mepy) (59)

TABLE 8.9

INFRARED DATA FOR THE METHOXIDE COMPLEXES (4000 – 600 cm^{-1})

FREE AMINE	ASSIGNMENT(50)	Cu(OMe)Clpy	Cu(OMe)Brpy
3080	20b	3105	3110
	8a + 19a	3088	3090
3054	2: 20a	3060	3064
		3040	3044
3036	13: 7b	3022	3030
		3000	3005
	CH_3str.(OCH_3)	2800	2805
1583	8a	1608	1608
1572	8b	1572	1571
1482	19a	1490	1490
1439	19b	1450	1449
1375	14	1364	1364
1288	3	1242	1242
1218	9a	1230 1220	1228
1148	15	1160	1160
1068	18a	1079	1077
1085	18b	1068	1068
	O-C Stretch	(1050)*	(1050)*
1030	12	1048	1046
992	1	–	–
986	17a	990	990
942	5	958	956
891	10a	888	885
886	10b	–	–
749	4	762	761
700	11	700	698
652	6b	652	652
605	6a	641	641

* = very broad band

TABLE 8.10

FAR INFRARED SPECTRA AND BAND ASSIGNMENTS FOR Cu(OMe)Clpy AND Cu(OMe)Brpy

Cu(OMe)Clpy cm^{-1}	Cu(OMe)Brpy cm^{-1}	$\dfrac{Cu-Br}{Cu-Cl}$	ASSIGNMENT
538(s)	540(s)	–	ν Cu-Oasym.
435(m)	435(m)	–	16b ligand vibration*
362(s)	356(s)	–	δO-Cu-O ?
266(s)	226(s)	0.85	νCu-Xasym,"short"
240(s)	244(s)	–	νCu-Nasym.
212(s)	176(s)	0.83	νCu-Xasym.,"long"
158(w)	160(m,sh)	–	δCu-O,δCu-N?
147(w)	104(w)	0.71	δCu-X
106(s)	79(s)	0.75	δCu-X
	51(v.w)	–	?

s = strong   v.w = very weak

m = medium   sh = shoulder

w = weak   * = based on reference (50)

TABLE 8.11

FAR INFRARED SPECTRA AND BAND ASSIGNMENTS FOR $[Cu(OMe)Cl2-mepy]_2$

VIBRATIONAL BANDS cm^{-1}	ASSIGNMENT
540 (s)	νCu-Oasym.
480 (s)	Ligand vibration 11*
434 (s)	Ligand vibration 16a*
396 (m)	Ligand vibration 15*
360 (m)	δO-Cu-O ?
273 (s)	νCu-Clasym., "short"
238 (s)	νCu-Nasym.
190 (m)	νCu-Clasym., "long"
158 (m)	δCu-O, δCu-N?
130 (m)	δCu-Cl
84 (s)	δCu-Cl

s = strong   * based on reference (50)

m = medium
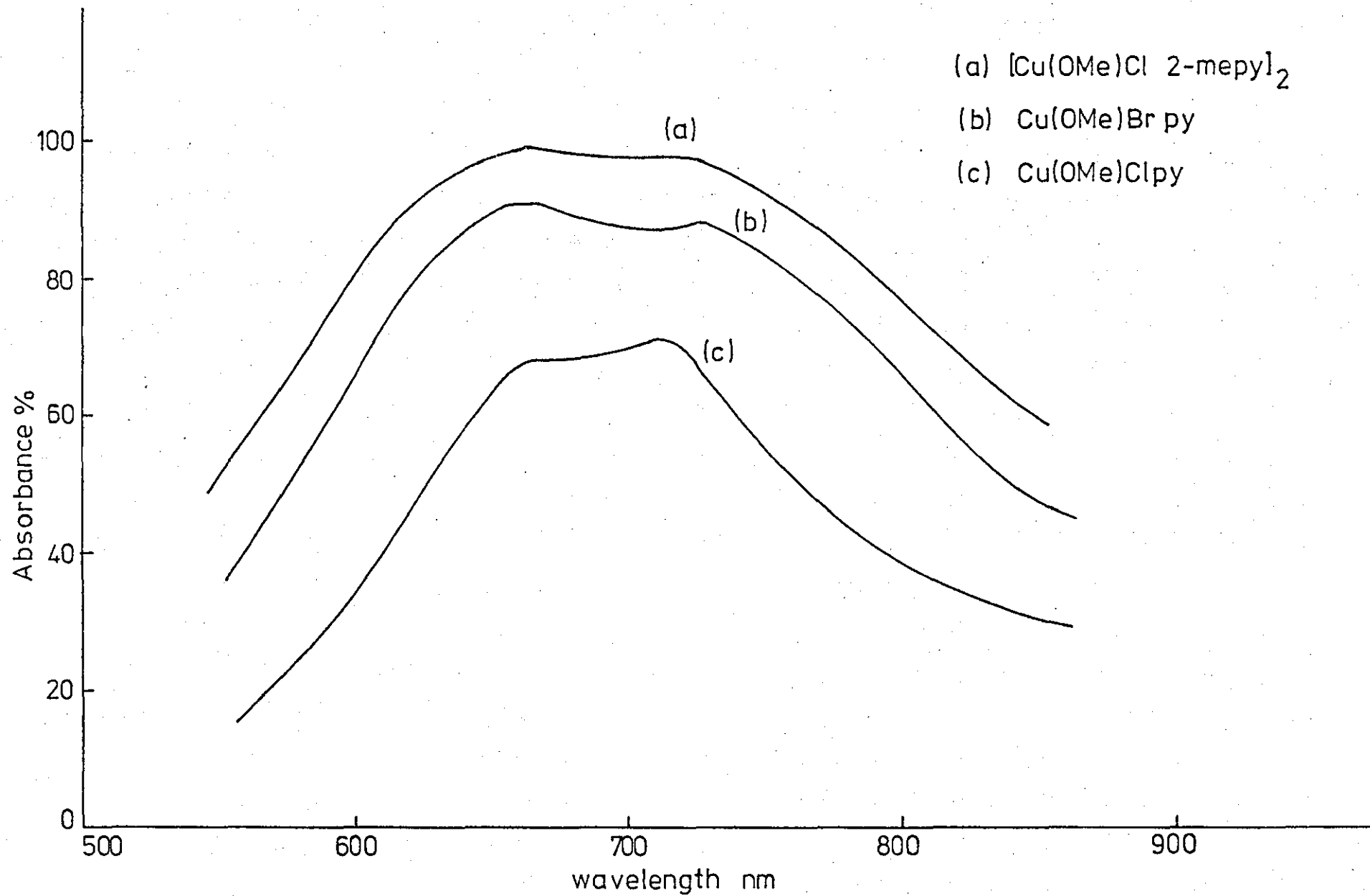
(a) [Cu(OMe)Cl 2-mepy]$_2$

(b) Cu(OMe)Br py

(c) Cu(OMe)Clpy

FIGURE 8.4. Reflectance spectra for methoxide complexes

The infrared spectrum of the complex ($4000 - 250$ cm^{-1}) showed the characteristic C-O band at 1015 cm^{-1} reported by Brubaker and Wicholas (23) and, in addition, bands at 525, 418 and 335 cm^{-1} which have not been reported before. On exposure to the atmosphere for a few minutes, hydroxide bands appeared in the infrared spectrum between 3300 and 3500 cm^{-1}, with a corresponding increase in copper and chloride percentages.

8.2.4 Oxidation of copper (I) chloride in solutions containing halide ions

The oxidation of copper (I) chloride was studied in alcohol solutions containing chloride (as tetramethylammonium chloride or zinc chloride) and bromide (as zinc bromide) ions, in order to obtain information on the conditions under which tetranuclear copper (II) complexes are formed. In addition, the oxidation of copper (I) chloride with chlorine in ethanol was studied.

(a) oxidation in the presence of $(CH_3)_4NCl$

Oxidation in the presence of tetramethylammonium chloride resulted in two products: one under anhydrous conditions and the other in the presence of water.

Anhydrous copper (I) chloride (0.01 mole) was slurried in anhydrous ethanol containing tetramethylammonium chloride (0.01 mole). The solution was stirred magnetically and dry oxygen passed through it for 12 hours. A brown complex formed, which reacted readily with atmospheric moisture and so was filtered using a filter stick, washed with anhydrous ethanol and diethyl ether and transferred to a dry-box for analysis. Analytical data for this complex are contained in table 8.12. The infrared spectrum showed, apart from the C-H and C-N bands of the tetramethylammonium cation, a medium intensity broad band at 1055 cm^{-1}, strong bands at 541 and 285 cm^{-1} and a weak band at 460 cm^{-1}.

TABLE 8.12

ANALYTICAL DATA FOR THE OXIDATION PRODUCTS OF COPPER (I) CHLORIDE -
TETRAMETHYLAMMONIUM CHLORIDE MIXTURES

	BROWN OXIDATION PRODUCT $[(CH_3)_4N]_2^+ Cu_4OCl_6(OEt)_2^{2-}$		ORANGE OXIDATION PRODUCT $[(CH_3)_4N]_4^+ Cu_4OCl_6^{4-} 2Cu_2(OH)_3Cl$	
	Found	Calc.	Found	Calc.
% Copper	35.28	35.24	37.42	37.70
% chloride	30.05	29.49	30.96	31.55
% nitrogen	4.1	3.9	4.1	4.2
% carbon	15.5	19.98	13.8	14.3
% hydrogen	4.3	4.8	4.1	4.1
$OH^- + O^{2-}$ meq./gm.	–	–	6.10	5.98

This reaction was repeated in ethanol (250 ml) containing water (2 ml), with aerial oxidation over a period of 24 hours. The product, an orange solid, was filtered washed with absolute alcohol followed by anhydrous diethyl ether, and dried in vacuo (2 torr) at 20°C. Analytical data are presented in table 8.12. It was found that the brown complex, formed by oxidation under anhydrous conditions reacted readily with atmospheric water vapour to produce an orange complex identical (analytical, x-ray and spectral data) to the orange product prepared in the presence of water. This orange complex had the stoichiometry $[(CH_3)_4N]^+Cu_2(OH)_2Cl_3^-$ and from x-ray powder diffraction and infrared spectral data (not listed) contained $[(CH_3)_4N]_4^+Cu_4OCl_{10}^{4-}$ and Paratacamite $Cu_2(OH)_3Cl$. Hence it can be formulated $[(CH_3)_4N]_4^+Cu_4OCl_{10}^{4-}:2Cu_2(OH)_3Cl$ (table 8.12).

This complex underwent a reaction with pyridine in ethanol to yield a buff coloured complex which from analytical, infrared and x-ray diffraction data was found to be $Cu_4OCl_64py:2Cu_2(OH)_3Cl$

Found, % Cu, 41.05: %Cl, 22.88: % C, 19.1: % H, 2.4: % N, 4.4.

Calc., % Cu, 41.45: %Cl, 23.13: % C, 19.6: % H, 2.1: % N, 4.6.

