NEW ASPECTS OF THE CHEMISTRY OF QUATERNARY ADDITION REAGENTS FOR THE ELECTROCRYSTALLISATION OF ZINC

Submitted by BARRIE SYDNEY JAMES, MARCH 1979,
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SUMMARY

The introduction of quaternary pyridinium derivatives as brightening agents for the electrodeposition of zinc from alkaline electrolytes is one of the significant recent advances in this field. This work describes the brightening effect of quaternary pyridinium derivatives, with differences in structure, on the zinc deposits obtained from alkaline cyanide and cyanide-free electrolytes. In addition chemical changes were found to be occurring in these solutions, which could be followed using ultra-violet and nuclear magnetic resonance spectroscopy. Analysis of the ultra-violet data has enabled the kinetics of these reactions to be deduced and this together with relevant information from the literature, has led to the hypothesis that the new species are bimolecular ethers. A correlation of the ultra-violet and electroplating results, suggests that these bimolecular ethers may be the brightening agents and not the materials originally added.

Since it proved impossible to isolate the bimolecular ethers, model compounds were employed to explore their co-ordination chemistry. The zinc complex of 2,2'-oxydibenzoic acid was prepared first, but elemental analysis and the infra-red spectrum did not give much structural information. It was thus decided to prepare the cobalt and copper complexes, in order that the magnetic susceptibilities (and hence magnetic moments) and diffuse reflectance spectra could be obtained. Unfortunately, these techniques gave very little extra structural information, consequently, the iron complexes were prepared in order that Mössbauer spectroscopy could be employed, but this only succeeded in further complicating the issue. Finally, the zinc and copper complexes of 2,2'-thiodibenzoic acid, 3,3'-oxydipropionic acid and 3,3'-thiodipropionic acid were prepared and investigated. Copper-3,3'-thiodipropionate proved of interest, since it exhibited antiferromagnetic behaviour, and a plot of $1/\chi$ against temperature almost fitted a theoretical curve, suggesting that the complex could possibly be a dimer, although higher clusters can not be discounted.

However, the structure of all the complexes is still in doubt and although a great deal is now known about them, further work is necesary before unambiguous structures can be assigned and this may ultimately depend on X-ray diffraction studies.

KEY WORDS: Zinc, Electrodeposition, Pyridinium,
Bimolecular ether, Carboxylate co-ordination.

CONTENTS

PART ONE QUATERNARY ADDITION REAGENTS

PART TWO MODEL COMPOUNDS

NEW ASPECTS OF THE CHEMISTRY OF QUATERNARY ADDITION REAGENTS FOR THE ELECTROCRYSTALLISATION OF ZINC.

INTRODUCTION

As copper came of age in its alloy bronze, so iron came of age in its alloy steel. Of all the metals known to man, iron and steel are most widely used, since no other metal can provide such a combination of cost, strength, ductility and ease of fabrication. They suffer, however, from one main drawback; except in the case of the stainless steel alloys, atmospheric corrosion or rusting occurs at a relatively rapid rate. As long as steel retains its pre-eminence as a material of construction, the need to protect it against the ravages of corrosion will not only continue, but progressively increase.

A great variety of methods of protection are available, paints are probably the most widely used, and impart protection by enveloping the steelwork with a non-corrodible coating. They are reasonably cheap and easy to apply and afford good protection, provided the envelope remains completely impervious. Once a crack develops protection is lost locally and attack on the exposed steel begins immediately. Since the formation of rust is accompanied by an expansion, the coating in the vicinity of the crack lifts to expose more steel and so once begun rusting spreads continuously. A more dependable method of protection is to apply a coating of zinc, not only is this more durable than paint and less subject to cracking, but based on its position in the electrochemical series, zinc behaves anodically towards the underlying steel and protects it sacrificially. This means that even though a small degree of damage may occur to the deposit or it may be slightly porous, rusting of the bared steel is prevented at the expense of the surrounding zinc coating.

Some 40% of the worlds output of zinc is used for the coating of steel, by a large variety of techniques which include; hot dip galvanising, spraying, the application of zinc or zinc chromate containing paints and electroplating. Zinc is electrodeposited on a very large number of components and fittings, encountered in everday life, which range through motor cars, office furniture, and electrical equipment, to domestic appliances. Zinc coatings are not applied exclusively to prevent articles from corroding in service but can play an extremely useful part in preventing corrosion during handling, transport and storage; ensuring that the product reaches the user in good condition. An example of this is the electrogalvanising of wood screws, The corrosion of such screws is not a serious problem once they have been installed, but even slightly rusted screws may be unsaleable, even though they may be quite satisfactory functionally.

Although the basic reason for the application of a zinc coating is to prevent corrosion, necessitating only the production of a sufficiently thick film. Developments in the art of bright zinc plating and improvements in the various post plating treatments, used industrially, has enabled durable finishes with an attractive appearance to be produced. This has resulted in zinc plating now being used for decorative applications, and is replacing the more expensive nickel-chromium finish, from many of its conventional uses.

Zinc can be plated from alkaline cyanide, alkaline cyanide free and acid baths.

The alkaline cyanide zinc plating electrolyte has been known for over fifty years and until the last decade was the majour producer of zinc plated articles, being known within the plating industry as "the workhorse of the plating trade". The robust nature of the electrolyte has resulted in it suffering much adverse chemical abuse, but still continuing to produce commercially acceptable bright electrodeposits.

The conventional high metal alkaline cyanide bright zinc plating bath has an extremely broad composition range for its basic inorganic constituents. A generally acceptable composition would fall within the limits:

	RACK	BARREL
Zinc as Zn^{2+}	30 - 40 gl^{-1}	30 - 40 gl^{-1}
Total Cyanide as NaCN	90 - 120 gl^{-1}	75 - 90 gl^{-1}
Sodium Hydroxide	75 - 85 gl^{-1}	80 - 95 gl^{-1}
Ratio NaCN to Zn	2.8 - 3.5 : 1	2.4 - 2.8 : 1
Ratio NaOH to Zn	2.0 - 2.5 : 1	2.4 - 2.8 : 1

Industrially two methods are available for providing a conductive path for the electric current to reach the articles to be electroplated and they are termed "Rack" and "Barrel" processes.

These two processes differ in the method by which the current is supplied to the article to be plated. In the "Rack" or "Vat" process, the workpiece is usually a large object, for example a hub cap or bumper bar. This is attached directly to the cathode bus bar, with copper wire or is wired (or "jigged") on to racks (or jigs), which are then hooked on to the cathode bar. Since it would be an expensive and time consuming task to wire up a large number of small objects, such as screws, nuts or washers. These articles are plated in a perforated barrel, which rotates in the electrolyte, hence the term "Barrel" plating.

Although the high metal - high cyanide alkaline plating baths have many advantageous characteristics, the most serious disadvantage is their high toxicity. Although cyanide can easily be destroyed by using a chlorine or hypochlorite treatment. The natural concern for the safety of the workers, the protection of the environment, coupled with the stricter limits on all effluent discharge set by Local Authorities. Together with the necessity for conservation of water and the higher cost of basic chemicals for solution maintenance and effluent treatment, have resulted in the development of medium metal - medium cyanide, low metal - low cyanide and cyanide free alkaline zinc plating solutions.

A typical range of constituents for the medium metal - medium cyanide and low metal - low cyanide zinc plating electrolytes are:

	LOW METAL - LOW CYANIDE	MEDIUM METAL- MEDIUM CYANIDE
zinc as Zn	6 - 10 gl^{-1}	20 - 25 gl^{-1}
total cyanide as NaCN	6 - 12 gl^{-1}	30 - 50 gl^{-1}
sodium hydroxide as NaOH	50 - 90 gl^{-1}	60 - 90 gl^{-1}
ratio Zn to NaCN	0·8 - 1 2 : 1	1·5 - 2 0 : 1

The low metal-low cyanide bath has three main disadvantages:

1. The high metal-high cyanide zinc plating solution needed very little attention, but the very low reservoir of metal and cyanide ions, in the new process necessitated much closer analytical control. A daily analysis for both zinc and cyanide being recommended, thus creating unfamiliar control problems and suggesting that this process should only be installed where on-the-spot laboratory facilities are available.

2. The lower metal content imposes current density restrictions, making its use in rack installations dubious, especially at high current densities.

3. The low reservoir of ions results in poor cleaning efficiency compared with the high metal-high cyanide electrolyte, making necessary, an adequate cleaning line prior to electroplating.

To overcome these problems, the basic formulation of the solution was gradually altered, so that a reasonable current density could be employed in a stable, easily controllable solution. The zinc, cyanide and sodium hydroxide concentrations were raised resulting in the medium metal-medium cyanide bath. A compromise between the high and low cyanide electrolytes.

The elimination of the extremely toxic cyanide ion and the resultant simplification of effluent disposal, were the main reasons for the development of the alkaline none-cyanide zinc plating electrolyte. The constituents of a typical solution are; zinc metal 5 to 15 gl^{-1} and sodium hydroxide 50 to 200 gl^{-1}, with optimum results being obtained by employing a zinc to sodium hydroxide ratio of 1 : 10. The first commercial sucess of such a plating solution dates back only ten years, since electro-deposits obtained by electrolysing a solution of composition indicated above, results in dark powdery deposits. It is only the recent development of suitable addition agents which has enabled bright, ductile deposits to be obtained, and so make this electrolyte commercially viable.

The last type of zinc electroplating solution to be considered are the, so called, acid zinc plating electrolytes since they operate around a pH of about 5, and tend to include the neutral zinc plating electrolytes, which operate about pH 7, but differ from the acid zinc plating electrolytes, in that they require the presence of a chelating agent. The acid zinc plating electrolyte usually contains zinc ions and a conducting salt such as ammonium or chloride ions, and a complex mixture of organic chemicals needed to produce a bright and ductile deposit. Since the addition-agent system is so complex, and is not relevant to this thesis, being of a different type to the brightening system used in the alkaline cyanide and none-cyanide plating electrolytes, no further reference will be made.

The alkaline cyanide zinc plating bath was first recorded by R.C. Snowdon[1] in 1907, who deposited zinc from a zinc sulphate solution, containing enough potassium cyanide to redissolve the precipitate obtained, when the solution was rendered alkaline. It was much later in 1921 when Blum, Liscomb and Carson[2] published what is probably the first authoritative investigation of cyanide zinc plating baths. They developed the pertinent fundamental chemistry and gave definite recommendations with respect to bath composition and operating conditions, but unfortunately their bath, while useful from the stand-point of operating characteristics was not readily amenable to the production of bright deposits.

The first bright alkaline cyanide zinc plating baths were introduced to the plating industry in 1935[3] and came into widespread use shortly after. The history of the development of this process, being then, the search for new addition agents, which have changed it from a bath producing dull, stained deposits with limited coverage into one which gives brilliant blue bright, readily marketable, low cost finishes with excellent coverage in low current density recesses.

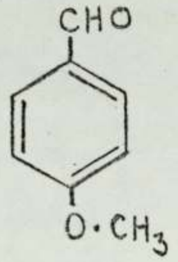
Numerous patents have been issued claiming novel addition agents, but a detailed list would only confuse the issue, because of the vague nature of many of the claims and the lack of any standards for the comparison of results obtained. Many of the compounds which are described as producing bright deposits in some patents, give only semi-bright deposits when compared to deposits obtained using one of the acknowledged "brightening" agents. The most adventageous brightening systems used commercially contain a mixture of chemical compounds. In many cases the mixtures act synergist-ically, that is, the correct combination of addition agents produce better results than those expected, based on the results achieved when they are used alone. The most profitable approach to this topic, which will be employed in this thesis, involves an appraisal of the main chemical types of addition agents, which more or less parallels the history of their development.

Initial efforts involved the addition of inorganic compounds of such elements as; nickel, molybdenum, tungsten, manganese, cobalt, mercury, chromium, aluminium, selenium and tellurium, used at concentrations ranging from trace amounts to concentrations of one or two grams per litre. Not all of these are equally effective, some being much more active than others. The oxidation state of the element is also important, for example chromium (VI) compounds have disasterous effects on the deposit, causing dullness and lack of plate, while chromium (III) compounds have a beneficial effect. Nickel(II) and molybdenum(VI) compounds are the addition agents most widely used, but these are usually used in conjunction with other types of addition agents. Nickel (II) at about ten parts per million, improve the brightness of an already bright plate. This type of addition agent is not extensively used, since the small quantities employed are difficult to control and an excess can cause the deposit to be brittle and also produce black stains, when the plated article is given a subsequent immersion in a "passivating solution".