This reaction confirms the stoichiometry of the orange product, as a replacement of the axial chlorides in $Cu_4OCl_{10}^{4-}$ by pyridine may be expected by comparison with similar reactions discussed in Chapter Five. The low copper, chloride and carbon analyses in the orange and yellow complexes may be due to the presence of water, which is difficult to verify from the infrared spectrum due to the strong OH bands of Paratacamite present. In the analogous bromide system, copper (I) bromide oxidised in the presence of tetramethylammonium bromide, no reaction occurred.

(b) <u>oxidation in the presence of zinc halides</u>

Copper (I) chloride (0.01 mole) was slurried in absolute ethanol

(150 ml) containing zinc (II) chloride (0.01 mole) and pyridine

(0.015 mole). Oxygen was passed through the solution for one hour,

after which time a yellow complex had formed. The product was

filtered, washed with ethanol, followed by anhydrous diethyl ether and

dried in vacuo (2 torr) at 20°C. The product was identified by

analytical and infrared data as the tetranuclear complex

$Cu_4OCl_6$4py (Found % Cu, 31.66: % Cl, 26.40. Calc. %Cu, 31.80,

%Cl, 26.61. γCu-O, 577 cm^{-1}.

The reaction was repeated in an ethanol solution containing zinc(II)

bromide (0.0025 mole). The product was identified in a similar

manner, as the tetranuclear mixed halide complex $Cu_4OCl_4Br_2$4py.

(Found % Cu, 28.41: % Cl, 15.60: %Br, 18.17. Calc. % Cu, 28.62:

% Cl, 15.97: % Br. 17.99 γCu-Oasym. 563 cm^{-1}).

(c) <u>oxidation of copper (I) chloride with chlorine in ethanol</u>

In an attempt to produce a "Cu_4OCl_6" solution, copper (I)

chloride (0.005 mole) was slurried in ethanol (100 ml) containing

water (2 ml). The solution was stirred and chlorine gas passed

through it. An exothermic reaction occurred and the solution had to

be cooled to prevent boiling. After about half an hour, the

solution had turned yellow and all the solid dissolved. Pyridine

(5 ml in 25 ml ethanol) was added, which resulted in a further

exothermic reaction and a bright yellow precipitate. The yellow

complex was filtered, washed with ethanol and diethyl ether and

dried in vacuo (2 torr) at 20°C. The product appeared to be

$[CuCl_4]^{2-}[pyH]_2^+$ (found % Cu, 17.51: % Cl, 38.90. Calc. % Cu, 17.38:

% Cl, 38.79), and is presumably formed via the chlorination of

ethanol which would produce H^+ and Cl^- ions. The infrared spectrum

of this complex indicated the presence of the pyridinium ion, with
bands at 1632, 1614, 1600, 1525, and 1331 cm^{-1} which have been
assigned (51) to N-H deformational modes. An identical yellow
complex was subsequently prepared by the reaction between
copper (II) chloride dihydrate and pyridine hydrochloride in ethanol.

8.2.5 Miscellaneous experiments

(a) attempted preparation of a pyridine complex of copper hydroxychloride

Attempts were made to prepare a complex of stoichiometry
Cu(OH)Clpy, by the reaction of copper hydroxychloride with pyridine
under various reaction conditions.

Copper hydroxychloride (0.01 mole) was refluxed in pyridine
(200 ml) for several days. After the time, the solution remained
colourless and an infrared spectrum of the suspended solid
showed that it was unchanged Cu(OH)Cl.

In a further experiment, copper hydroxychloride (0.01 mole)
was placed in a pyrex tube containing pyridine (0.02 mole).
The tube was sealed and heated in a furnace to 200°C for 2 days.
After this time, the reaction products were examined and found to
consist of a large amount of metallic copper, a black tar and
some unreacted pyridine. No copper complexes could be isolated
from the mixture.

(b) attempted measurement of the reduction potential of $Cu_4OCl_6$4py

In conjunction with experiments concerning the oxidation of
copper (I) chloride complexes to form tetranuclear copper (II)
compounds, an attempt was made to measure the reduction potential
of $Cu_4OCl_6$4py. Comparisons with other copper (II) complexes could
then be made, which might produce relevant information with regard
to the possibility of tetranuclear complexes being involved in
catalytic oxidation reactions.

These studies were made in acetonitrile in which the complex
was moderately soluble, and which had a fairly high decomposition
potential. In an initial study, no reversible potential was
observed at : a platinum electrode for the complex, which would have
indicated a reversible potential for the system. The polarisation
curves for $Cu_4OCl_6 4py$ in acetonitrile were studied using a
Chemical Electronics TR70/2A potentiostat, hanging mercury drop and
lead electrodes, in an acetonitrile, solution containing sodium
perchlorate as a background electrolyte and with an $Ag/AgClO_4$
reference electrode. Linear potential sweeps were made and the
polarisation curves recorded on an X-Y plotter. No reduction
potential was observed for the tetranuclear complex before the
solvent decomposition.

8.2.6 Analytical procedures and reagents

Copper, halide, mixed halide, hydroxide and C, H and N analyses,
infrared spectra, reflectance spectra and X-ray powder diffraction
data, were obtained as previously described. In addition, the infrared
spectrum of $Cu(OMe)Brpy$ was recorded by the P.C.M.U. between 20 and
200 cm^{-1}, without polythene optics in order to determine accurately the
position of the band at about 80 cm^{-1}. Pyridine analyses were obtained
by utilising an absorption band in the U.V. spectra of solutions of
pyridine complexes in HCl. This band, at 255 nm, obeys Beer's Law and
so can be used to determine the amount of pyridine in the complex. In
practice, a sample of the complex (ca. 0.02 - 0.05 g) was dissolved
in concentrated hydrochloric acid (10 ml) and the solution made up to
one litre. The optical density of this solution was measured using a
Hilger spectrophotometer with matched 1 cm. silica cells. The amount
of pyridine in the complex could then be estimated by reference to a
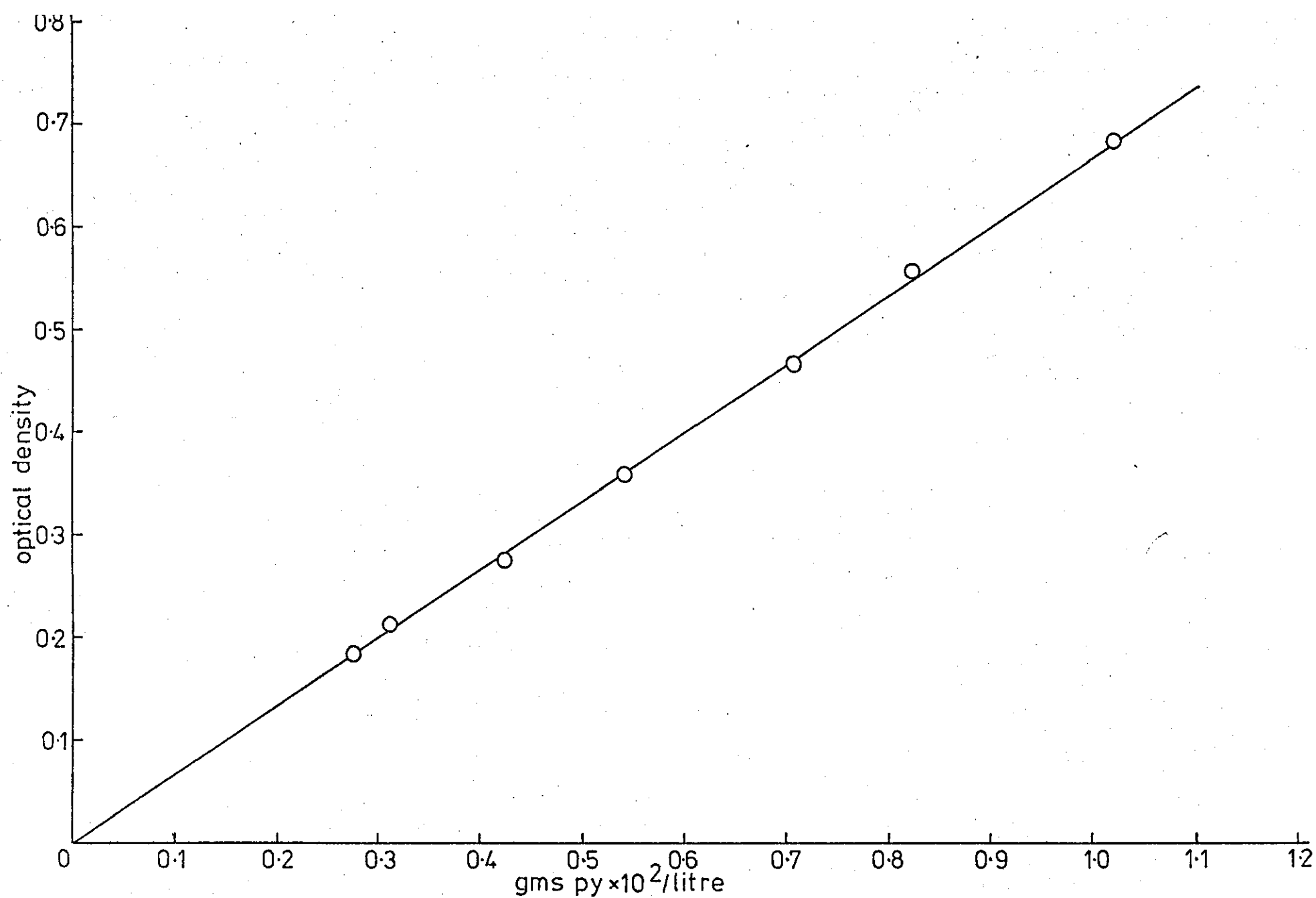calibration graph, which had been made using standard copper halide-

FIGURE 8. 5.   Calibration graph for pyridine analysis

pyridine complexes ($CuCl_2 2py$ and $CuBr_2 2py$). This graph is shown in figure 8.5. Water was determined by a standard method (172), using the Karl Fisher Reagent. Magnetic moments were determined by the Gouy method (173).
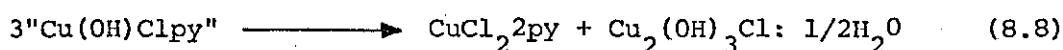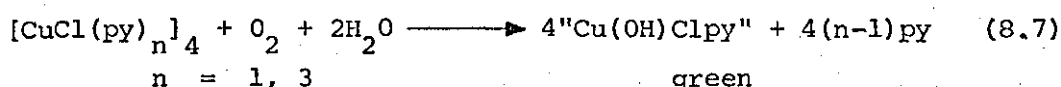
The copper reagents, tetramethylammonium halides and solutions were dried and/or purified as previously described. Gasses were dried by passing them through columns of molecular sieve type 5A. Anhydrous copper (II) chloride was prepared by the reaction of the dihydrate complex with thionyl chloride (174). The anhydrous pyridine (20 ppm water) used for the oxygen absorption experiments, was obtained by leaving the dry solvent in contact with molecular sieve type 4A for several months. All other reagents were of analytical grade and used without further purification.

8.3 Discussion

8.3.1 Oxidation of copper (I) halide – pyridine complexes and solutions

The oxidation of the complexes CuClpy, CuCl3py and CuBr3py with wet air proceeds fairly rapidly. The results of oxidation experiments (tables 8.1 – 8.4) indicate that the oxidation of both mono- and trispyridine complexes of copper (I) chloride results in the formation of similar copper (II) complexes. The oxidation of these two complexes is complete within about half an hour and data suggest that, although the products remain apparently unchanged for some time (up to about 16 hours), in the presence of wet air they eventually give rise to further hydrolysis products. Analytical data for the initial oxidation product (table 8.1) indicate a copper to chlorine ratio of 1:1, but x-ray powder diffraction data (table 8.2) show the presence of $CuCl_2 2py$ only. Infrared data (table 8.3) indicate the presence of hydroxide groups, with a strong OH band between 3600 and 3200 cm^{-1} and a band at 450 cm^{-1} which can be

assigned to a Cu-O vibration (discussed in Chapter Seven).

Consequently, a copper hydroxide complex is present in addition to

$CuCl_2 2py$, but it may be in an amorphous state and show only diffuse

x-ray powder diffraction lines which were not resolved by the

diffractometer. After a further reaction with water, data indicate that

the blue complex formed after about 64 hours reaction, consists of a

mixture of paratacamite, $Cu_2(OH)_3Cl$, and $CuCl_2 2py$ (tables 8.1 - 8.3).

The oxidation reaction was confirmed as involving 1/4 mole of oxygen per

mole of copper (I) chloride in the presence of water and, in addition,

this stoichiometry also applies under anhydrous conditions (figure 8.3).

Analytical data (table 8.1) are in agreement with a stoichiometry of

Cu(OH)Clpy for the green complex formed by the initial oxidation reaction,

and $CuCl_2 2py$: $Cu_2(OH)_3ClxH_2O$, x = ca. 1/2, for the blue complex formed

after about 64 hours contact with wet air. This leads to an overall reactio

scheme shown in equations 8.7 and 8.8 based on the assumption that the

copper (I) chloride-pyridine complexes can be formulated as tetramers

(discussed in Chapter Two).

$$[CuCl(py)_n]_4 + O_2 + 2H_2O \longrightarrow 4"Cu(OH)Clpy" + 4(n-1)py \quad (8.7)$$
$$n = 1, 3 \qquad \qquad green$$

$$3"Cu(OH)Clpy" \longrightarrow CuCl_2 2py + Cu_2(OH)_3Cl: 1/2H_2O \quad (8.8)$$

"Cu(OH)Clpy" can probably be formulated $CuCl_2 2py$: $Cu(OH)_2$

This scheme is in agreement with the weight gains and losses

reported in table 8.1: the theoretical weight changes and analyses

for this reaction scheme are shown in table 8.13. The weight losses for

the trispyridine complex are not in very good agreement with theoretical

values, which is probably due to the fact that the copper(I)-pyridine comple

contained only 2.94 pyridines per copper atom. The product from the

oxidation of copper (I) chloride in non-aqueous solutions (table 8.6)

was identical to the green oxidation product "Cu(OH)Clpy", and this

complex was probably the one isolated by Finkbeiner et al. (7) from
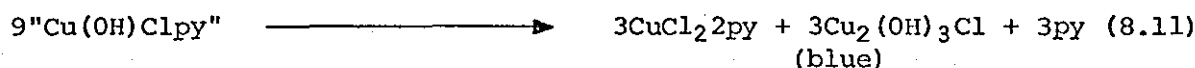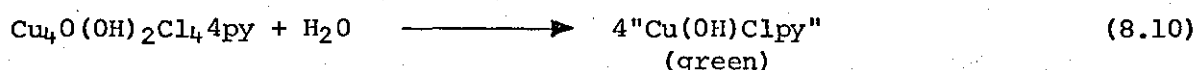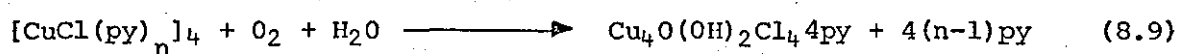
TABLE 8.13

THEORETICAL DATA FOR THE OXIDATION OF COPPER (I) HALIDE-PYRIDINE COMPLEXES

REACTION		REACTION CONDITIONS	WEIGHT CHANGE %	PRODUCT COMPOSITION		
				% COPPER	% HALOGEN	% PYRIDINE
$[CuClpy]_4 \longrightarrow$	$4"Cu(OH)Clpy"$	wet air	+ 9.6	32.57	18.17	40.54
$3[CuClpy]_4 \longrightarrow$	$4[CuCl_2 2py:Cu_2(OH)_3Cl\ 1/2H_2O]$	wet air	- 3.6	37.00	20.64	30.71
$[CuCl3py]_4 \longrightarrow$	$4"Cu(OH)Clpy"$	wet air	- 42.0	32.57	18.17	40.54
$3[CuCl3py]_4 \longrightarrow$	$4[CuCl_2 2py:Cu_2(OH)_3Cl\ 1/2H_2O]$	wet air	- 48.9	37.00	20.64	30.71
$[CuCl3py]_4 \longrightarrow$	$(CuCl_2 CuO)_2 5py$	dry oxygen	- 38.8	30.87	17.22	48.03
$[CuBr3py]_4 \longrightarrow$	$4"Cu(OH)Brpy"$	wet air	-37.1	26.52	33.35	33.02
$3[CuBr3py]_4 \longrightarrow$	$4[CuBr_2 2py:Cu_2(OH)_3Br\ 1/2H_2O]$	wet air	- 44.0	29.39	36.96	24.39

o-dichlorobenzene solution. A similar reaction scheme to that shown

in equations 8.7 and 8.8 can be applied for the oxidation of CuBr3py in

wet air, although this necessitates the inclusion of a hydrated product

$(CuBr_2 2py:Cu_2(OH)_3Br \ 1/2H_2O)$ which is unusual for copper (II) bromide

complexes. Reflectance spectra for these complexes (table 8.4) is

in agreement with the presence of $CuX_2 2py$ in the oxidation products,

but further information from these spectra is precluded by the broad

nature of the bands. The isolation of complexes with definite

stoichiometries from the products of the oxidation of copper (I)

halide-pyridine complexes, or from solutions containing copper (I)

chloride and pyridine is not always possible for, although these

oxidation products invariably have copper to chlorine ratios of 1:1,

they may contain non-stoichiometric amounts of pyridine caused by the

replacement of the amine by water. A similar situation was discussed

in Chapter Seven with respect to the hydrolysis of the tetranuclear

methanol complexes, which resulted in non-stoichiometric amounts of

methanol in the hydrolysis product.

Finkbeiner at al. (7) and Hay (16) reported that neither the

complex $CuCl_2 2py$ nor basic copper salts have catalytic activity for the

oxidative coupling of phenols, which implies that the products of

equations 8.7 and 8.8 are not the active catalysts. It is probable

that a complex is formed initially by the oxidation of copper (I)

chloride-pyridine compounds in the solid state or in solution, that

then reacts to produce the green complex of stoichiometry Cu(OH)Clpy.

In order to investigate this possibility, the oxidation of CuClpy was

studied by a gravimetric technique. The results of this experiment

(table 8.5) indicate that the initial oxidation involves one molecule

of oxygen and one molecule of water per four copper atoms (theoretical

weight gain equivalent to 50 m.wt. units). This initial weight gain

was followed by a loss in weight which eventually produced a blue complex.

The overall weight loss (4.8%) was similar to that observed for CuClpy

during other oxidation reactions (4.3%, table 8.1), and close to the

theoretical value of 3.6% (table 8.13). It is suggested on the basis

of these results that the oxidation of copper (I) chloride-pyridine

complexes and copper (I) chloride and pyridine in solution, proceeds

via the formation of a tetranuclear copper (II) complex, which will

contain mixed bridging chloride and hydroxide anions. This complex

then undergoes a rapid hydrolysis reaction, to produce the partially

amorphous complex "Cu(OH)Clpy", which will further react in the presence

of water to form $CuCl_2 2py$ and $Cu_2(OH)_3Cl$. This complete reaction

scheme is shown in equations 8.9 to 8.11 below.

$$[CuCl(py)_n]_4 + O_2 + H_2O \longrightarrow Cu_4O(OH)_2Cl_4 4py + 4(n-1)py \qquad (8.9)$$

$$Cu_4O(OH)_2Cl_4 4py + H_2O \longrightarrow 4"Cu(OH)Clpy" \qquad (8.10)$$
$$\text{(green)}$$

$$9"Cu(OH)Clpy" \longrightarrow 3CuCl_2 2py + 3Cu_2(OH)_3Cl + 3py \quad (8.11)$$
$$\text{(blue)}$$

$$n = 1 \text{ or } 3$$

The observed weight changes and product compositions for the

formation of the green and blue complexes of equations 8.10 and 8.11

above (table 8.1), are in good agreement with the theoretical data for

these reactions (table 8.13). However it was not possible to isolate

the tetranuclear complex $Cu_4O(OH)_2Cl_4 4py$, due to the very fast hydrolysis

reaction it apparently undergoes in the presence of water. This

hydrolysis reaction (equation 8.10) is similar to the hydrolysis of the

tetranuclear methanol complexes discussed in Chapter Seven, in which

the central oxygen atom of the Cu_4O cluster, reacts with one molecule

of water to form two hydroxide molecules. This reaction was not observed

(as a further weight increase) in the gravimetric studies on the oxidation of CuClpy (table 8.5). However, under these conditions, which were somewhat different (with respect to percentage oxygen and P_{H_2O}) to those employed in the oxidation experiments reported in Table 8.1, it is probable that the stages in the reaction represented by equations 8.10 and 8.11 were occuring almost simultaneously. Under these circumstances, loss of pyridine may well have masked the weight increase due to a reaction with water. The tetranuclear complex $Cu_4O(OH)_2Cl_44py$ is presumably present in pyridine solutions containing oxidised copper (I) chloride: however, an attempt to observe the $\nu Cu-O$ asym. band of this complex in such solutions was unsuccessful. If this band is as high as 600 cm^{-1}, it will be obscured by the strong vibration at 605 cm^{-1} in unco-ordinated pyridine, and so it may not be resolved in this solvent.

Although the oxidation of copper (I) halide-pyridine complexes under anhydrous conditions is not strictly relevant to the isolation of the catalyst complex (enough water is always present during the oxidative coupling of phenols to allow equation 8.9 to occur), these reactions have been studied. The two bromide complexes were not fully oxidised under these conditions. The oxidation of CuCl3py in dry oxygen results in a black/green complex, the infrared spectrum of which indicates that it probably contains $CuCl_22py$ and has copper-oxygen bands (a very broad band at 450 cm^{-1}). On the basis of analytical data and weight changes on oxidation (table 8.1), the complex can be formulated $(CuCl_2CuO)_25py$. Theoretical data is presented in table 8.13. There was some indication that the products from the oxidation of CuClpy under anhydrous conditions would undergo a reaction with water vapour, to yield the blue complex $CuCl_22py$: $Cu_2(OH)_3Cl$: $1/2H_2O$ produced by the oxidation with wet air. Consequently, the complex $(CuCl_2:CuO)_25py$

may not be a simple mixture of $CuCl_2 2py$ and CuO, but a more complex

polynuclear compound.