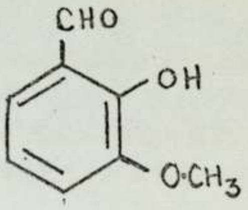
Another class of addition agents which have been known for some time, are the naturally occuring organic polymers; mainly animal proteins used in the form of glue or gelatine. These are used at concentrations of one or two grams per litre and are extremely effective at producing bright zinc plate at low current densities, but since they are easily hydrolysed in the highly caustic electrolyte, must be replaced frequently, and the breakdown products of the hydrolysis reaction can cause problems. They are not particularly effective when used alone and so are usually used in conjunction with other addition agents, since they will brighten low current density areas, which tend to be dull with certain other addition agents.

Other types of polymer known for some time are the polyvinyl alcohols, which are available in a variety of molecular weights and degrees of hydrolysis. These polymers have a definite brightening action when used by themselves, but are usually used in combination with other addition agents, because the deposits produced alone have a distinct yellow tinge. This discolouration can be removed by a subsequent dipping operation, but would not yield such clear and bright deposits, as those produced, when used in the correct combination with other addition agents. The most suitable molecular weight and degree of hydrolysis of the polyvinyl alcohol, depends on the other addition agents employed. The effect of a change in the molecular weight or degree of hydrolysis, is not very large, all grades produce a bright plate, but some are more successfully employed at removing minor faults.

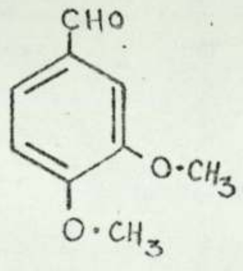
One of the milestones in the development of bright zinc deposits from an alkaline zinc electrolyte has been the use of Aromatic Aldehydes as addition agents, the most effective being; anisaldehyde, vanillin, piperonal and veratraldehyde.



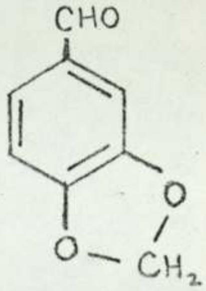
p-anisaldehyde



o-vanillin



veratraldehyde



piperonal

With the introduction of these addition agents, for the first time very bright zinc deposits could be obtained. These chemicals co-operate efficiently with the addition agents described previously, the most effective combination being with polyvinyl alcohols. The Aromatic Aldehydes are used in concentrations of 0.5 to 1.0 grams per litre, an excess not being detrimental, in fact improvement can be obtained by using higher concentrations. The limiting factor being the cost, since these materials tend to be rather expensive, and the material used commercially is usually chosen not because it is the best, but usually the cheapest. Some correlation between the brightness of the deposit and the structure of the aromatic aldehyde used have been observed, but no quantitative data is available, the results being mainly subjective. Veratraldehyde and piperonal produce the brightest deposits, while benzaldehyde has little or no effect. Anisaldehyde is probably the most widely used materials, since it produces acceptably bright deposits and is relatively cheap. Small amounts of the more expensive aromatic aldehydes are sometimes incorporated in commercial mixes, in order to boost the brightness, without making the cost prohibative.

The aromatic aldehydes are usually added in the form of their bisulphite addition complex, since the are usually water insoluble. This complex is readily destroyed by the highly alkaline electrolyte, consequently these compounds probably exist eventually, in solution, as the cyanide addition complex.

Aromatic ketones and aliphatic aldehydes have some effect when used in alkaline zinc plating electrolytes, but the brightness of the deposits, are nowhere as beneficial as those obtained when using the aromatic aldehydes.

The publication of British patent 1,049,132 granted to the Udylite Corporation in 1966 and British patent 1,170,058 granted to E.I. DuPont de Nemours and Company in 1969, which introduced a new and valuable family of addition agents, these being quaternary pyridine derivatives.

The main claim of British patent 1,049,132 comprises an aqueous alkaline cyanide zinc bath, for the electrodeposition of lustrous zinc in which is dissolved at least one quaternary nitrogen compound, containing at least one carboxylic ester, carboxamide, substituted carboxamide, carboxy or nitrile group.

The preferred pyridine compounds quoted are methyl, ethyl or propyl nicotinate (claims 4,5 and 6) and the preferred quaternising agents being methyl, ethyl, propyl or allyl chloroacetate or chloropropionate and alpha chloroacetamide or beta chloropropionitrile (claim 7).

The quaternary pyridine compounds mentioned in the claims being:

(i) N-allyl-3-ethylcarboxylate pyridinium bromide (claim 8)

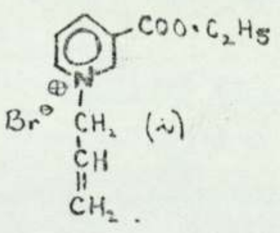
(ii) N-methylcarboxymethyl-3-ethylcarboxylate pyridinium chloride (claim 9)

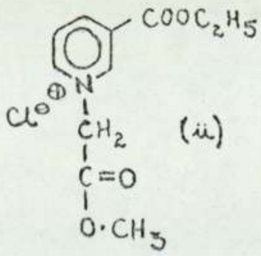
(iii) bis-1,4-xylylene-3,3'-ethylcarboxylate pyridinium chloride (claim 11)

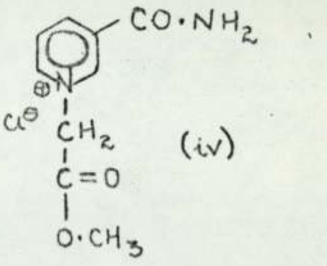
(iv) N-methylcarboxymethyl-3-carboxamide pyridinium chloride (claim 13)

and

(v) N-benzyl-3-ethylcarboxylate pyridinium chloride (claimed twice 10 and 12)


(i)


(ii)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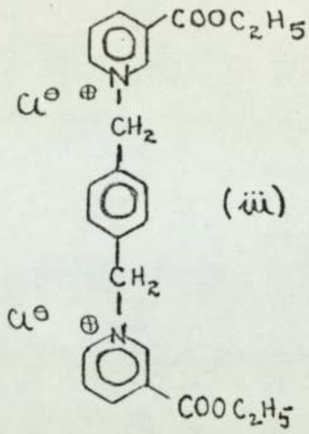
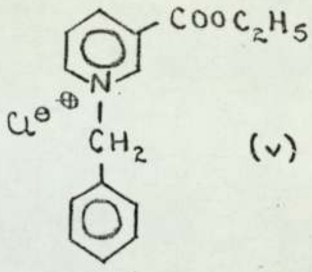


(iii)



(v)

The specified quaternary nitrogen compounds make possible the electrodeposition of mirror bright zinc deposits from alkaline cyanide zinc baths over a wide current density range. They co-operate to an unexpected degree with other known addition agents, for example aromatic aldehydes, polyvinyl alcohol and modified polyvinyl alcohol (such as oxidised or ethoxylated), peptones and very specifically with very small concentrations of the inorganic salts of manganese, molybdenum, trivalent chromium and iron, and with combinations of these materials, to give even brighter and more uniform deposits than those achieved alone.

The other British patent 1,170,058 for which an application was made 21 months after British patent 1,049,132, claims the addition of an aromatic betaine, which has a quaternary nitrogen atom directly bonded to 3 or 4 carbon atoms (at least one of which is a member of an aromatic nucleus), and a carboxylic or sulphonic acid group attached to the quaternary nitrogen atom through a carbon linkage, containing from one to six carbon atoms. The heterocyclic ring systems, which can provide the quaternary nitrogen atom include pyrrole, indole, quinoline and isoquinoline, as well as pyridine. The only compound quoted in the claims is 1-benzyl pyridinium-3-carboxylate (claim 17), although examples of other heterocyclic betaines are illustrated in the body of the patent.

1-benzyl pyridinium-3-carboxylate is also covered, in the first claim of British patent 1,049,132 and is the compound most widely used commercially. Although other members of this family can produce brighter deposits than 1-benzyl pyridinium -3-carboxylate, it has the advantage that not only does it produce adequately bright deposits, but it can easily be prepared from cheap, readily available materials, namely nicotinic acid and benzyl chloride.

The aromatic betaines can be used alone, but are preferably used in combination with an organic polymer that is soluble in the bath. The presence of the polymer being particularly desirable when the bath is used above room temperature, since plating baths at 50°C., are not unknown in summer. Examples of suitable polymers, include synthetic polymers such as polyvinyl alcohol (or modified polyvinyl alcohols) or polyethylene imines, and natural polymers such as gelatine, glue, peptone, gums and agar-agar, as well as protein substances such as egg albumin and milk protein hydrolysate. The polyvinyl alcohols, prepared by the partial hydrolysis of polyvinyl acetate, having molecular weights in the range 5,000 to 20,000 and a degree of hydrolysis of 87 - 89 %, are quoted as providing particularly stable plating baths and co-operate most efficiently with the aromatic betaines. Table 1 (from British patent 1,170,058), illustrates this co-operative effect in the results obtained, on varying the concentration of a partially hydroylsed (87 - 89 %) polyvinyl alcohol, having a molecular weight of about 16,800; with zero and 0.8 grams per litre of 1-benzyl-3-carboxy pyridinium chloride.

TABLE 1

	Amount of Betaine Added	Amount of PVA Added	Product Quality
a	0	$0.13\ gl^{-1}$	Dull on all surfaces
b	$0.8\ gl^{-1}$	0	Very desirable product, bright on all surfaces
c	$0.8\ gl^{-1}$	$0.004\ gl^{-1}$	Brightness about the same as (b), increase in shininess of plate
d	$0.8\ gl^{-1}$	$0.04\ gl^{-1}$	Product about same as (c)
e	$0.8\ gl^{-1}$	$0.08\ gl^{-1}$	Plate very bright and shiny, improvement over (c)
f	$0.8\ gl^{-1}$	$0.13\ gl^{-1}$	Plate has an extremely bright and liquid appearance even in low current density areas, overall mirror like quality

The following mainly historical coverage of addition agents used in alkaline cyanide zinc plating electrolytes, is almost complete, lacking only one recent development, which will be described later. A slight digression, into the field of none cyanide zinc plating addition agents, is in order, because the first commercial plating baths began to appear at this time.

The alkaline none-cyanide zinc plating bath without the benefit of addition agents, produces a deep black powdery deposit over almost the entire acceptable range of operating current densities. Early attempts to develop a substitute for cyanide, in this system, centred about other complexing or chelating agents, such as, sodium gluconate, ethylenediamine tetraacetic acid (edta) and triethanolamine. These compounds were used in large amounts, up to 30 grams per litre, together with conventional cyanide brighteners, which mainly consisted of aromatic aldehydes, polyvinyl alcohols, gelatine and metallic ions. Baths of this type gave a reasonable zinc deposit, but decidedly inferior in brightness and uniformity of plate when compared to the traditional cyanide containing processes. The processes were tolerated however, because they no longer contained cyanide, thus removing the toxic hazard of this material, and simplifying effluent disposal since there was no longer any cyanide to destroy. One big disadvantage was that the concentration of iron in the bath quickly built up, since it was effectively complexed by the addition agents, resulting in the deposition of a zinc-iron alloy. This alloy in the range of approximately 100-150 p.p.m. of iron, became blue-black and ultimately dark grey-black upon subsequent bright dipping, making the process totally unacceptable. Another, even more insidious problem which involved the waste disposal system, began to appear in the complexed type of alkaline none-cyanide zinc plating installations, after one or two months of operation. When, as is almost often the case, a plating company had other plating processes in operation, especially copper, the complexing agents from the drag out of the none-cyanide zinc system, when mixed with the general effluent, tied up any copper or nickel, so tightly that it could not be precipitated (and so removed), by conventional waste treatment methods. Thus, while the alkaline none-cyanide process was originally conceived to solve a waste treatment problem, it created a monster of its own, obliterating the original reason for its development.

The most notable advance in this field came with the publication of British patent 1,219,932 granted to Lea-Ronal Inc., in 1971. This invention concerns the addition, to an alkaline zincate electrolyte, of the water soluble reaction product of an alkylene polyamine, (containing one or more tertiary, or quaternary amine groups), with an epihalohydrin. The two materials used to illustrate the invention, in the examples in the body of the patent, being 1,3-dimethylaminopropylamine and epichlorhydrin (1-chloro-2,3-epoxypropane). These polymers have a molecular weight above 250 and should preferrably be in the range 4,000 to 5,000. This material is a weak complexant and so poses no problems of effluent disposal, but when used at concentrations of approximately one gram per litre, produces a bright and very commercially desirable finish. The brightness of the deposit can be improved by combination of the polymer with aromatic aldehydes or pyridinium betaines, smaller concentrations being used to produce the same or better results than those obtained from cyanide containing electrolytes.

Since this development several patents[4], have been granted, which describe other similar nitrogen containing polymers, for use in alkaline none-cyanide zinc plating baths.

The latest and probably the most noteworthy advance in the development of alkaline cyanide, none-cyanide and acid zinc plating processes, has been the publication, in patent form, of some japanese work. This describes a series of quaternary heterocyclic polymers, the most active addition agent being the polymer obtained from the reaction between imidazole and epichlorhydrin.