8.3.2   The structure of Cu(OMe)Clpy and Cu(OMe)Brpy

The catalyst complex of stoichiometry Cu(OMe)Clpy, prepared by

Finkbeiner at al. (7) by the oxidation of a copper (I) chloride-pyridine

mixture in methanol, has already been discussed in Chapter One, where

it was pointed out that the structure proposed for this complex was

not in agreement with what is now known concerning the co-ordination

chemistry of copper.   Recently, Roubaty et al. (26) reported a proton

NMR study of the complex and proposed the structure shown in figure 8.6.

There are several aspects of this latest paper which are unsatisfactory

not only in terms of the chemistry of copper, but with respect to

analytical data, NMR data and incorrect data concerning past papers.

Roubaty et al. reported that the complex obtained by the oxidation of

a copper (I) chloride-pyridine mixture in methanol, was an unstable,

diamagnetic compound of ill-defined stoichiometry (copper to chlorine

ratio 1:1 to 1:1.26).   They assigned a single peak at 9.95τ in the

proton NMR spectrum of the complex in dimethylformamide, to co-ordinated

pyridine, suggesting that the shift from the normal resonances at

1.50, 3.01 and 2.64τ for the α, β and γ protons, was due to the fact

that pyridine was π-bonded to the copper atoms, in a manner similar to

metallocene complexes.   The formation of this type of compound is

without substantiating evidence in the field of copper chemistry and,

from the point of view of the pyridine molecule which normally σ-bonds

through the lone pair of electrons on the nitrogen, is unlikely.   The

shift in the proton resonances of the cyclopentadiene anion on

co-ordination to form a "sandwich" type complex like ferrocene, is of

the order of $2-3\tau$ and a similar shift might be expected for the pyridine

protons in a purely π-bonded complex.   Roubaty et al. reported a shift

of 7 - 8τ for these protons and failed to satisfactorily explain why
they should appear as a single resonance. The apparent diamagnetic
characteristics of the complex were explained by the formation of a
copper-copper bond (figure 8.6) " similar to that in copper (II) acetate
dihydrate". However, the copper-copper interactions in this latter
complex results in a magnetic moment of 1.4 B.M. at room temperature (70).
No mention was made of the effect of the bridging oxygen atom on the
magnetic properties of the complex. Finally, Roubaty et al. reported no
infrared data for the complex and the work of Finkbeiner et al. and other
workers in the field of oxidative coupling reactions was misquoted.
It seems likely that the complex obtained by Roubaty et al. from
the oxidation of copper (I) chloride, bore little relation to that
described by Finkbeiner et al. (7) and this may have resulted in
anomalous NMR data which has been misinterpreted.

The complexes obtained in this investigation from the oxidation
of a copper (I) halide-pyridine mixture in methanol, have the
stoichiometry Cu(OMe)Xpy, X = Cl,Br (table 8.7). Infrared data
(table 8.9) and reflectance spectra (figure 8.4) indicate that they are
closely related to the complex [Cu(O)Me)Cl2-mepy]$_2$ reported by Gill
and Sterns (59), the crystal structure of which (25) was discussed in
Chapter One and is shown in figure 8.7. The infrared spectra of the
pyridine complexes (table 8.9) indicate that they contain the methoxide
group, having a band at 2,800 cm^{-1}(chloride) and 2805 cm^{-1} (bromide)
and a band at 1050 cm^{-1} (both complexes). These bands have been
assigned (59) to νC-H in O-CH$_3$ and νO-C in O-CH$_3$ respectively, and
appear at 2799 and 1055 cm^{-1} in the 2-methyl pyridine complex. There
were no bands in the region 3200-3600 cm^{-1} which might be assigned to
OH vibrations, indicating that the complexes contained no methanol.
The pyridine vibrational bands in these complexes appear in similar
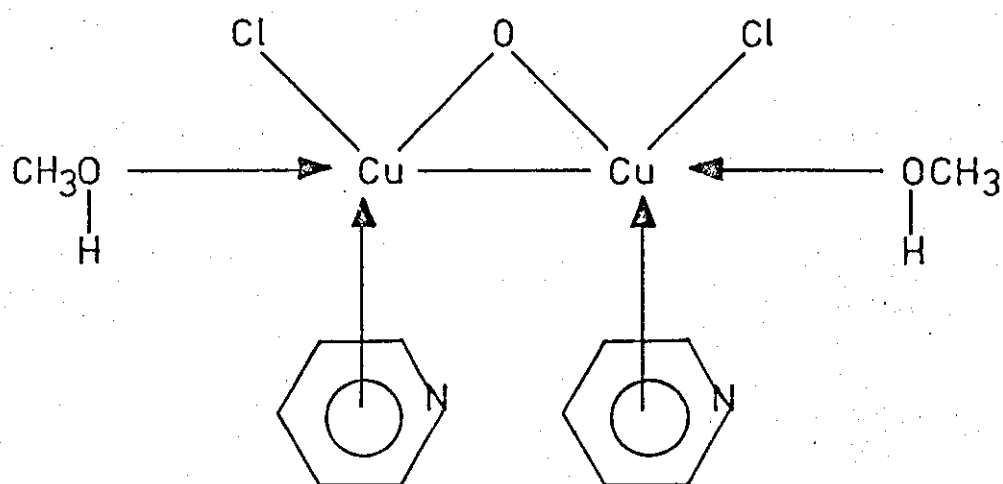positions to these bands in both the bispyridinedihalo copper (II)

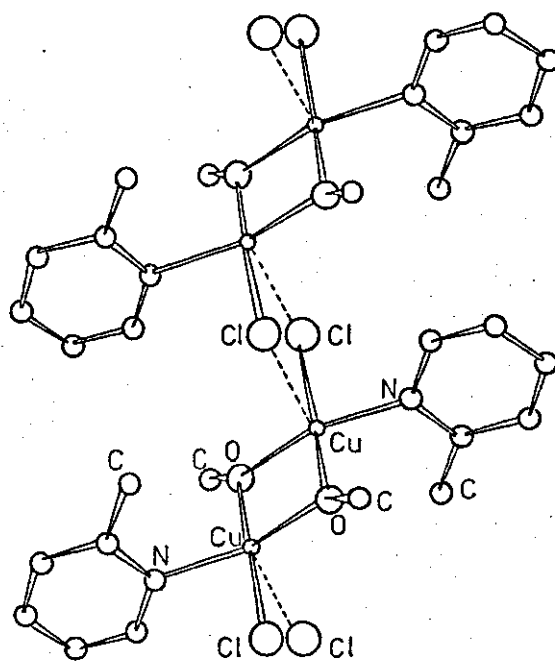FIGURE 8.6. The structure of the methoxide catalyst
(Roubaty et al.).

FIGURE 8.7 The crystal structure of [Cu(OMe)Cl2-mepy]$_2$
after M.Sterns. (25)

complexes and in the tetranuclear copper (II) complexes containing axial pyridine ligands (Chapter Four), which indicates that in these methoxide complexes, the pyridine is co-ordinated in a similar manner through the nitrogen. The magnetic moment of the two complexes (0.66 and 0.64 B.M.for chloride and bromide respectively), indicates that they contain bridging methoxide groups similar to those in $[Cu(OMe)Cl2-mepy]_2$, the magnetic moment of which was reported to be 0.62 B.M. (59). The reflectance spectra for the three methoxide complexes (figure 8.4) reveal that all three contain copper in a similar stereochemical environment; the 2-methylpyridine complex contains five co-ordinate copper in a distorted tetragonal pyramidal configuration (figure 8.9), and the pyridine complexes must contain copper atoms with a similar stereochemistry. The x-ray powder diffraction data (table 8.8), show that the two pyridine complexes are isomorphous, and some similarities to the powder pattern of the 2-methylpyridine complex can also be observed. However, all three complexes are not strictly isomorphous. Finally, the 2-methylpyridine complex can be prepared by the oxidation of copper (I) chloride - 2-methylpyridine mixtures in methanol in addition to the method of Gill and Sterns (tables 8.7 and 8.8).

From these data it is evident that the two pyridine complexes are structurally similar to the 2-methylpyridine complex, and it is proposed that the complexes Cu(OMe)Clpy and Cu(OMe)Brpy consist of centrosymmetrical dimeric units with bridging methoxide groups, the dimers being joined into infinite chains by long copper-halogen bonds.

The far infrared spectra of the two pyridine complexes and the 2-methylpyridine complex has been measured (tables 8.10 and 8.11), and assignments can be made for the observed vibrational bands in a similar manner to those made for the tetranuclear complexes (Chapter Six). On the assumption that all three methoxide complexes are structurally similar and can be considered as $Cu_2X_2Y_2L_2$ units (X = halide,

Y = OMe, L = amine), 18 vibrations may be expected. These molecules belong to the C_i point group and so the vibrations will consist of A_g species which are Raman active, and A_u species which will be infrared active. The molecules possess a centre of symmetry and so there will be no coincidences, which means that nine infrared bands should be observed and, in addition, the symmetrical stretching vibrations will be infrared inactive for the same reason. The complexes will show assymmetric stretching vibrations due to "long" (bridging) as well as "short" (terminal) Cu-X bonds. Similar "long" and "short" Cu-X bonds are present in complexes of stoichiometry $CuX_2 2L$, X = Cl,Br, L = py, 4-mepy, 1,4-dithiane, 1,2,4-triazole, semi-carbazide and thiosemicarbazide, (50, 139, 143). The "short"Cu-X vibrations have been assigned to bands at 270 - 330 cm^{-1} and 230-260 cm^{-1} for chloride and bromide complexes respectively, whilst the corresponding values for the "long" bonds are 220-270 cm^{-1} and 180 - 240 cm^{-1} (139, 143). In the methoxide complexes, νCu-X asym. for the short bond can be assigned to bands at 266 and 226 cm^{-1} in the chloride- and bromide-pyridine complexes and at 273 cm^{-1} in the 2-methylpyridine complex (tables 8.10 and 8.11). For the "long" Cu-X bonds, νCu-X asym. is assigned to bands at 212, 176 and 190 cm^{-1} for the three complexes.

The assymmetric Cu-0 stretching vibration has already been assigned to the strong band at 540 cm^{-1} in the 2-methylpyridine complex (59), and strong bands at 538 and 540 cm^{-1} in the pyridine complexes can be similarly assigned. This band appears at 525 cm^{-1} in the complex Cu(OMe)Cl prepared for comparative purposes. The strong band which appears at about 360 cm^{-1} in all three complexes is at too constant a frequency to be a copper-halogen vibration and too high for a copper-nitrogen vibration (discussed in Chapter Six). Consequently, it may be associated with a Cu-0 bending vibration.

This mode appears at 250 cm^{-1} in the complex Cr(OMe)$_3$ which also

contains bridging methoxy groups (175). A similar intensity band

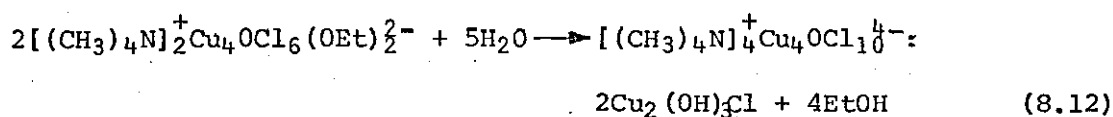appears at 335 cm^{-1} in Cu(OMe)Cl.

The Cu-N assymmetric stretching vibration can be assigned to

the strong band which appears at about 240 cm^{-1} in all three complexes,

due to its constant position. This is in agreement with the usual

frequency for this vibration in copper complexes (Chapter Six). The

weak to medium bands that appear about 160 cm^{-1} in all three

complexes can be assigned to either δCu-O or δCu-N vibrations. Due

to the uncertainty in the position of δCu-O (discussed in

Chapter Six), no definite assignment can be made for this band. The

remaining bands in these complexes have been assigned to bending or

deformation modes associated with Cu-X vibrations, due to their low

frequency and the $\frac{Cu-Br}{Cu-Cl}$ ratios.

The assignments of the vibrational bands for these three complexes,

support the postulate that they are all structurally similar, eight

bands were resolved for the two chloride complexes, and nine for the

bromide complex (the latter complex only was studied without

polythene optics, which gave improved resolution) and all bands could

be correlated except the weak band at 51 cm^{-1} in Cu(OMe)Brpy.

8.3.3 Oxidation of copper (I) chloride in the presence of halide ions

The oxidation of copper (I) chloride in the presence of halide

ions and a co-ordinating ligand, produces tetranuclear copper (II)

complexes as major reaction products. With tetramethylammonium chloride

in the presence of water, the product is a 1:2 mixture of

$[(CH_3)_4N]_4^+Cu_4OCl_{10}^{4-}$ and $Cu_2(OH)_3Cl$. In the absence of water, the reaction

is more complicated. The product may again contain the tetranuclear

decachloride complex with infrared bands at 951 cm^{-1} (C-N), 541 cm^{-1} (Cu-O)

and 285 cm^{-1} (axial Cu-Cl). In addition, a broad band at 1055 cm^{-1} with

a shoulder at about 1020 cm^{-1} can be assigned to the νC-O vibration,
which has been observed in copper ethoxide and ethoxychloride
complexes (23). Analytical data (table 8.12) suggest the stoichiometry
$[(CH_3)_4N]_2^+Cu_4OCl_6(OEt)]^{2-}$ for this oxidation product. The poor carbon
and hydrogen analyses (table 8.12) were probably due to the fact that
the complex reacts readily with atmospheric water vapour, to form a
1:2 mixture of the decachloride complex and Paratacamite, with
presumably the loss of ethanol. The C,H and N analyses were obtained
outside this laboratory, and any precautions that were taken to avoid
contact with the atmosphere were apparently unsuccessful. Nitrogen
analysis, which would be relatively unaffected by this hydrolysis
reaction, indicates a copper to nitrogen ratio of 4:2.1 which is in
agreement with theoretical data (within experimental error). The
stoichiometry proposed for this complex is in agreement with its
reaction with water vapour shown in equation 8.12 below

$$2[(CH_3)_4N]_2^+Cu_4OCl_6(OEt)]^{2-} + 5H_2O \longrightarrow [(CH_3)_4N]_4^+Cu_4OCl_{10}^{4-}:$$

$$2Cu_2(OH)_3Cl + 4EtOH \qquad (8.12)$$

Copper alkoxides and alkoxyhalides react readily with water vapour
to form copper hydroxide compounds (cf. the methoxide complexes in
8.3.2 above and references 23, 24 and 176). Until further information
is available (such as x-ray powder diffraction and magnetic data), it
remains uncertain whether this oxidation product is a mixture of the
tetranuclear decahalide complex and a copper ethoxide compound, or
whether it could be a tetranuclear complex containing bridging ethoxide
groups and axial chloride atoms.

The results of the oxidation of copper (I) chloride in the
presence of zinc halides, indicate that under reaction conditions in
which a copper to halogen ratio of at least 1:1.5 is present, tetranuclear
copper (II) complexes are the major reaction products.

The attempted preparation of a pyridine complex of copper hydroxychloride (8.2.5.above), indicates that the copper reactant or product may have too great a lattice energy for a reaction to occur with pyridine in solution, but that at high temperatures and pressures some reaction takes place: it may be possible that under the right conditions, the tetranuclear complex $Cu_4O(OH)_2Cl_4 4py$ postulated above could be isolated from reactions involving copper hydroxychloride and pyridine.

The failure to observe a reduction potential for the complex $Cu_4OCl_6 4py$ (8.2.5 above) may be due in part to difficulties experienced whilst working in a non-aqueous solvent such as acetonitrile. The copper complex was not very soluble in acetonitrile (ca. 6%) and the mercury electrode did not function correctly, due to the tendency of the solvent to "creep" up the capillary and separate the mercury thread. It is possible that more meaningful results could be obtained in other non-aqueous solvents.

8.4 Conclusions

The oxidation of copper (I) chloride in the presence of halide ions leads to the formation of tetranuclear copper (II) complexes. The oxidation of copper (I) halide-pyridine complexes both in the solid state and as well as in solution, appears to yield similar products. Some evidence is offered which suggests that this oxidation proceeds via a tetranuclear complex of stoichiometry $Cu_4O(OH)_2Cl_4 4py$, which then undergoes a further reaction with water to yield $CuCl_2 2py$ and a basic copper salt; a reaction which so far has precluded the possibility of isolating the tetranuclear complex. This complex is in all probability the active catalyst species in the copper catalysed oxidative coupling of phenols, and will be discussed in relation to these coupling reactions

in Chapter Ten. The analogous copper (I) bromide-pyridine system

appears to undergo a similar oxidation reaction.

In addition, the structure of the catalyst complex Cu(OMe)Clpy

has been resolved along with the analogous bromide complex, and shown

to have a similar dimeric structure to that of [Cu(OMe)Cl2-mepy]$_2$.

This catalyst complex will also be discussed in Chapter Ten.

CHAPTER NINE

FURTHER STUDIES ON MIXED HALIDE COMPLEXES OF COPPER (II)

9.1 Introduction

It was mentioned in Chapter Three that the addition of a stoichiometric amount of pyridine to an ethanolic "Cu_4OCl_6" solution, produced a mixture of Cu_4OCl_64py, $CuCl_22py$ and $Cu_2(OH)_3Cl$. A similar reaction involving a "$Cu_4OCl_3Br_3$" solution was attempted in order to prepare the mixed halide complex CuClBr2py. It was necessary to avoid the production of large quantities of the tetranuclear or hydroxide species during this preparation, and so several different reaction conditions were used. The best results were obtained by a reaction between $Cu_4OCl_3Br_34py$ and pyridine in methylethylketone at $-78°C$, which produced a bright green complex containing only small amounts of these two species (as indicated by the infrared spectrum). The bispyridine dihalo copper (II) complexes are usually purified by recrystallisation from DMF solution, and a similar method was used for the green complex prepared from $Cu_4OCl_3Br_34py$. This, however, resulted in a bright green crystalline solid which did not contain a 1:1 chlorine to bromine ratio. Under these circumstances, it was decided to investigate the recrystallisation of 1:1 mixtures of $CuCl_22py$ and $CuBr_22py$, in order to ascertain whether the difference in the solubility of the two species resulted in a crystal mixture containing a greater proportion of either one. The results of these studies are described in this chapter, as well as an attempt to prepare CuClBr2py from an ethanolic solution of "CuClBr": the preparation of this latter species was described in Chapter Four.

9.2 Experimental and results

9.2.1 Preparation from $Cu_4OCl_3Br_34py$

$Cu_4OCl_3Br_34py$ (0.005 mole) was slurried in methylethylketone
(200 ml) containing pyridine (0.05 mole). The solution was maintained at
-78°C with stirring for one hour. After this time, a bright green complex
had formed which was filtered, washed with ethanol and dried in vacuo.
An infrared spectrum of this solid showed that it contained some
unreacted tetranuclear complex and, in addition, a hydroxide compound.
About 2g of the solid was dissolved in DMF (20 ml) at 100°C and
recrystallised by allowing the solvent to evaporate over a period of
several days. The product, a bright green crystalline solid, was
washed with ethanol followed by diethylether and dried as above.
The complex had the stoichiometry $Cu_4Cl_5Br_38py$.

9.2.2 Preparations from $CuCl_22py-CuBr_22py$ mixtures

Copper (II) chloride dihydrate (0.05 mole) and copper (II) bromide
(0.05 mole) were dissolved in ethanol (500 ml) and pyridine (0.3 mole
in 100 ml EtOH) added with stirring. A khaki solid precipitated which
was filtered, washed with ethanol and diethyl ether and dried in vacuo
as above. X-ray powder diffraction data indicated that the khaki solid was
a mixture of $CuCl_22py$ and $CuBr_22py$.

A portion of this solid (ca. 5 gms) was dissolved in DMF (50 ml)
at 100°C and allowed to crystallise slowly at room temperature for
about 2 hours. The crystalline product was then filtered and washed
with ethanol and diethyl ether and dried as above. A bottle green solid
crystallised as 1 cm needles with a stoichiometry $Cu_3Cl_4Br_26py$. A
microscopic examination of the crystals showed no evidence for the
separate existence of $CuCl_22py$ (blue needles) and $CuBr_22py$ (green needles).

A further 5 gms of khaki solid was dissolved in DMF at 100°C
and recrystallised quickly by lowering the ambient temperature to 0°C.

The product, a bright green crystalline solid, was washed and dried

as described above, and had a stoichiometry $Cu_5Cl_6Br_4$10py. The complex

had crystallised as 2 mm needles and a microscopic examination again

showed no $CuCl_2$2py or $CuBr_2$2py.

9.2.3 Preparation from "CuClBr"

It was mentioned in Chapter Four that a pure sample of CuClBr had not

been prepared by the method of Batsanov et al. (102), which involved

the oxidation of copper (I) chloride by bromine in ethanol. This

failure may have been due to the further reaction of CuClBr with excess

bromine present, which may occur during the evaporation stage of the

preparation when the concentration of bromine and CuClBr will be very

high. Consequently, it was considered likely that a complex of

stoichiometry CuClBr2py could be prepared by adding pyridine to the

ethanolic solution immediately after the oxidation reaction.

Copper (I) chloride (0.01 mole) was slurried in ethanol (200 ml)

containing bromine (0.0075 mole). The solution was stirred and slowly

turned brown. After 40 minutes, it was filtered to remove any

unreacted CuCl, and pyridine (0.025 mole in 50 ml EtOH) added with

vigorous stirring. A green complex precipitated and was filtered and

washed with ethanol and diethyl ether, and dried as above. The

product had the stoichiometry CuClBr2py.