Brightness

Despite the vast array of addition agents used to obtain a bright deposit from alkaline cyanide and none-cyanide zinc plating electrolytes, very little work has been published concerning the mechanism of the brightening action. A historical difficulty in dealing with this problem, was the lack of a clear definition of "brightness", in terms of physical magnitudes.

Three possibilities exist with respect to the reflection of light at a surface. Firstly, when the light is reflected diffusely, the surface has a matt appearance. Secondly, when the light is reflected directionally, the surface has a mirror appearance. Thirdly (a mixed effect), when there is mostly directionally reflected light and only a small proportion of the light is reflected diffusely, then the surface appears bright.

Most of the early work has centred around a vague definition of brightness, in terms of visual appearance, but more recently the reflecting power, as measured by the amount of light specularly reflected off a surface*, i.e. at an angle equal and opposite to that of incidence with respect to the normal to the geometrical surface, has been used.
(* or more precisely, the illumination of the monitoring detector at constant illumination of the reflecting surface)
The results obtained are inadequate for characterising unequivocally the property perceived by the human eye as brightness, since a stronger impression of brightness does not necessarily correspond to a higher intensity of mirror reflected light. A more precise definition, not involving the actual reflectivity of the surface, would be in terms of the ratio between specularly and diffusely reflected light.

A surface which is termed smooth, in common usage, generally appears rough when studied under the microscope, and it is this micro-roughness which is responsible for diffuse reflectance. When the nature of the surface is studied under the optical or electron microscope, only a small part of the surface is viewed at any one time, while the human eye evaluates the entire surface.

The question arises as to what scale of surface roughness is responsible for the introduction of scattering in the reflected light. On intuitive grounds the surface will be effectively smooth, from the point of view of reflectivity, when the order of magnitude of the irregularities becomes less than the wavelength of the radiation being used.

Weil and Paquin[6], found a linear relationship between the logarithm of the amount of light specularly reflected by a surface (under well standardised conditions), and the fraction of the surface which contains no irregularities larger than 0.15 nm.,(1500 Å).

The ratio[7] of diffuse reflection to total reflection is often given by ($4\pi\sigma/\lambda$)^2 where σ is the root mean square roughness and λ is the wavelength of the light (0.4 to 0.8 nm.,) or other electromagnetic radiation. This implies that the surface is somewhat brighter in light of longer wavelength.

Work with metals other than zinc, mainly copper, nickel and chromium, has led to the proposal of two major theories to explain the brightness of electrodeposits.

One theory advanced by a number of workers[8], states that electrodeposits are bright if their microstructure consists of crystallites smaller than the wavelength of visible light, that is, smaller than 0.4 nm.

The alternative theory, with its own share of supporters[9], suggests that there is a high degree of preferred orientation so that the crystal faces presented to the surface are essentially parallel, so that even large grained deposits will be bright.

It has been demonstrated in recent years[10], that bright metal deposits can be relatively coarsely crystalline, so that the occurance of a fine structure is not an essential precondition for brightness. It has also been shown[11], that metal coatings crystallising without any grain orientation can be bright, so that a particular orientation of the crystallites cannot be considered to be the cause of brightness.

Little information has been published regarding the microstructure and metallurgical properties of zinc electroplate. Fischer[12] concluded that the macroscopic structure of zinc electrodeposited from a cyanide electrolyte, is of the so-called "field orientated texture type", basing his classification on optical microscopy which showed the fibrous appearance and X-ray diffraction which showed (1011) texture.

Hasko [13] verified the fibrous appearance but reported (1120) texture for deposits from a range of cyanide electrolytes.

Todt[14] analysed the carbon content of zinc deposits, finding about 0.1 per cent for three commercial alkaline baths and 1.0 per cent for an acid bath.

Recent workers[15] have examined thin zinc foils deposited from alkaline cyanide electrolytes (covering a wide range of compositions), an alkaline none-cyanide electrolyte and an acid electrolyte, by transmission electron microscopy. They have shown the grain structure of the deposits to be columnar and to have grain diameters of 0.1 to 0.4 μm for deposits from the cyanide electrolytes and 0.04 to 0.1 μm from the none-cyanide electrolyte. The dominating crystallo -graphic orientation parallel to the plating surface was (1120), and the carbon content 0 to 0.5 per cent.

PART ONE

INVESTIGATION OF THE ACTION OF QUATERNARY PYRIDINIUM DERIVATIVES IN ZINC PLATING ELECTROLYTES

PART ONE

INVESTIGATION OF THE ACTION OF QUATERNARY PYRIDINIUM DERIVATIVES IN PLATING ELECTROLYTES

The following pyridine derivatives were bought or prepared, for testing in alkaline cyanide and alkaline none-cyanide zinc plating electrolytes.

Nicotinic acid (B.D.H.)
Homarine hydrochloride (Aldrich Chemical Co. Ltd.)

Prepared

1-Benzyl-3-carboxypyridinium chloride
1-Benzyl-4-carboxypyridinium chloride
1-Propyl-3-carboxypyridinium bromide

Attempts were made to prepare a sample of 1-benzyl-2-carboxypyridinium chloride (and bromide) but only 2-carboxypyridinium hydrochloride (and hydrobromide) were isolated.

1-Benzyl-3-carboxypyridinium chloride

This material was first reported by Gautier and Renault[16] who obtained it by acid hydrolysis of 1-benzyl-3-carbamoyl pyridinium chloride, but unfortunately no further preparative details are given in the publication. Other preparative methods have been detailed by Anderson and Berkelhammer[17] and Kolyer[18], but a modified method was used as described below.

30.8 grams (0.25 mole) of nicotinic acid was suspended in 100 cm^3 of distilled water and about 50 cm^3 of 20% sodium hydroxide solution was slowly added with vigorous stirring, to dissolve the nicotinic acid and give a solution with a resultant pH of 7. The solution was transferred to a 250 cm^3 round bottomed flask, with stirrer and reflux condenser, 30 cm^3 (0.26 mole) of benzyl chloride was added and the suspension, stirred vigorously for 10 hours at 80-90°C. After cooling, the solution was acidified with dilute hydrochloric acid and the resultant white precipitate, filtered off and recrystallised twice from boiling water, yielding 51.8 grams (83%).

The crystals had a faint pink tinge and melted at 181.5-182.5°C., (dec), agreeing with Kolyer[18] (180-181.5°C.,dec) and also Anderson and Berkelhammer[17] (183-184.5°C.,dec) but raising some doubt regarding the results obtained by Gautier and Renault[16] (196-197°C.,dec.)

The elemental composition and the infra-red spectrum were obtained and the compound was titrated with standardised 0.1 molar sodium hydroxide solution, to a phenolphthalein end point.

This compound (and others described later) was dried in a vacuum desiccator, over P_4O_{10} for at least two days.

1-Propyl-3-carboxypyridinium bromide

This material was first reported by Gautier and Renault[16] obtained by the acid hydrolysis of 1-propyl-3-carbamoyl pyridinium bromide, but an alternative procedure was adopted, as described below.

30.8 grams (0.25 mole) of nicotinic acid was suspended in 100 cm^3 of distilled water and about 50 cm^3 of 20% sodium hydroxide solution,,was slowly added with vigorous stirring, to dissolve the nicotinic acid and give a solution with a pH of 7. The solution was then transferred to a 250 cm^3 round bottomed flask, equipped with a stirrer and a reflux condenser. 25 cm^3 (0.275 mole) of 1-bromopropane was then added and the suspension, stirred for 16 hours at 80-90°C. After cooling 50 cm^3 of approx., 47% hydrobromic acid (approx. 0.58 mole), was added, but no precipitate obtained. The solution was evaporated down to 40 cm^3 and allowed to cool. The crystals produced on cooling were filtered off and recrystallised from a methanol-ethyl acetate mixture, yielding 21.8 grams (36%), with a melting point of 158-160°C., (lit.[16] 111°C.).

The elemental compositon and the infra-red spectrum were obtained and the material titrated with standardised 0.1 molar sodium hydroxide solution to a phenolphthalein end point.

1-Benzyl-4-carboxypyridinium chloride

No mention of this compound was found in the literature, it was prepared as follows.

30.8 grams (0.25 mole) of isonicotinic acid (pyridine-4-carboxylic acid) was suspended in 100 cm^3 of distilled water and about 50 cm^3 of 20% sodium hydroxide solution was added slowly, with vigorous stirring, to dissolve the isonicotinic acid and then to adjust the pH to 7. 30.0 cm^3 (0.26 mole) of benzyl chloride was added and the resultant suspension stirred for 10 hours at 80-90°C. After cooling the solution was acidified with concentrated hydrochloric acid and the white precipitate produced, filtered off and recrystallised twicw from a propan-2-ol/ethyl acetate mixture, yielding 53.7 grams (76%) of white crystals melting point 135-137°C.

The elemental compositon and the infra-red spectrum were obtained and the compound titrated with standardised 0.1 molar sodium hydroxide solution to a phenolphthalein end point.

1-Benzyl-2-carboxypyridinium chloride (and bromide)

No reference could be found in the literature regarding this compound and so an analogous method to that used for the preparation of 1-benzyl-3-carboxypyridinium chloride was employed.

30.8 grams (0.25 mole) of picolinic acid (pyridine-2-carboxylic acid) was dissolved in 50 cm^3 of distilled water and the pH adjusted to 7, with approximately 50 cm^3 of 20% sodium hydroxide solution. The solution was then transferred to a 250 cm^3 round bottomed flask, equipped with a stirrer and a reflux condenser. 30.0 cm^3 (0.26 mole) of benzyl chloride was added and the suspension stirred for 10 hours at 80-90°C. After cooling the solution was acidified with 40 cm^3 of concentrated hydrochloric acid, but since no precipitate was obtained, the solution was evaporated down to about 40 cm^3.

The above procedure was repeated using 31.0 cm^3 (0.26 mole) of benzyl bromide and 50 cm^3 of 47% hydrobromic acid.

The material obtained from these procedures, was filtered off, recrystallised twice from a propan-2-ol / ethyl acetate mixture, then dried in a vacuum desiccator over P_4O_{10} for 2 days.

A melting point and infra-red spectrum was obtained, and each compound was titrated with standardised 0.1 molar sodium hydroxide solution.

A further attempt to prepare 1-benzyl-2-carboxypyridinium chloride (and bromide) was made using the free acid.

30.8 grams (0.25 mole) of picolinic acid was dissolved in 50 cm^3 of distilled water and transferred to a 250 cm^3 round bottomed flask equipped with a stirrer and reflux condenser. 50 cm^3 of propan-2-ol was measured in, then 30.0 cm^3 (0.26 mole) of benzyl chloride or 31.0 cm^3 (0.26 mole) of benzyl bromide and the mixture stirred for ten hours at 80-90°C. After cooling the solution was acidified with 40 cm^3 concentrated hydrochloric acid (or 50 cm^3 of 47% hydrobromic acid) and evaporated down to about 40 cm^3. The precipitate obtained in each case was filtered off, recrystallised twice from propan-2-ol / ethyl acetate mixture and dried in a vacuum desiccator over P_4O_{10}.

The melting points and infra-red spectra were obtained an and the materials titrated with standardised 0.1 molar sodium hydroxide solution to a phenolphthalein end point.

Pyridine-2-carboxylic acid, hydrochloride (& hydrobromide)

These two compounds were prepared by dissolvine 12.3 grams (0.1 mole) picolinic acid in 15 cm^3 distilled water, then adding an excess of the appropriate acid (20 cm^3 conc., hydrochloric acid and 35 cm^3 47% hydrobromic acid) and then stirring at 40°C., for one hour. The solids which precipitated on cooling, were filtered off and the filtrates evaporated to 10 cm^3 and the further crops of crystals filtered off. The two crops of crystals were combined, recrystallised from propan-2-ol / ethyl acetate and dried in a vacuum desiccator over $P_4 O_{10}$, for at least two days.

The melting points and infra-red spectra were obtained and the materials titrated with standardised 0.1 molar sodium hydroxide solution.

Preparation of Standard Electrolytes

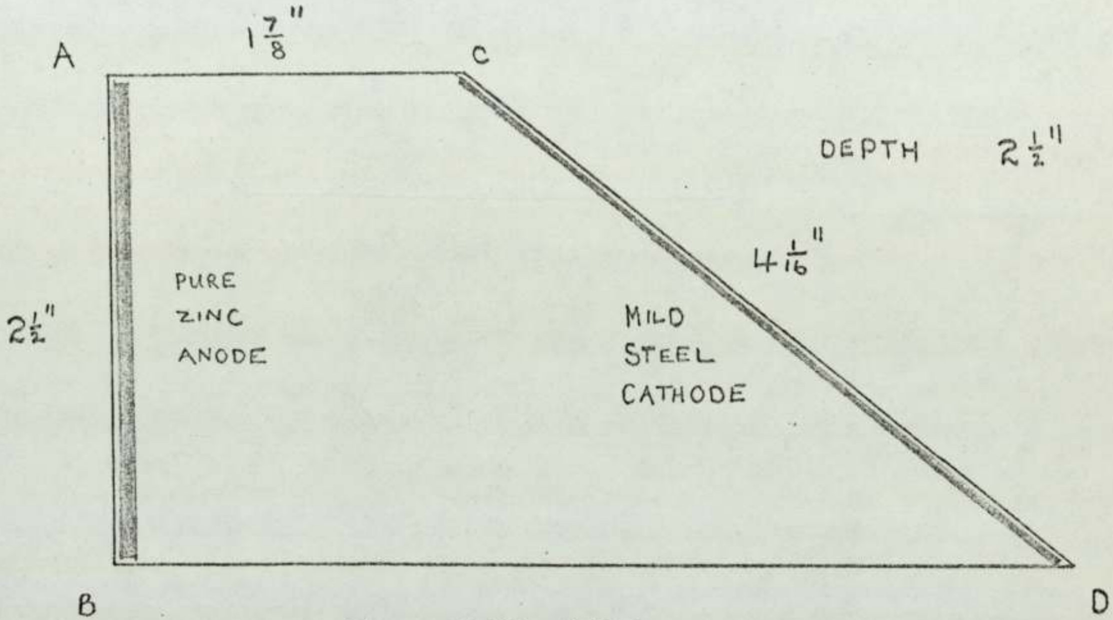
5 litres of a high metal - high cyanide zinc plating electrolyte, was prepared using zinc oxide, sodium hydroxide and sodium cyanide, the composition being adjusted until it gave the following analysis; zinc as metal 80 grams per litre, sodium hydroxide as NaOH 155 grams per litre and sodium cyanide as NaCN 230 grams per litre. This solution is twice the concentration of a normal electrolyte and needs to be diluted 50:50 before use.

About 0.5 grams per litre of sodium polysulphide solution was added, with continuous mixing to minimise the local precipitation of zinc sulphide, and the solution was electrolysed for eight hours at a current density of about 2 to 5 amperes per square foot.* These two operations being necessary to remove any metallic contamination, mainly lead and cadmium, which would cause dullness and other faults.

* These are the units used within the plating industry, the S.I. unit is the ampere per square decimetre which is equivalent to 9.29 amperes per square foot.

5 litres of a none-cyanide zincate electrolyte was prepared from zinc oxide and sodium hydroxide, the composition being adjusted until analysis gave 20 grams per litre of zinc as zinc metal and 220 grams per litre of sodium hydroxide as NaOH. The solution was electrolysed for ten hours at 2 to 5 amperes per square foot, to remove any metallic contamination.

Plating tests using the above electrolytes were carried out in a Hull cell[19], a device used to show the variation in appearance of the electrodeposit at varying current densities, this being achieved by virtue of the placement of the cathode at a fixed angle with respect to the anode. This results in a plating cell with a trapezoidal plan, the dimension of which are illustrated in the diagram below.



THE HULL CELL.

A supply of current (a steady one ampere), is necessary between the Anode and the Cathode.

It can be seen from the diagram, that the equipotential lines are not parallel, with the result that the current density is higher at C than at D. The current distribution for this arrangement has been determined and standard charts are available, so that the cathode panel can be compared with a chart in order to relate the appearance of the deposit to a particular current density.

The general method for testing the quaternary pyridinium compounds in a Hull cell was as follows:

125 cm^3 of electrolyte solution was poured into a 250 cm^3

measuring cylinder, the desired amount of addition agent (usually as an aqueous solution) introduced, and the resultant mixture diluted to the 250 cm^3 mark with distilled water. This solution was then transferred to a 400 cm^3 wide mouthed beaker, stirred thoroughly with a glass rod and the temperature adjusted to 25°C.

A mild steel panel 3" by 4" by 0.01" (the cathode), on which the zinc is electroplated, was then cleaned using the following sequence;

1. degrease with acetone
2. water swill
3. anodic cleaner - such as Activax*
4. water swill
5. dilute hydrochloric acid dip (approx. 50% by volume)
6. water swill
7. second stage anodic clean - such as 10-55 Cleaner*
8. water swill
9. water swill

* Trademark for further details see Canning Handbook on Electroplating

The electrolyte was then poured into the Hull cell, the cleaned mild steel panel inserted, and a current of one ampere passed for 15 minutes, the voltage being regulated (manually or electronically) so that the current remained constant.

After 15 minutes the current was switched off and the panel removed from the Hull cell. After swilling thoroughly in cold running water, the panel was partially immersed in a 1% nitric acid solution for 10 seconds, so that about half of the zinc plated area was immersed. The panel was then swilled in cold running water and dried in a stream of hot air.

The reason for only dipping half the panel was in order that a comparison could be made between the dipped and undipped zinc electrodeposit. The dilute nitric acid dip, removes any surface films and leaves a brighter finish.

Proprietry dips contain other additives, which increase the brightness even more.

In the cyanide electrolyte, the pyridine derivatives were tested alone at 0.5 and 1.0 gl^{-1}, then at 1.0 gl^{-1} with 1.0 gl^{-1} of polyvinylalcohol. Fresh base being used for each test and the Hull cell and anode being cleaned thoroughly, before the introduction of a new compound.

A different approach was adopted with the alkaline none-cyanide electrolyte, because of the poor deposits obtained without any addition agents, and the fact that by themselves the pyridine derivatives have very little effect. Consequently, all the tests were made with the addition of 4.0 gl^{-1} of Polymin G35 (a polyethyleneimine obtained from B.A.S.F.), which when used at this concentration alone, gives a electro-deposit comparable to that obtained from the alkaline cyanide electrolyte.

The pyridine derivatives were tested at concentrations of 0.5 and 1.0 gl^{-1}, the solution containing 1.0 gl^{-1} being retained for 100 hours, then a fresh panel being plated at 25°C.

Ultra-violet experiments

The following experiments were performed using a Pye-Unicam SP 500 spectrophotometer in 1 cm silica cells.

50 cm^3 of a solution containing 20 gl^{-1} Zn^{2+} and 200 gl^{-1} NaOH (in distilled water) was pipetted into a 100 cm^3 standard flask. 10 cm^3 of a 5% solution of 1-benzyl-3-carboxy pyridinium chloride (pH 6.5) was then added, the mixture diluted to the mark with distilled water, and shaken vigorously to mix thoroughly. The optical density was then recorded at wavelengths of 230 to 400 nm in steps of 5 nm.

The optical density was again recorded at the same wavelengths, after the solution had been allowed to stand for 25 hours.

The above procedure was repeated, without the Zn^{2+} ions.

Action of hydroxide ions on 1-benzyl-3-carboxypyridinium chloride

50 cm^3 of 20% sodium hydroxide solution and 10 cm^3 of 0.5% 1-benzyl-3-carboxypyridinium chloride solution (pH 6.5), were diluted to 100 cm^3 with distilled water. The optical density was then recorded at 330 to 400 nm at intervals of 10 nm., this being assumed to be zero time. The optical density at these wavelengths was again recorded after 1,2,3, 5,6, 7½ and 30 hours.

Effects of Temperature

A different procedure was adopted for the following experiments, since it was found that the heat of dilution produced by using the procedure described above, caused the initial results to be anomalous.

0.2 grams of 1-benzyl-3-carboxypyridinium chloride was weighed out accurately and dissolved in 100 cm^3 of 10% sodium hydroxide solution, in a 150 cm^3 beaker. The sodium hydroxide solution and the beaker having been kept in a water bath at 20°C., prior to this operation for about one hour. After vigorously stirring the solution for about one minute to ensure that the pyridine derivative had completely dissolved, it was transferred to the SP 500 spectrophotometer and thermostated at 20°C., throughout the experiment. The optical density at 360 nm., was then recorded every minute on the minute for 15 minutes.

The experiment was then repeated at 25, 30 and 35°C.

Effects of Varying the Concentration of Sodium Hydroxide

0.2 grams of 1-benzyl-3-carboxypyridinium chloride was weighed accurately and dissolved in 100 cm^3 of 10% sodium hydroxide solution. The sodium hydroxide solution had been equilibrated at 20°C., for one hour prior to commencement of the experiment and the cell holders were maintained at 20°C., throughout the experiment. The optical density was measured at 360 nm., every five minutes for 35 minutes, the readings rising above 1.0 after this time.

The experiment was then repeated using 70 cm^3 (7 grams of NaOH), 50 cm^3 (5 grams of NaOH) and 10 cm^3 (1 gram of NaOH), of 10% sodium hydroxide solution diluted to 100 cm^3 in a graduated flask. The solutions produced above being equilibrated at 20°C., for one hour prior to commencement of the experiment. The optical density being then measured every five minutes for 50 minutes, or until the optical density went above 1.0.

Effect of Varying the Concentration of 1-benzyl-3-carboxy pyridinium chloride

The experimental procedure described above was repeated using 100 cm^3 of 10% sodium hydroxide solution, but using 0.5, 0.1 and 0.05 grams of 1-benzyl-3-carboxypyridinium chloride. The optical density being measured at 360 nm, every five minutes for 60 minutes, or until the optical density became greater than 2.0 .

Effect of Zn^{2+} on the Production of the Maximum at 360 nm

The experimental procedure described above was repeated with 2.1 grams of zinc chloride (10 gl^{-1} Zn^{2+}) and 0.2 grams of 1-benzyl-3-carboxypyridinium chloride, being added to 100 cm^3 of 10% sodium hydroxide solution, thermostated at 20°C. The optical density being measured at 360 nm., every five minutes for 35 minutes.

Effect of Other Pyridine Derivatives

0.4 grams of 1-Propyl-3-carboxypyridinium bromide was weighed out accurately and dissolved in 100 cm^3 of 10% sodium hydroxide solution. The optical density was then measured from 320 to 400 nm., in steps of 10 nm., immediately and then after 1½, 2, 4, 6, 22, 25, 30 and 48 hours.

The experiment was then repeated with;

(i) 0.5 grams of 1-Benzyl-4-carboxypyridinium chloride
and
(ii) 0.5 grams of Nicotinic acid

in 100 cm^3 of 10% sodium hydroxide solution.

The experiment was repeated with 0.5 grams of 1-benzyl -3-carboxy pyridinium chloride dissolved in 100 cm^3 of 10% sodium hydroxide solution. The optical density being measured at 400 to 600 nm., in steps of 10 nm., initially and then after 1, 3, 5, 6, 7 and 25 hours.

Combined Plating and U.V. Experiments

5 litres of a none-cyanide zincate electrolyte was prepared, containing 20 gl^{-1} of zinc metal and 200 gl^{-1} of sodium hydroxide, and purified by electrolysis. 4 grams of Polymin G35 (a polyethyleneimine available from B.A.S.F.) and 0.05 grams of 1-benzyl-3-carboxypyridinium chloride, was dissolved in 500 cm^3 of the above electrolyte, and the mixture diluted to one litre with distilled water. 250 cm^3 of the resultant solution was poured into a Hull cell and a cleaned steel panel plated for 15 minutes using a current of one ampere. Simultaneously with this plating test, a sample of the remaining solution was used to determine the optical density at a wavelength of 360 nm.
The above procedure was then repeated using unplated solution after 24 and 170 hours.

The above experiment was repeated using 0.5 grams of 1-propyl-3-carboxypyridinium bromide and then again using 1.0 grams of nicotinic acid. In both sets of experiments 4 grams of Polymin G35 was also present.

Comparison of the Rate of Production of the Maximum at 360 nm for 1-Benzyl and 1-Propyl, 3-carboxypyridinium compounds

0.1 grams of 1-benzyl-3-carboxypyridinium chloride was dissolved in 100 cm^3 of 10% sodium hydroxide solution and the optical density at 360 nm., measured every five minutes for one hour.

The experiment was then repeated using 0.4 and 1.0 grams of 1-propyl-3-carboxypyridinium bromide.

Nuclear Magnetic Resonance Experiments

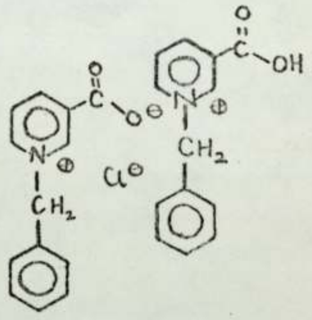
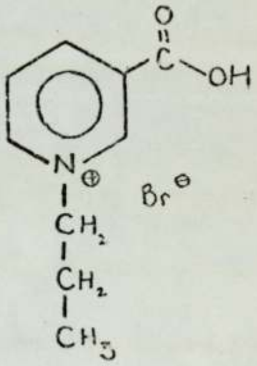
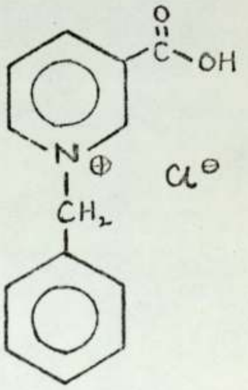
To a suspension of 1.0 grams of 1-benzyl-3-carboxy pyridinium chloride in 3.0 cm^3 of deuterium oxide (D_2O), was added 0.2 cm^3 of 52% NaOD in D_2O and the mixture agitated for about one minute. A further 0.2 cm^3 of 52% NaOD in D_2O was added and the mixture agitated until all solid material had dissolved.