Analytical data for all the complexes described above are

contained in table 9.1. X-ray powder diffraction lines for the

complexes (except $Cu_4Cl_5Br_3$8py) are listed in table 9.2. The

reflectance spectra for these mixed halide complexes all showed one

broad band with maxima about 675 nm. $CuCl_2$2py and $CuBr_2$2py also

show one broad absorption band at 695 and 700 nm respectively. The

infrared spectra of the mixed halide complexes showed the presence of

co-ordinated pyridine, with the vibrational bands at almost identical

TABLE 9.1

ANALYTICAL DATA FOR MIXED HALIDE COMPLEXES

Complex	Analyses						
	% Copper		% Chloride		% Bromide		Cu:Cl:Br
	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cu_4Cl_5Br_3 8py$	18.88	19.49	13.23	13.59	19.08	18.39	4:5.0:3.2
$Cu_3Cl_4Br_2 6py$	19.73	19.72	14.70	14.67	16.30	16.53	3:4.0:2.0
$Cu_5Cl_6Br_4 10py$	19.20	19.36	13.12	12.96	19.28	19.48	5:6.0:4.0
$CuClBr2py$	18.64	18.85	10.06	10.52	24.00	23.71	1:1.0:1.0

TABLE 9.2

X-RAY POWDER DIFFRACTION DATA FOR MIXED HALIDE COMPLEXES, $CuCl_2 2py$ AND $CuBr_2 2py$

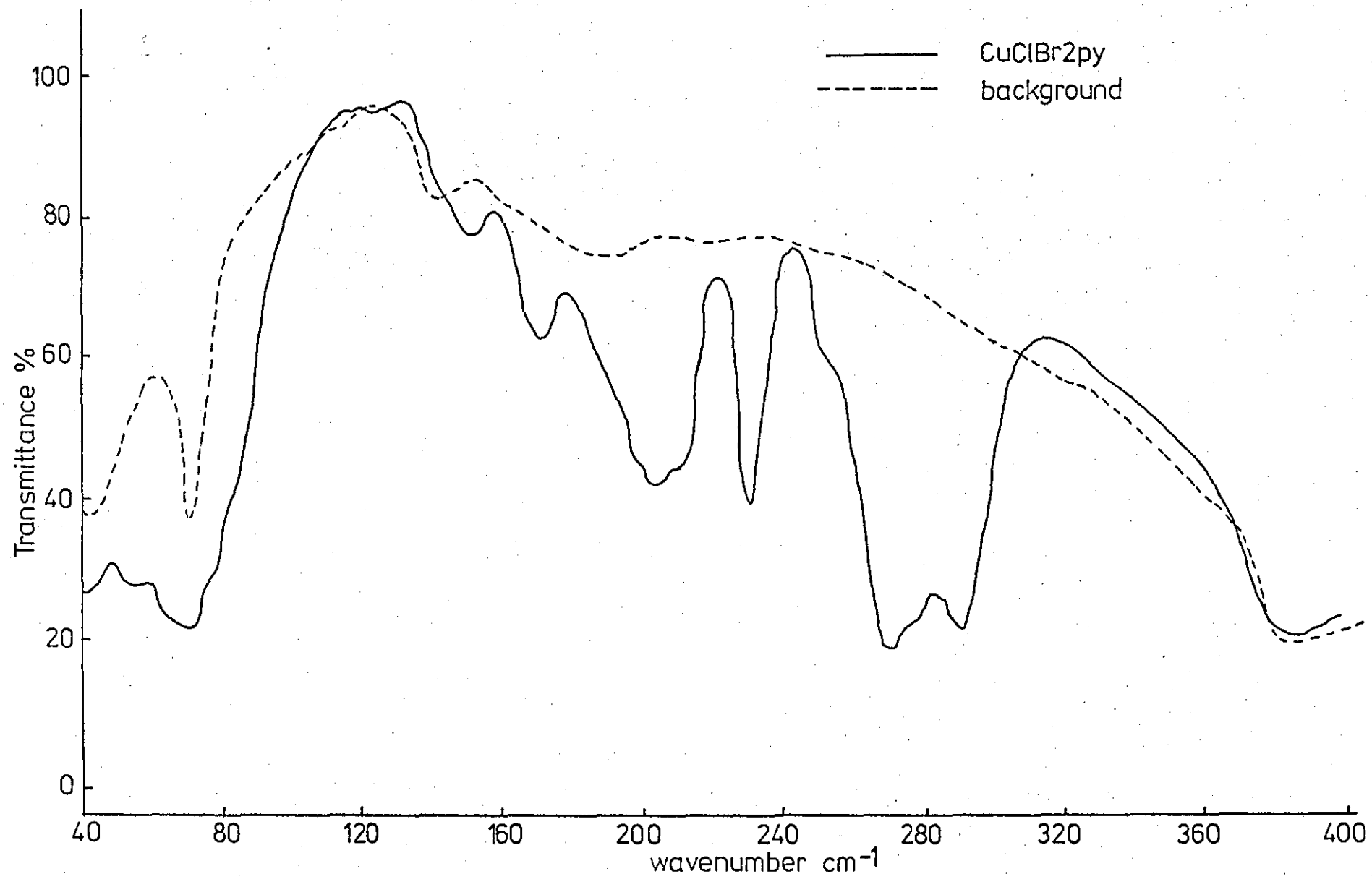| CuCl₂2py		CuBr₂2py		Cu₃Cl₄Br₂6py		Cu₅Cl₆Br₄10py		CuClBr2py	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
8.45	80	8.80	100	8.59	60	8.57	40	8.76	100
7.60	100	7.54	80	7.72	100	7.70	100	7.52	15
6.07	10	6.05	2	6.10	2	6.10	5	4.77	15
4.74	30	4.80	10	4.77	20	4.78	5	4.35	2
4.14	10	4.44	2	4.18	10	4.19	10	4.03	2
3.82	15	4.17	2	3.85	20	3.85	15	3.86	20
3.80	15	4.06	5	3.52	5	3.50	2	3.63	2
3.46	5	3.90	15	3.45	15	3.45	15	3.38	5
3.41	10	3.74	2					3.33	1
3.24	2	3.40	10						
3.08	2	3.20	2					3.14	5
3.01	5	3.05	2	3.00	2			3.00	5
2.94	2	3.03	2	2.89	5	2.90	2	2.91	10
2.87	2	2.97	2						
2.83	2	2.93	5						
2.75	5	2.75	2			2.66	2	2.67	5
2.66	2	2.69	5						
		2.65	2	2.53	5	2.54	2	2.54	5
		2.59	2						

FIGURE 9.1. The far infrared spectrum of CuClBr2py

frequencies to those in the bispyridine dihalo copper (II) complexes

(Chapters Two and Four). There is little difference between the frequency

of the pyridine ring vibrations in $CuCl_2 2py$ and $CuBr_2 2py$ (table 2.2),

and these vibrations in the mixed halide complexes generally lie in-

between those in the dichloro and dibromo complexes. The far infrared

spectrum of the complex CuClBr2py is shown in figure 9.1. The only

other far infrared spectrum that has been measured is that of $Cu_4Cl_5Br_3 8py$

which was identical to that of CuClBr2py. Band assignments for CuClBr2py

vibrations are contained in table 9.3 along with the assignments made for

the vibrational bands of $CuCl_2 2py$ and $CuBr_2 2py$, which have been

reported by Goldstein et al. (50).

Copper and mixed halide analyses, infrared and reflectance

spectra and x-ray powder diffraction data were obtained as previously

described. All copper reagents and solvents were purified and/or

dried by methods described in previous chapters.

9.3   Discussion

The reaction between an ethanolic solution of copper (II) chloride,

copper (II) bromide and pyridine, results in the precipitation of a

khaki complex that is readily identified by x-ray powder diffraction

data, to be a mixture of $CuCl_2 2py$ and $CuBr_2 2py$. However, the

recrystallisation of this mixture from DMF solution results in the

formation of complexes that are not simple crystal mixtures of the two

bispyridinedihalo copper (II) species, although they are apparently

isomorphous with these compounds (table 9.2). The chlorine to bromine

ratio of these mixed halide complexes (table 9.1) depends on the rate

of crystal formation, which itself is controlled by the rate of cooling

of the solution. This suggests that the composition of the product is

controlled by the solubilities of individual chloride and bromide

complexes in solution and hence, the products may be polymeric mixtures

TABLE 9.3

INFRARED BAND ASSIGNMENTS FOR CuClBr2py, CuCl$_2$2py and CuBr$_2$2py

CuClBr2py cm^{-1}	CuCl$_2$2py cm^{-1} (50)	CuBr$_2$2py cm^{-1}(50)	Assignment (50)
290, 252	287	256	νCu-Xasym"short"
270, 274	266	268	νCu-Nasym.
233, 210	229	204	νCu-Xasym."long"
204, 196	200	196	δCu-N
171, 150	177	132	δCu-X
80, 55	90	60	δCu-X

of $CuCl_2 2py$ and $CuBr_2 2py$ units. The formation of this type of mixed halide complex has not been reported before, but can be correlated with a recent investigation by Bell et al. concerning x-ray diffraction studies on aqueous copper (II) chloride solutions (177). They found that the copper complexes present in aqueous solutions of copper (II) chloride, depended on the solute concentration, and that in 3.18 and 4.35M $CuCl_2$, the major species present were $Cu_3Cl_6 8H_2O$ and $Cu_5Cl_{10} 12H_2O$ respectively. Similar polymeric complexes with bridging chloride atoms have already been established in the crystalline state, with complexes such as $Cu_3Cl_6 2MeCN$, $Cu_5Cl_{10} 2C_3H_7OH$ and $Cu_2Cl_4 2MeCN$ (178). An analogous situation could exist in the present system, where polymeric $CuCl_2 2py$ and $CuBr_2 2py$ units may be present in DMF solution and, on crystallisation, this leads to the formation of a polymer containing a mixture of individual $CuCl_2 2py$ and $CuBr_2 2py$ units [the bispyridinedihalo copper (II) complexes themselves have been shown to be polymeric in the solid state, the copper atoms being joined into infinite chains by "long" and "short" Cu-X bonds (179, 180)]. These individual units may be present as mixtures of monomers, dimers, trimers etc., resulting in a variety of possible stoichiometries, with individual units joined into polymeric chains by mixed chloride-bromide bridges. The other possibility for the structure of these mixed halide complexes, arises from the fact that the bispyridinedihalo copper (II) complexes might be completely dissociated in DMF solution, leading to a crystalline complex containing a random distribution of chloride and bromide ions. This, however, might be expected to result in the formation of complexes in which the chlorine to bromine ratio was non-integral unless very large repeat units were considered and, as this does not appear to be the case with these present mixed halide complexes, it is considered that a structure of this type is unlikely.

The complex CuClBr2py, prepared from an ethanolic CuClBr solution, may contain mixed $CuCl_2 2py$ and $CuBr_2 2py$ structural units or alternatively CuClBr2py units, The far infrared spectrum of this complex (figure 9.1), shows vibrational bands which can be correlated with the assignments made for $CuCl_2 2py$ and $CuBr_2 2py$ (table 9.3). The copper-nitrogen vibrations associated with both dichloro and dibromo complexes appear to be present in the mixed halide complex, which may indicate that $CuCl_2 2py$ and $CuBr_2 2py$ units, rather than CuClBr2py units, are present, since the latter structure might not be expected to exhibit vibrational bands due to two different Cu-N bonds. In addition, both CuClBr2py and $Cu_4Cl_5Br_3 8py$ have identical infrared spectra which indicates similar structural units.