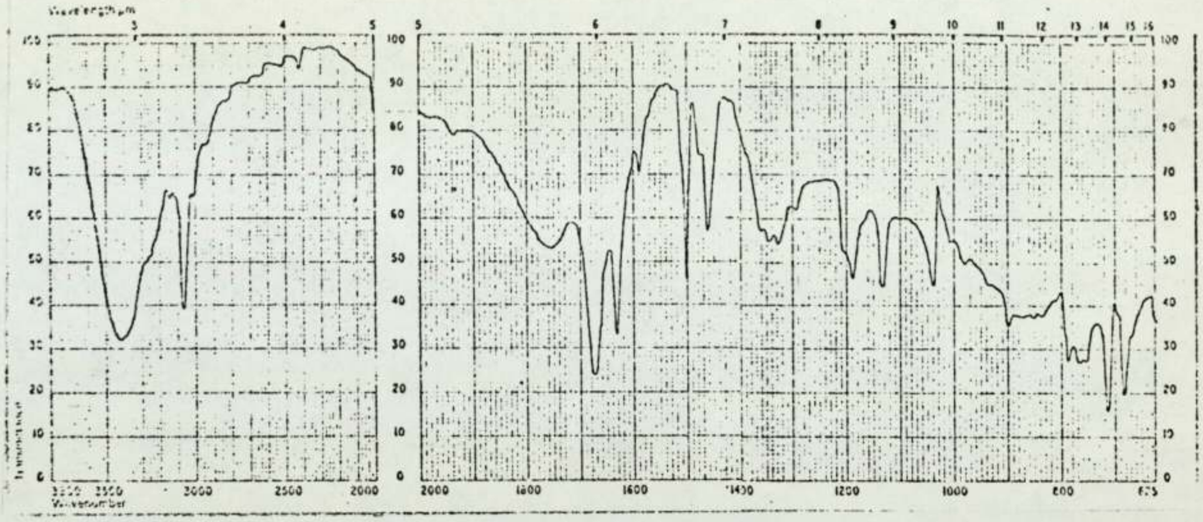
The nuclear magnetic resonance spectrum was then obtained using a Varian HA 100D spectrometer, using Trimethylsilane (TMS) in a sealed capillary tube as an external standard.

The solution was stored for nine days in a dark cupboard and the spectrum again determined.

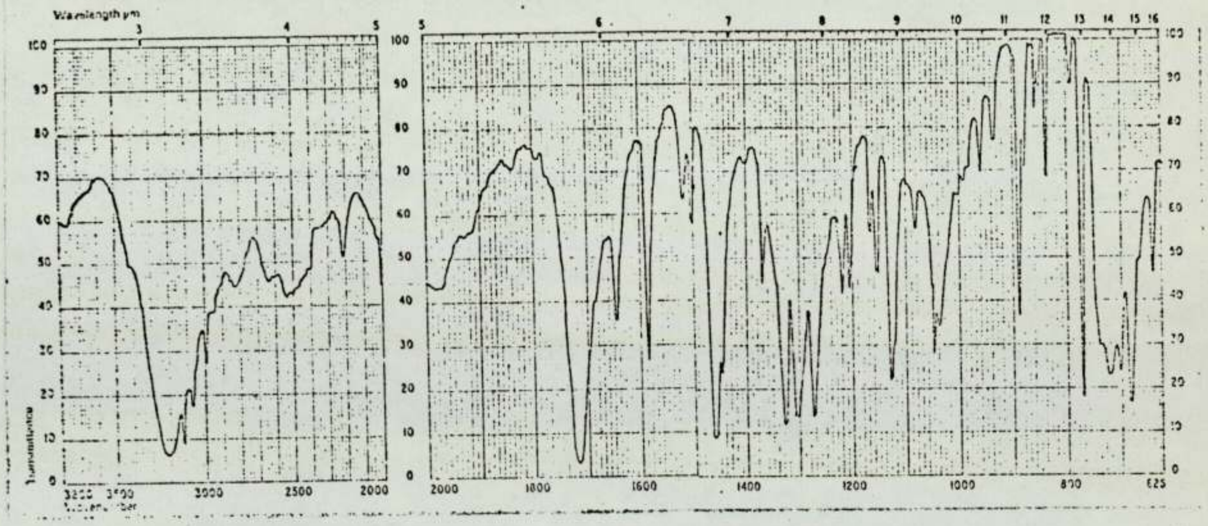
The above preparative procedure was then repeated and the spectrum recorded. 1.6 cm^3 of 52% NaOD in D_2O was then added and the solution agitated. The spectrum was recorded after 2 and 9 days. then finally at the end of one month.

TABLE 2 Elementary Analysis, Equivalent Weight (eq. wt.) & Structure of Pyridine Derivatives.

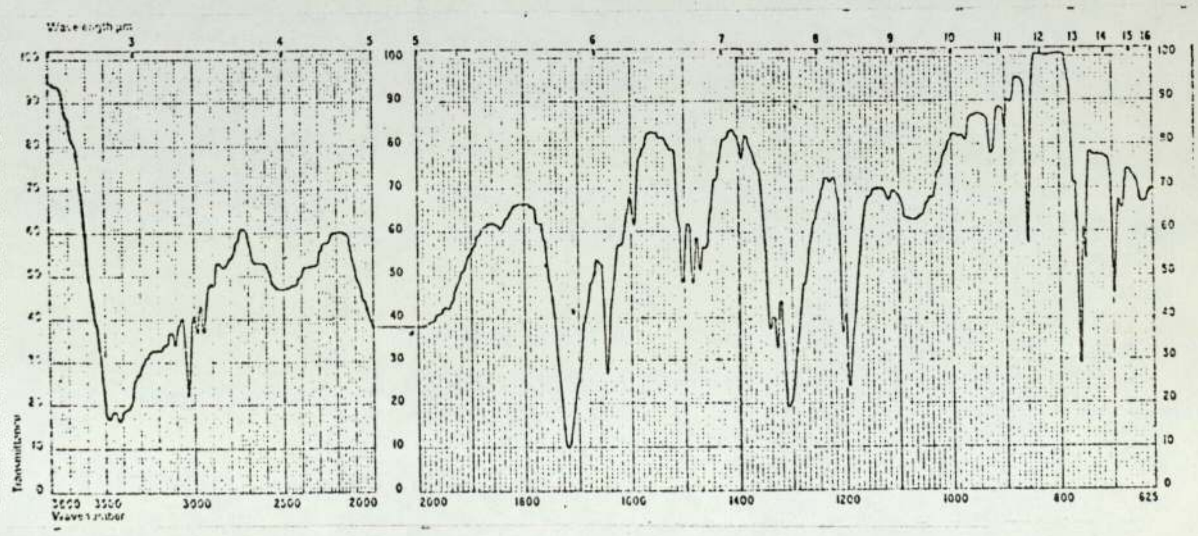
COMPOUND	FOUND	CALCULATED	STRUCTURE
1-BENZYL 3-CARBOXY PYRIDINIUM CHLORIDE	64·19 63·81 % C 5·79 5·74 % N 5·12 5·17 % H 7·3 % Cl 479 480 eq. wt.	64·93 % C $5{\cdot}82_5$ % N 5·24 % H 7·37 % Cl 480·95 eq. wt.	
1-PROPYL 3-CARBOXY PYRIDINIUM BROMIDE	42·90 43·42 % C 5·86 5·91 % N 4·78 4·80 % H 32·32 % Br 245 246 eq. wt.	43·91 % C 5·71 % N 4·91 % H 32·50 % Br. 246·16 eq. wt.	
1-BENZYL 4-CARBOXY PYRIDINIUM CHLORIDE	61·98 61·70 % C 5·76 5·72 % N 4·96 5·26 % H 13·10 % Cl 252 250 eq. wt.	62·53 % C 5·61 % N 5·61 % H 12·82 % Cl 249·7 eq. wt.	



1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE



1-BENZYL-4-CARBOXYPYRIDINIUM CHLORIDE



1-PROPYL-3-CARBOXYPYRIDINIUM BROMIDE

RESULTS

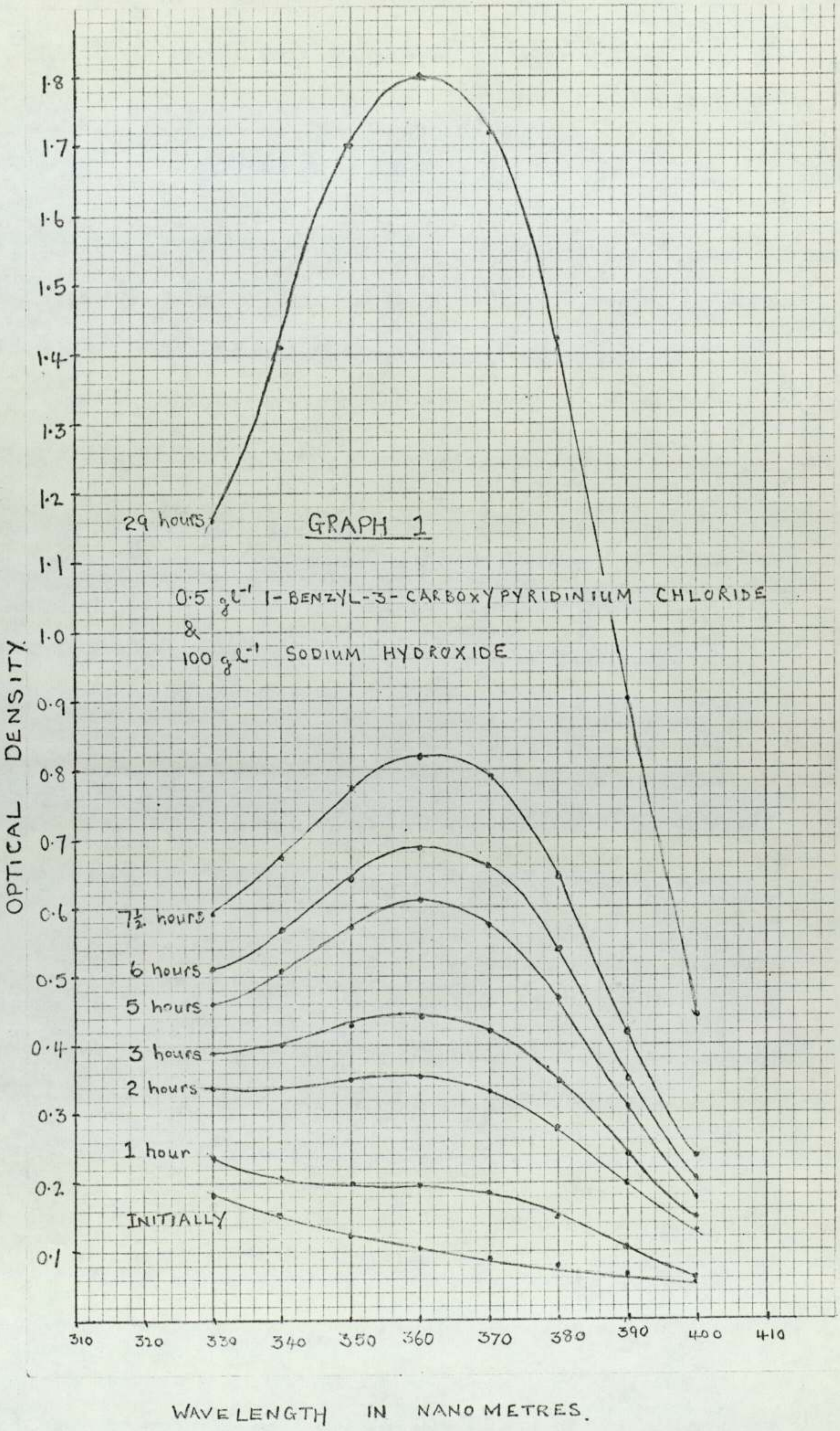
The results of the elemental analysis and the equivalent weight determinations, for the pyridine derivatives, are given in Table 2. The only unexpected result being those obtained for 1-benzyl-3-carboxypyridinium chloride. The equivalent weight for this compound was found to be 479-480, almost double the expected value. This result in conjunction with the elemental analysis, suggested that the structure must be a dimer as illustrated in Table 2.

1-benzyl-2-carboxypyridinium chloride (or bromide) could not be prepared by the methods described. The only material that could be isolated, was the hydrochloride (or hydrobromide) of pyridine-2-carboxylic acid, which was readily identified by its equivalent weight and infra-red spectrum.

Results of the U.V. Experiments

The optical density measurements obtained at wavelengths of 230 to 400 nm. (in steps of 10 nm.), for 0.5 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride dissolved in a standard none-cyanide zincate electrolyte, can be seen in Appendix (i). Immediately after make up, only the expected maximum at 263 nm., was observed, although it was necessary to dilute the solution ten times in order to obtain measurable optical densities. After 25 hours, the optical density at 260 nm., had increased from 0.97 to 1.57, but more interestingly a new maximum had appeared at about 360 nm.

Almost identical results were obtained when the above procedure was repeated in the absence of zinc ions, as can be seen in Appendix (i).



GRAPH 1

0·5 gl^{-1} 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE
&
100 gl^{-1} SODIUM HYDROXIDE
OPTICAL DENSITY.
WAVELENGTH IN NANOMETRES.
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
310
320
330
340
350
360
370
380
390
400
410
29 hours
7½ hours
6 hours
5 hours
3 hours
2 hours
1 hour
INITIALLY

Action of Hydroxide Ions on 1-Benzyl-3-carboxypyridinium chloride

The results of this experiment are illustrated in graph 1, the experimental details being found in the Appendix. The graph depicts the growth of a maximum at about 360 nm.

Effect on Maximum of Variation in Temperature, Concentration of Hydroxide Ions and Concentration of 1-Benzyl-3-carboxypyridinium chloride

The results of these experiments are illustrated in graphs 2, 3 and 4, the actual experimental values being recorded in the Appendix. An increase in any of these quantities produces an increase in the rate of production of the maximum at 360 nm. The initial portion of the graphs being linear but curvature becoming noticeable as the reaction proceeds.

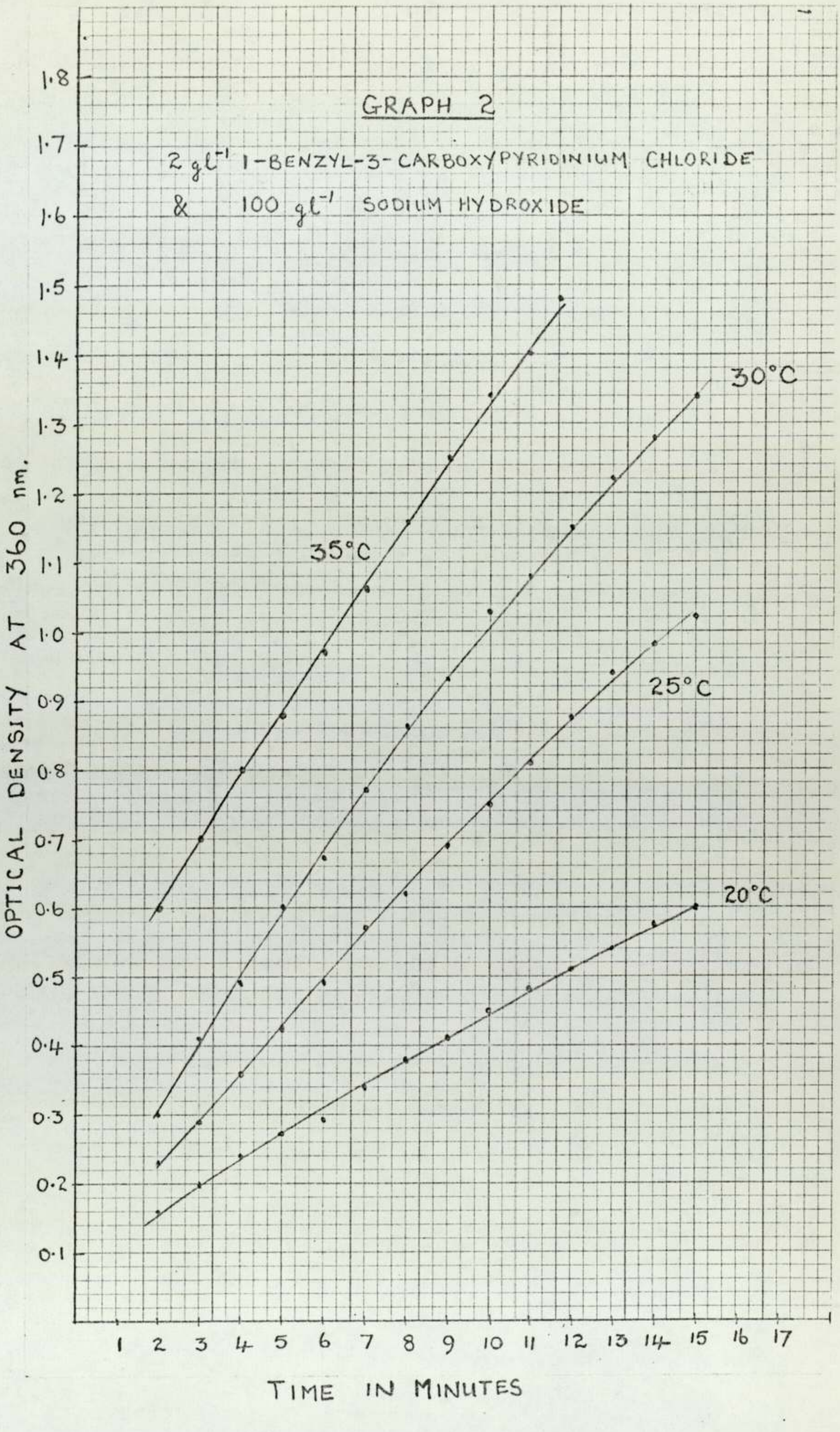
Using a method described by Eisenthal and Katritzky[20] it was possible to determine the reaction order with respect to hydroxide ion and 1-benzyl-3-carboxypyridinium chloride concentration.

Let; $\text{rate} = k_{obs}\left[OH^-\right]^n \left[Py^+\right]^m$

where, Py^+ = concentration of 1-benzyl-3-carboxypyridinium chloride

hence, $\log \text{rate} = \log k_{obs} + n\log\left[OH^-\right] + m\log\left[Py^+\right]$

Thus, by constructing log-log plots of the initial rate (in optical density units per second, calculated from the slope of the initial linear portions of the appropriate curves) against different concentrations of hydroxide ion and 1-benzyl-3-carboxypyridinium chloride. It is possible to