This investigation raises doubts concerning the validity of the conclusions reached by Batsanov et al. (102) on the composition of CuClBr. From the data reported by these workers, the complex they prepared could contain either polymeric CuClBr units or polymers consisting of $CuCl_2$ and $CuBr_2$ units. If the latter structure were present, the complex cannot be considered to be a true mixed halide compound, as this would contain individual copper atoms joined to both chlorine and bromine atoms by " short" Cu-X bonds.

Further studies concerning this phenomenon of mixed crystallisation are required in order to clarify the conditions under which various mixed halide complexes can be isolated, and to determine the nature of the structural units present.

CHAPTER TEN

CONCLUSIONS

In Chapter Eight it was postulated that the tetranuclear

copper (II) complex $Cu_4O(OH)_2 X_4 4py$ X = Cl,Br containing mixed halide-

hydroxide bridging anions, was the initial reaction product from the

oxidation of copper (I) halide-pyridine complexes in the presence of

water. It was also suggested that this tetranuclear complex was an

active catalyst in phenolic coupling reactions. In this chapter,

these postulates are discussed in terms of the tetranuclear complexes

themselves and also with respect to their rôle in the phenolic

oxidative coupling reactions. In addition, some suggestions are made

for further work in this particular field of copper chemistry.

10.1   Tetranuclear copper (II) complexes containing mixed bridges

The existence of stable tetranuclear copper (II) complexes

containing mixed bridging halides has been reported in Chapters Four

and Five and, in addition, some evidence was presented from exchange

reactions that the tetranuclear cluster will tolerate the presence of

hydroxyl groups. Copper complexes containing bridging hydroxide groups

are well known and hence the existence of the complex $Cu_4O(OH)_2X_4 4py$ is

in accord with what is now known of the co-ordination chemistry of

copper. Throughout this investigation, tetranuclear copper (II) complexes

have been shown to be common products from the oxidation of copper (I)

halides (mainly the chloride), usually in the presence of excess

halide ions and in alcohol solution. It has been suggested that the

mechanism of formation of these complexes from copper (II) halides,

involves the condensation of dimeric hydroxy bridged copper complexes

(Chapter Three and reference 61). It was observed during the preparation

of tetranuclear complexes from both copper (I) and copper (II) chloride,

that copper hydroxide complexes, noticeably $Cu_2(OH)_3Cl$, were obtained

as bi-products (Chapters Three and Eight). It is possible that

tetranuclear copper complexes containing hydroxide or alkoxide groups

are formed as intermediates in both these preparations. In the case of

the oxidation of copper (I) chloride in the presence of halide ions in an alcohol-pyridine solution (8.2.4), a redox reaction involving water or solvent molecules may lead to the formation of tetranuclear complexes such as $Cu_4O(OR)_2Cl_4 4py$ where R = H or Et. An anionic exchange (Cl^- for OR^-) would then produce the hexahalide complex (or mixed halide, with Br^- in solution). A tetranuclear ethoxide complex of similar stoichiometry may have been isolated from the oxidation of copper (I) chloride in ethanol, in the presence of tetramethylammonium chloride (Chapter Eight).

The preparation of, for example, an ethanolic "Cu_4OCl6" solution from $CuCl_2 2H_2O$ and CuO, may involve the formation of dimeric hydroxy bridged copper complexes, as suggested by Belford et al. (61). Two of these hydroxide units could then lose water to form a complex such as $Cu_4O(OH)_2Cl_4 4EtOH$ which would undergo anionic exchange with the excess chloride ions present, to form $Cu_4OCl_6 4EtOH$. For preparations involving anhydrous reagents, the intermediate species is again probably a tetranuclear alkoxide complex. It was mentioned in Chapter Eight that the oxidation of copper (I) chloride in the presence of water vapour may also be considered as proceeding via the formation of a tetranuclear complex such as $Cu_4O(OH)_2Cl_4$ (equations 8.3 to 8.5).

The oxidation of copper (I) halide-pyridine mixtures to form tetranuclear compounds such as $Cu_4O(OH)_2Cl_4 4py$ (Chapter Eight), has been substantiated by indirect evidence only. The kinetics of this reaction have not been studied, but several workers have suggested that the reaction is second order with respect to copper concentration (9, 37), based on the kinetics reported by Ruthven and Kenney for the oxidation of copper (I) chloride in melts (36). The oxidation scheme proposed in this investigation would require the reaction to be fourth order with respect to copper concentration. However, the conclusion

reached by Ruthven and Kenney for the oxidation in melts of sodium and lanthanum chloride, need not necessarily apply in the presence of pyridine and water, especially considering that a similar oxidation in a melt of K_2CuCl_4 results in the tetranuclear complex $K_4^+ Cu_4OCl_{10}^{4-}$ (62).

In Chapter Two it was mentioned that the molecular weight of copper (I) halides in pyridine had been measured in these laboratories and results indicated that tetrameric or higher units were present. Further studies (54) showed that when oxygen was allowed to react with a copper (I) chloride-pyridine solution, the molecular weight of the species in solution increased from 484 to 524, an indication that the oxidised species is also polymeric in nature: the change from "$(CuCl)_4$" to "$Cu_4O(OH)_2Cl_4$" corresponds to a molecular weight change from 396 to 446.

Further studies on the oxidation of copper (I) halide-pyridine solutions and complexes will be needed to confirm the existence of the tetranuclear species $Cu_4O(OH)_4X_4 4py$ and related compounds. The isolation of a complex such as $Cu_4O(OH)_2Cl_4 4py$ may be possible from the oxidation of copper (I) chloride-pyridine complexes in the solid state, in the presence of a stoichiometric amount of water vapour (one mole of $CuCl_npy$ to one quarter of a mole of water). This, however, will require a stringent control of the reaction conditions. It may also be possible to isolate tetranuclear copper complexes containing mixed halide-hydroxide bridges by exchange reactions similar to those described in Chapter Five. This would involve the reaction between, for example, an alcoholic tetramethylammonium hydroxide solution and $[(CH_3)_4N]_4^+ Cu_4OBr_{10}^{4-}$ in alcohol, with subsequent removal of the solvent or addition of pyridine to produce the tetranuclear complex. A similar reaction involving tetramethylammonium thiocyanate or cyanate could lead to the isolation of cluster complexes containing other bridging anions.

10.2 $Cu_4O(OH)_2Cl_44py$ as an oxidative catalyst

The proposed reactions scheme for the oxidative C-O

coupling of substituted phenols, involving the tetranuclear complex

$Cu_4O(OH)_2Cl_44py$ as the active catalyst species, is shown in figure 10.1.

The scheme is basically similar to that proposed by Price and Nakaoka (9)

for disubstituted phenols and Smith (37) for thiophenols, in that

it is a four stage cyclic reaction which will be mechanistically

similar to enzymic oxidation reactions (Chapter One). The proposed

oxidation mechanism is discussed in terms of the most common catalyst

used, namely a copper (I) chloride-pyridine mixture.

The copper (I) complex (figure 10.1) is shown in tetrameric

form(from the arguments discussed in Chapter Two) with one or three

molecules of co-ordinated pyridine per copper atom depending on the

pyridine to copper ratio in the solution, thus producing four or six

co-ordinate copper complexes. It was noted by Tsuchida et al. (10)

that the maximum rate of oxygen consumption of a copper (I) halide-

pyridine mixture, occured at a pyridine to copper ratio of 3:1.

This is in accord with the observations reported in Chapter Two

concerning the relevant oxidation rates of mono and trispyridine

complexes of copper (I) halides. In the presence of oxygen and water,

the copper (I) complex oxidises forming the tetranuclear complex

$Cu_4O(OH)_2Cl_44L$, the axial ligands (L) can be either pyridine, or

solvent molecules if the latter has sufficiently strong donor properties.

In the presence of an excess of phenol monomer, the axial ligands are

replaced by phenol molecules and the tetranuclear species thus

formed undergoes a redox reaction forming a copper (I) complex with

co-ordinated phenoxy radicals. The reduction of copper (II) to

copper (I) probably results in the formation of four phenol radicals

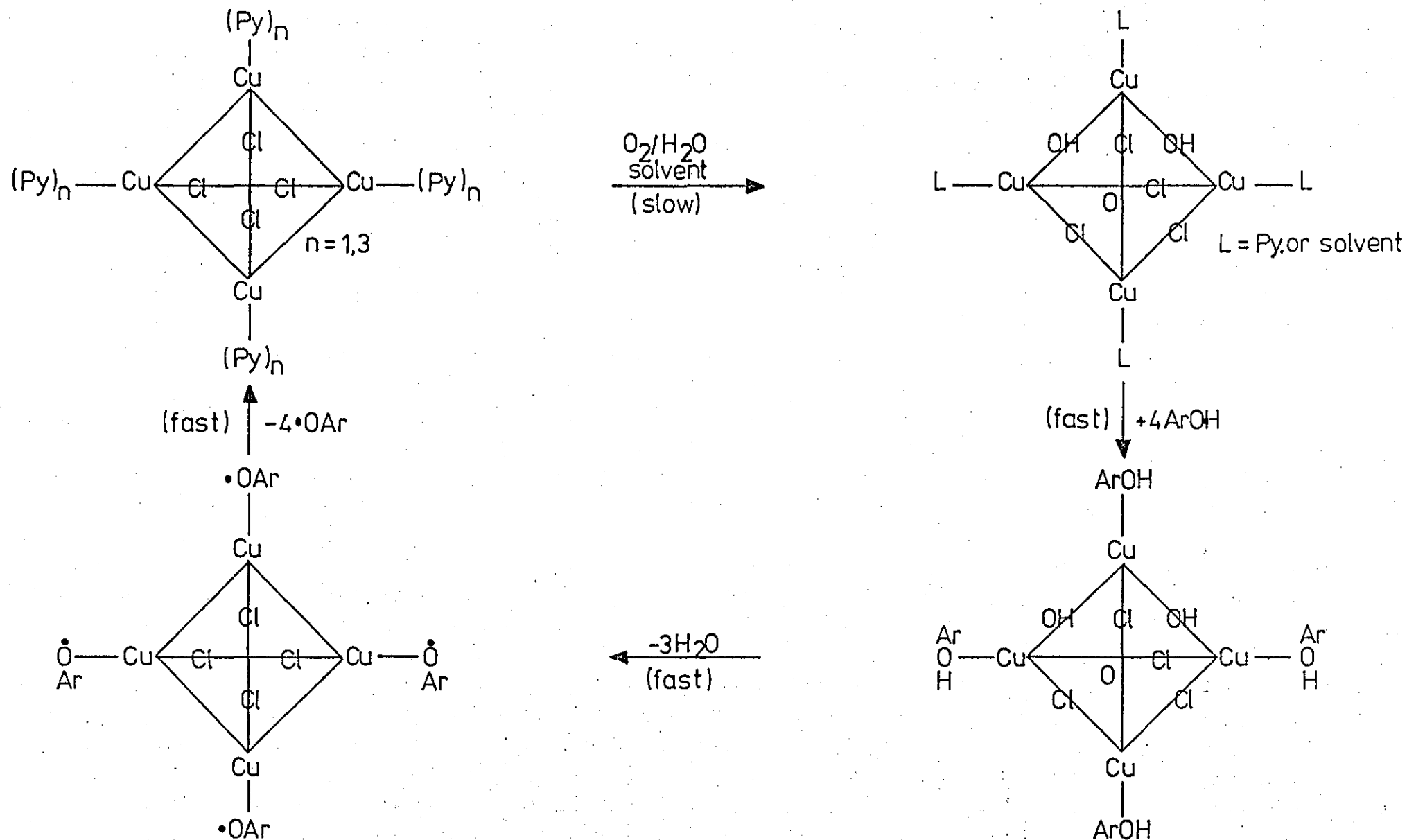which then lose H^+. The four protons can then combine with the bridging

FIGURE 10.1.   Proposed oxidative coupling reaction scheme, involving a tetranuclear copper(II) catalyst.

hydroxide groups and the central oxygen atom, forming four molecules of water in a similar way to that proposed for the thermal decomposition of $Cu_4OCl_6 4py$, in which the central oxygen atom combines with two hydrogen atoms from different pyridine molecules and thus allows the formation of chloropyridine and CuCl (Chapter Four). This particular reaction requires the tetranuclear phenol complex to be unstable to a redox reaction at room temperature, a postulate which is not unlikely considering the copper (II) complexes with ethylamine and related ligands (discussed in Chapter Four) which also undergo redox reactions at low temperatures. In the presence of high pyridine to copper ratios, where C-O coupling predominates, the pyridine will displace the phenoxy radicals from the copper (I) complex and these will then participate in C-O coupling, in a manner similar to that described by Price and Nakaoka [figure 1.5 and reference (9)]. At low pyridine to copper ratios however, there will be insufficient ligand available to replace all the aryloxy radicals and so they remain co-ordinated to the copper complex and C-C coupling results, as suggested by Price and Nakaoka in their reaction mechanism (figure 1.6).
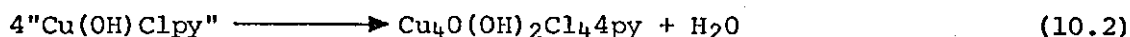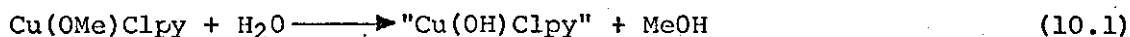
This reaction scheme is in accord with the observed kinetics of the coupling reaction, which is first order with respect to both copper concentration and oxygen partial pressure and, in agreement with the observation that the reaction is zero order with respect to monomer concentration (9, 18), the rate determining step will be the oxidation of copper (I) to copper (II) as suggested by Price and Nakaoka (9).

The suggestions that have been put forward to explain the effect of monomer structure on the rate of the coupling reaction, discussed in Chapter One, will also apply in this present reaction scheme. Monomers containing bulky groups in the 2, 6-positions will physically prevent the formation of a stable complex with the tetranuclear copper(II) catalyst so that pyridine is preferentially co-ordinated, whilst electron withdrawing or donating groups in the phenyl ring will retard or enhance the redox reaction by altering the oxidation potential of the monomer.

The effect of the amine structure on the oxidative coupling reaction is more complicated. Most workers have tended to attempt to explain the effect of different amines on the polymerisation rate or product formation, in relation to the active (Copper(II)) catalyst. If, as mentioned above, the rate determining step in the reaction is the oxidation of copper (I) to copper (II), the amine may effect this stage of the reaction only. In the reaction scheme shown in figure 10.1, the amine is probably not even co-ordinated to the copper (II) complex, since it was suggested in Chapter Five that when tetranuclear copper (II) complexes are present in solution, the axial ligands are usually replaced by solvent molecules. Therefore, it is proposed that the effect of different amines on the oxidative coupling reaction is mainly concerned with their effect on the oxidation potential of the copper (I)-amine complex and, to a lesser extent, with the ability of the amine to replace the phenoxy radicals in the copper (I) - phenoxy complex. This latter factor will affect the extent ofC-0 and C-C coupling, as well as the rate of formation of the copper (I)-amine complex (and hence the rate of polymerisation). It has been observed that amine structure affects both reaction rate and product formation (11, 12), but as little information is available of the effect of various amines on the stability of copper (I) halides towards oxidation, the validity of the above argument remains in doubt at present.

The slow rate of polymerisation in the presence of polar solvents (10) can be explained by a stabilisation of the copper (I) complex by solvent molecules, thus preventing the oxidation reaction in a similar manner to that suggested by Tsuchida et al. (10). Alternatively a polar solvent may prevent the co-ordination of the monomer to the tetranuclear catalyst and again lower the reaction rate.

The successful use of the catalyst complexes Cu(OMe)Clpy and [Cu(OH)TMED]$_2$Cl$_2$ by Finkbeiner et al. (7) and De Jongh et al. (20) respectively, requires some explanation in terms of the reaction scheme proposed in the present investigation. The methoxide complexes Cu(OMe)Xpy X = Cl,Br, discussed in Chapter Eight, were found to be sensitive to moisture, undergoing an hydrolysis reaction. It is suggested that the complex Cu(OMe)Clpy when used as a catalyst, reacts with water in the solution to form a dimeric hydroxy bridged copper complex which will then dehydrate, forming the catalyst complex Cu$_4$O(OH)$_2$Cl$_4$4py as described in 10.1 above. These reactions are shown below in equations 10.1 and 10.2.

$$Cu(OMe)Clpy + H_2O \longrightarrow "Cu(OH)Clpy" + MeOH \qquad (10.1)$$

$$4"Cu(OH)Clpy" \longrightarrow Cu_4O(OH)_2Cl_4 4py + H_2O \qquad (10.2)$$

This reaction path will be favoured since the complex Cu(OMe)Clpy is insoluble in the solvents used for oxidative coupling reactions (7) as might be expected for a polymeric compound of this nature, whereas the tetranuclear catalyst complex is more likely to be soluble. The dehydration reaction (equation 10.2 above) is analogous to the reaction of the basic salt Cu$_4$(OH)$_2$Cl$_6$4H$_2$O which forms the tetranuclear hexahalide complex when dissolved in ethanol (Chapter Seven). A similar dehydration reaction can be proposed for the complex [Cu(OH)TMED]$_2$Cl$_2$ in solution, again with the formation of a tetranuclear copper complex. Hence these two "catalyst" species may be regarded only as copper complexes that readily form the reactive catalyst complex Cu$_4$O(OH)$_2$Cl$_4$4L in solution and they probably play no active role in the oxidative coupling reactions in their original form.

The presence of water as an initial reactant in the oxidative coupling reaction is necessary for the formation of the tetranuclear

active catalyst complex (figure 10.1). The oxidation of copper (I)

chloride under these conditions only requires one quarter of a mole

of water per mole of copper for the formation of the tetranuclear

complex. In terms of the quantity of copper (I) halide that is

generally used in phenolic coupling reactions and the volume of

solution present, there only needs to be 1 to 100 ppm of water in the

reaction mixture for such a reaction scheme to take place. Normal

methods of drying will rarely produce a solvent containing less than

100 ppm of water, and even stringent drying techniques acting on an

hygroscopic solvent such as pyridine, will not give a product

containing less than 20 ppm of water (see Chapter Eight).

Consequently, there will always be enough water present in the reaction

mixture to ensure the formation of some tetranuclear complex,

although at the beginning of the oxidative coupling reaction, there

may not be enough to convert all the copper (I) complex into an

active catalyst species which may account for the slow initial reaction

rate observed by several workers (10, 18). The concentration of

monomer in the reaction mixture will initially be greater than the

concentration of water, and this may prevent the fast hydrolysis

reaction (equation 8.10) taking place with subsequent deactivation

of the catalyst, until the final stages of the reaction. Drying

agents, such as molecular sieve or magnezium sulphate which are

usually employed during these polymerisation reactions, will also

prevent hydrolysis of the catalyst complex. It has been shown,

however, that large amounts of water in the reaction mixture will

deactivate the copper catalyst (11, 12), in agreement with the

observations reported in Chapter Eight.

Finkbeiner et al. (7) reported the tetranuclear complex Cu_4OCl_64py

to have some catalytic activity for the oxidative coupling of

disubstituted phenols, but the rate of reaction was considerably slower compared with a conventional copper (I)-amine catalyst system. Although this tetranuclear hexahalide complex may be a catalyst in its own right, it is more likely that the formation of large amounts of the catalyst, $Cu_4O(OH)_2Cl_44L$, is prevented in this system by the presence of a 1:1.5 copper to chlorine ratio which, during the oxidation stage of the reaction (figure 10.1), results in the production of Cu_4OCl_64L as a major product. A similar low reaction rate has been observed whilst using calcium chloride as a drying agent (11); here again the major product from the oxidation of copper (I) chloride in the presence of halide ions would be the tetranuclear hexahalide complex, as discussed in Chapter Eight.

Although this investigation has been concerned with the copper (I) chloride-pyridine catalyst system, Copper (I) bromide has also been used to produce an active catalyst species under the same conditions (7,11), In general, reaction rates are very much slower which is in accord with the fact that the copper (I) state is more stable to oxidation in copper (I) bromide and this will affect the rate determining step of the coupling reaction. It seems likely, from the results of the oxidation reactions reported in Chapter Eight, that a tetranuclear copper (II) complex containing mixed halide and hydroxide bridges is the active catalyst for oxidations involving copper (I) bromide as well.

The reaction scheme proposed for the oxidative coupling of phenols (figure 10.1) is in agreement with the observed kinetic properties of the system, and in addition, it can explain many of the effects on reaction rate and product formation observed under different reaction conditions. The major advantage of this reaction scheme over the ones proposed by earlier workers (Chapter One), is that it is viable in terms of the known co-ordination chemistry of copper. No attempt has been made in this investigation

to study the actual mechanism of C-C or C-O coupling as, all that

is required of the catalyst species is to provide a mechanism for

the generation of phenoxy radicals. The actual mechanismsof radical

coupling are somewhat in dispute, but they have been discussed in

detail by several workers (1, 2, 4, 7-15, 37).

Further work is required to evaluate the validity of the

reaction scheme shown in figure 10.1. If the catalyst complex

$Cu_4O(OH)_2Cl_44py$ can be isolated by one of the methods described in

10.1 above, the relevance of the above reaction scheme could be

ascertained from a study of the reaction between the catalyst

complex and a phenol. Alternatively it may be easier to first study

the reaction between the tetranuclear hexahalide complexes and

phenols with respect to any redox reaction that may take place, as

it may be possible to isolate tetranuclear complexes containing axial

phenol ligands at low temperatures.

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