GRAPH 2
2 gl⁻¹ 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE
& 100 gl⁻¹ SODIUM HYDROXIDE
OPTICAL DENSITY AT 360 nm.
TIME IN MINUTES
35°C
30°C
25°C
20°C
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
1
2
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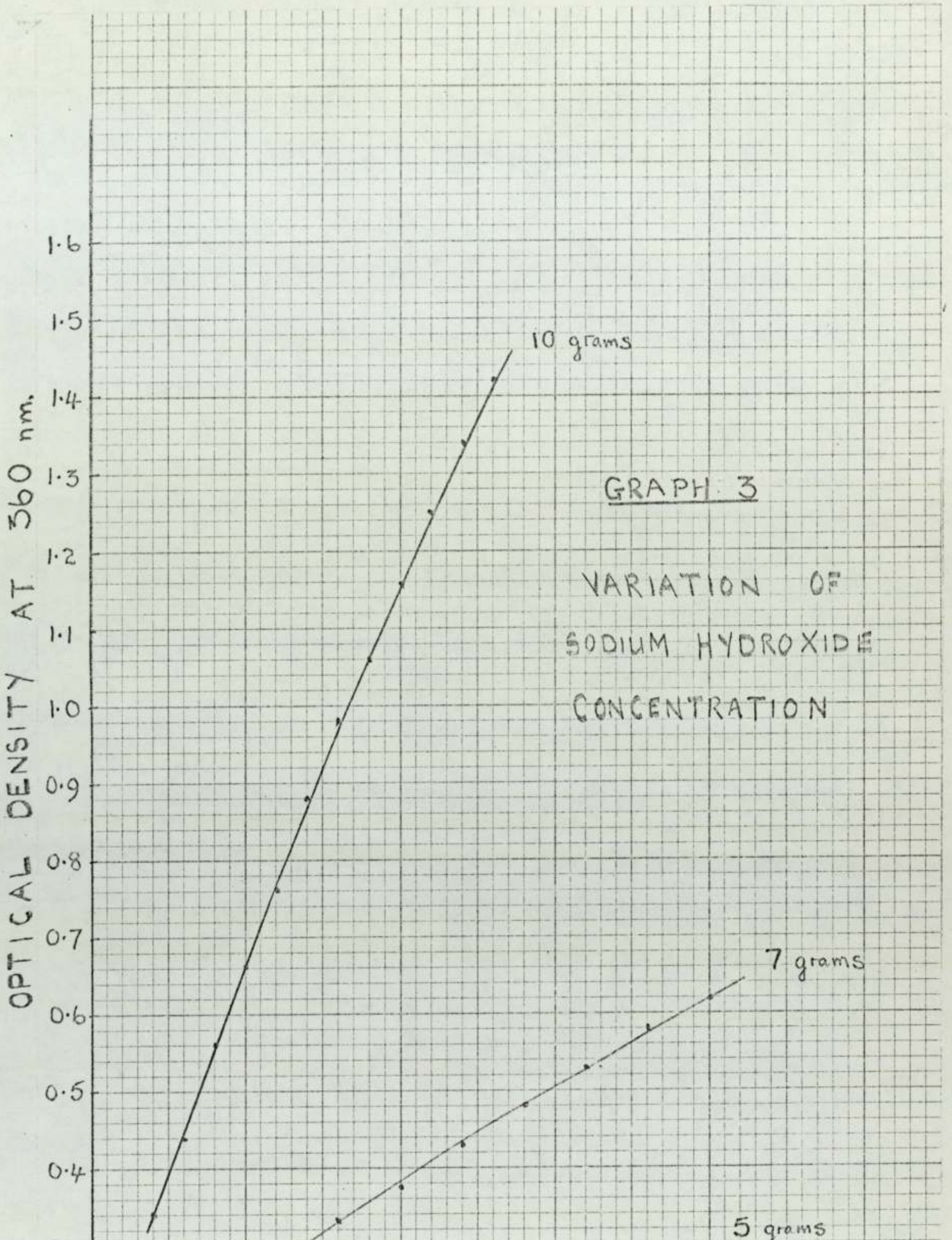
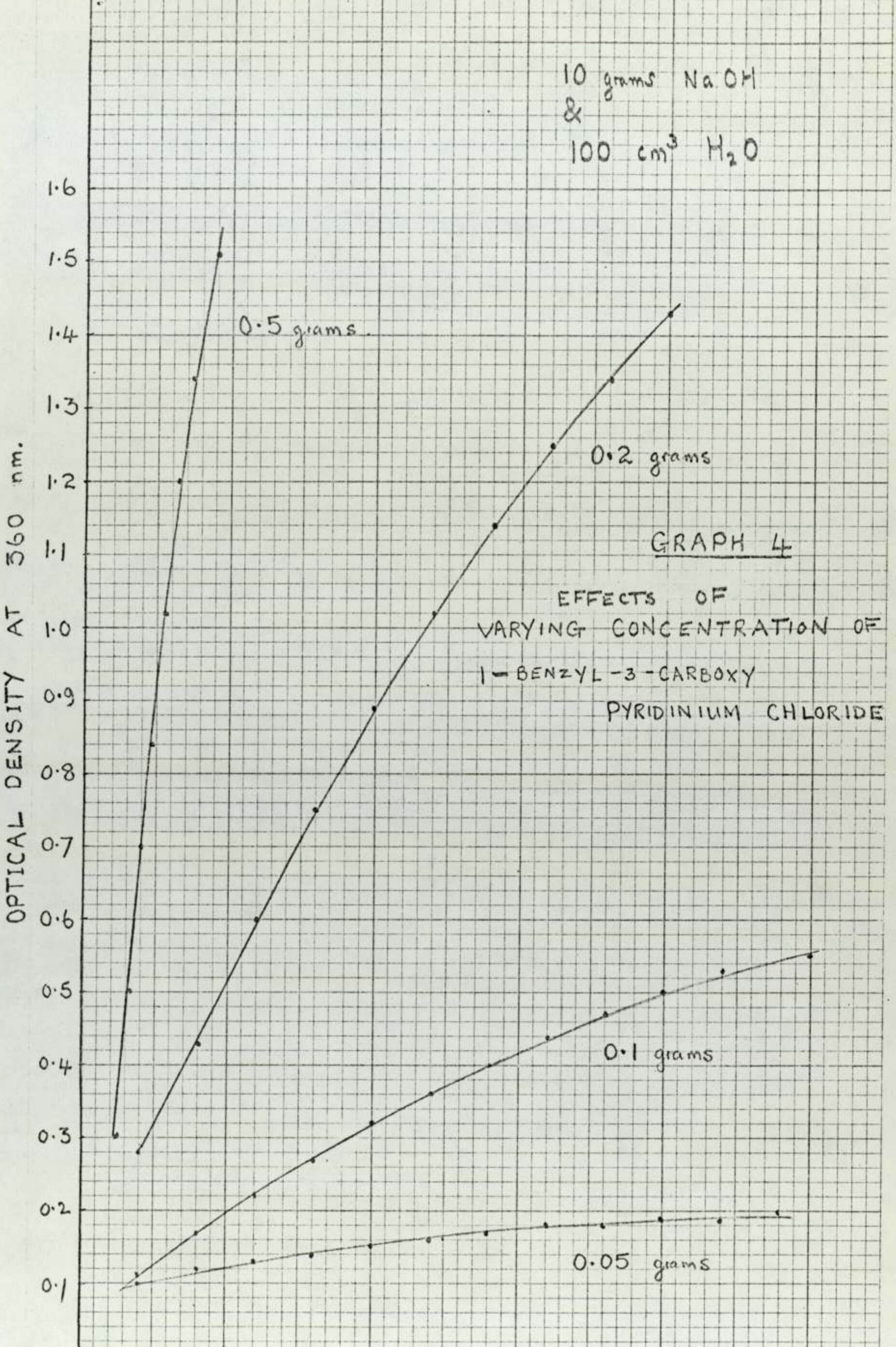
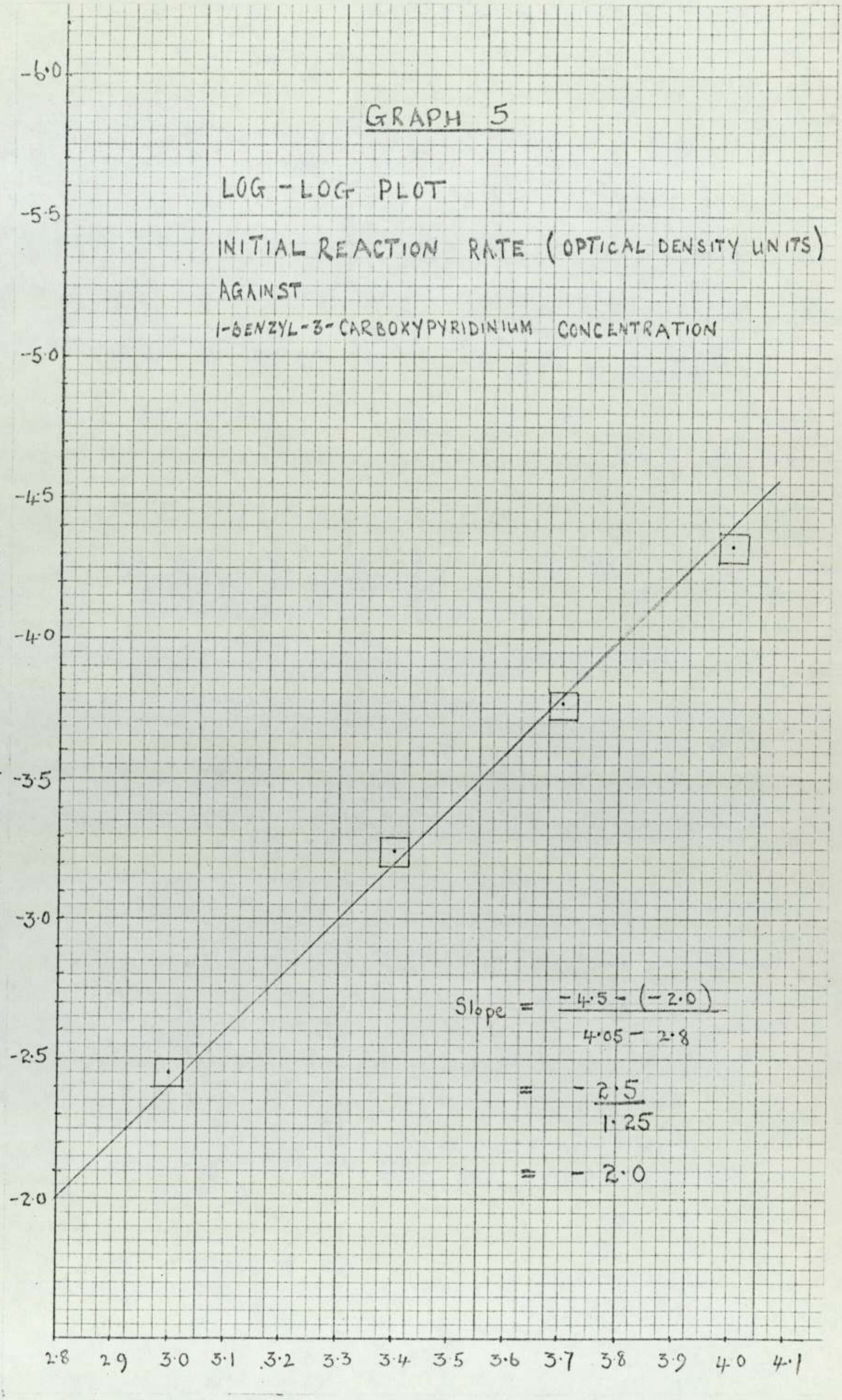
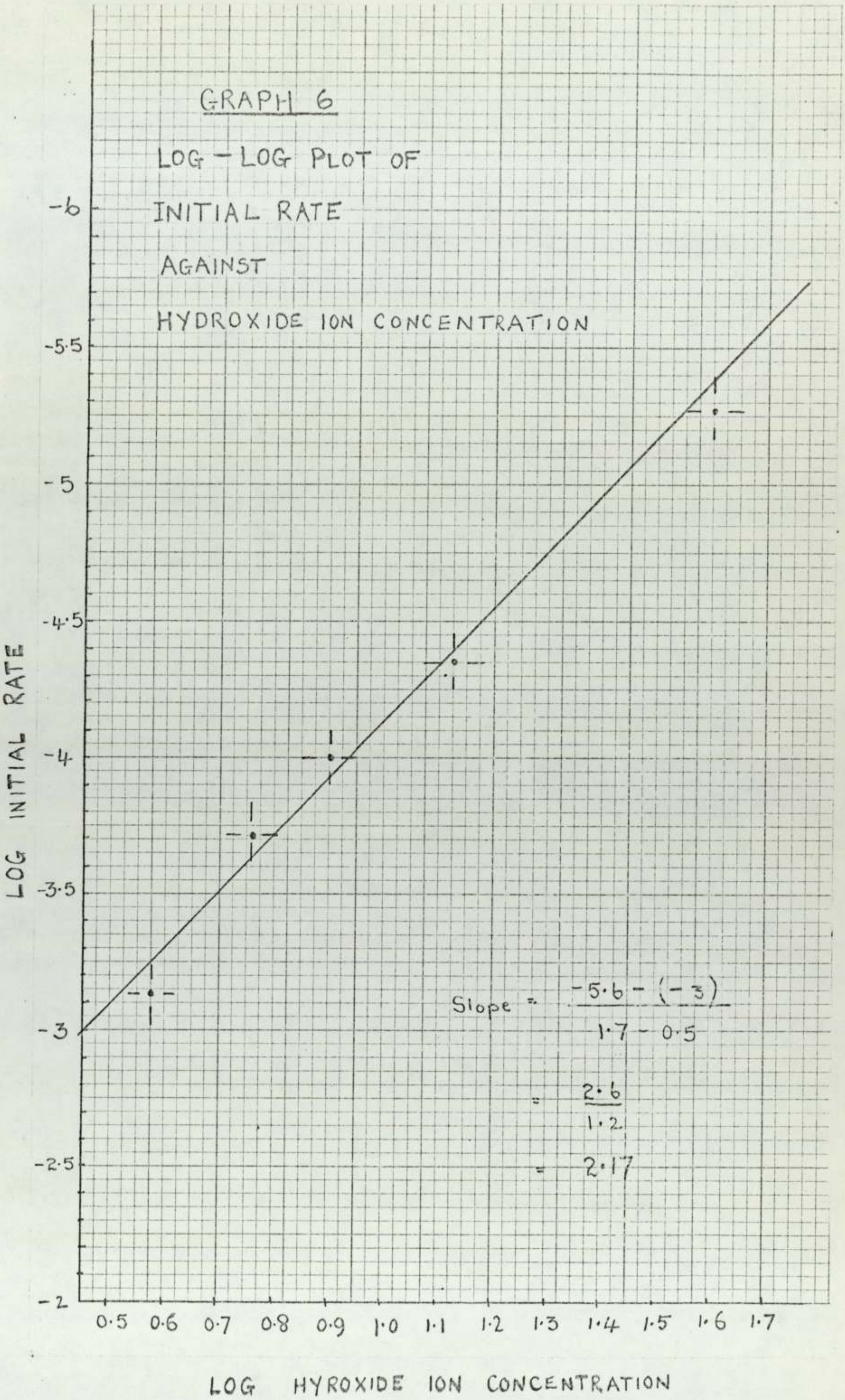

GRAPH 3
VARIATION OF SODIUM HYDROXIDE CONCENTRATION
OPTICAL DENSITY AT 360 nm.
TIME IN MINUTES
10 grams
7 grams
5 grams
3 grams
1 gram
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
1·2
1·3
1·4
1·5
1·6
5
10
15
20
25
30
35
40
45
50
55
60


10 grams Na OH
&
100 cm^3 H_2O
0·5 grams.
0·2 grams
0·1 grams
0·05 grams
GRAPH 4
EFFECTS OF
VARYING CONCENTRATION OF
1-BENZYL-3-CARBOXY
PYRIDINIUM CHLORIDE
OPTICAL DENSITY AT 360 nm.
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
5
10
15
20
25
30
35
40
45
50
55
60
TIME IN MINUTES


GRAPH 5
LOG - LOG PLOT
INITIAL REACTION RATE (OPTICAL DENSITY UNITS)
AGAINST
1-BENZYL-3-CARBOXYPYRIDINIUM CONCENTRATION
Slope = (-4·5 - (-2·0)) / (4·05 - 2·8)
= -2·5 / 1·25
= -2·0
LOGARITHM OF INITIAL RATE
-6·0
-5·5
-5·0
-4·5
-4·0
-3·5
-3·0
-2·5
-2·0
2·8
2·9
3·0
3·1
3·2
3·3
3·4
3·5
3·6
3·7
3·8
3·9
4·0
4·1
LOGARITHM 1-BENZYL-3-CARBOXY PYRIDINIUM ION CONCENTRATION.



GRAPH 6

LOG - LOG PLOT OF INITIAL RATE AGAINST HYDROXIDE ION CONCENTRATION

$$\text{Slope} = \frac{-5\cdot6-(-3)}{1\cdot7-0\cdot5} = \frac{2\cdot6}{1\cdot2} = 2\cdot17$$

determine n and m the orders of reaction for hydroxide ion and 1-benzyl-3-carboxypyridinium chloride, respectively. The results obtained are illustrated in graphs 5 and 6.

Results of the Plating Experiments

In the Cyanide Electrolyte

At 0.5 gl^{-1} 1-benzyl-3-carboxypyridinium chloride gave a bright uniform zinc deposit, which had a yellowish tinge, before immersion in a 1% nitric acid solution. Increasing the concentration to 1.0 gl^{-1} gave an increase in brightness.

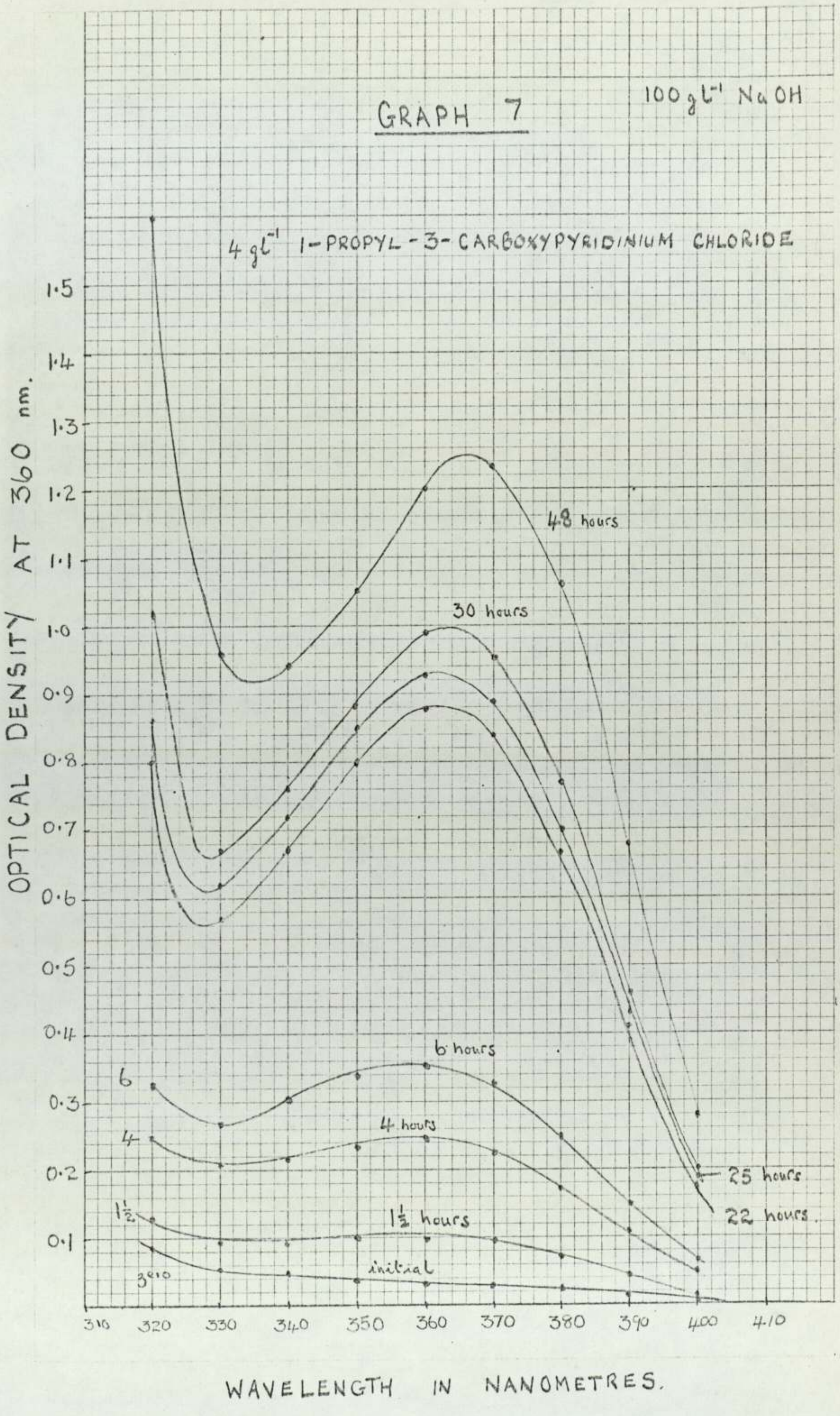
At 0.5 gl^{-1} 1-propyl-3-carboxypyridinium bromide gave a bright uniform zinc deposit, which had a yellowish tinge, before dipping. Increasing the concentration to 1.0 gl^{-1} produced an improvement in brightness, but inferior to that obtained from 0.5 gl^{-1} 1-benzyl-3-carboxypyridinium chloride.

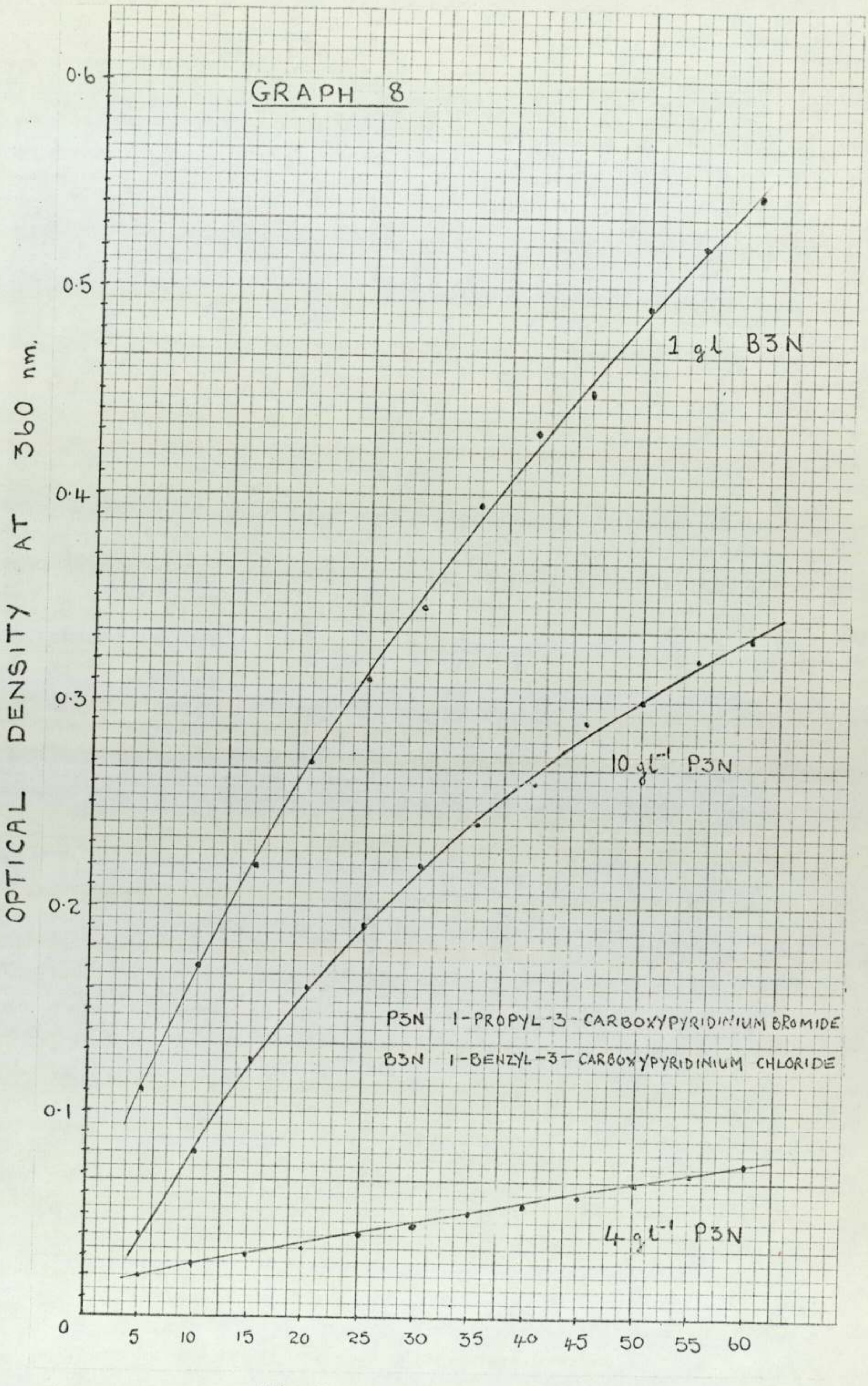
Both nicotinic acid and 1-benzyl-4-carboxypyridinium chloride at 0.5 gl^{-1}, gave deposits identical to that achieved from the electrolyte alone. Increasing the concentration to 1.0 gl^{-1} produced no improvement.

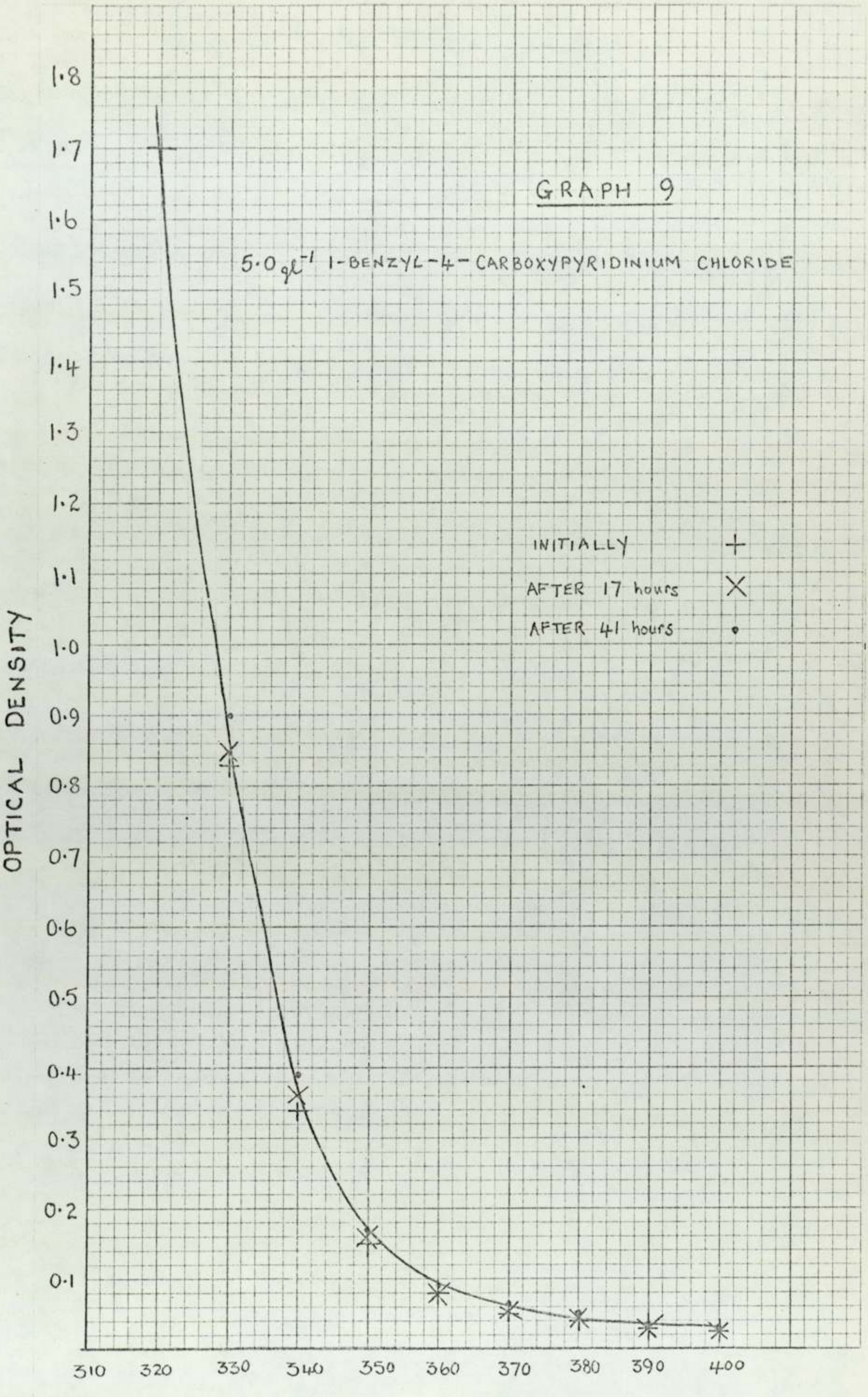
In the None-cyanide Electrolyte

At 0.5 gl^{-1} 1-benzyl-3-carboxypyridinium chloride gave a very bright uniform zinc deposit, but increasing the concentration to 1.0 gl^{-1} produced very little improvement. At 0.2 gl^{-1} the deposit was still very bright and uniform, being superior to that produced by 0.5 gl^{-1} in the cyanide electrolyte.

At 0.5 gl^{-1} 1-propyl-3-carboxypyridinium bromide and homarine hydrochloride (2-carboxy-1-methylpyridinium chloride), gave a deposit slightly better to that obtained from the


GRAPH 7
100 gl^{-1} NaOH
4 gl^{-1} 1-PROPYL-3-CARBOXYPYRIDINIUM CHLORIDE
OPTICAL DENSITY AT 360 nm.
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
48 hours
30 hours
25 hours
22 hours.
6 hours
4 hours
6
4
1½
1½ hours
initial
zero
310
320
330
340
350
360
370
380
390
400
410
WAVELENGTH IN NANOMETRES.


GRAPH 8
OPTICAL DENSITY AT 360 nm.
0.6
0.5
0.4
0.3
0.2
0.1
0
5
10
15
20
25
30
35
40
45
50
55
60
TIME IN MINUTES
1 gl B3N
10 gl⁻¹ P3N
4 gl⁻¹ P3N
P3N 1-PROPYL-3-CARBOXYPYRIDINIUM BROMIDE
B3N 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE



WAVELENGTH IN NANOMETRES.

electrolyte, without them. At 1.0 gl^{-1} an improvement was noticed, but the deposit produced was inferior to that obtained using 0.2 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride.

Nicotinic acid and 1-benzyl-4-carboxypyridinium chloride at 0.5 and 1.0 gl^{-1}, gave Hull cell panels similar to those obtained from the electrolyte, without them.

Effect of Hydroxide Ion on other Pyridine Derivatives

4.0 gl^{-1} of 1-propyl-3-carboxypyridinium bromide dissolved in 100 gl^{-1} of sodium hydroxide, exhibited a maximum at about 360 nm.,(but centred at 355 not 365 nm.) the intensity of which increased with time, as illustrated in graph 7.

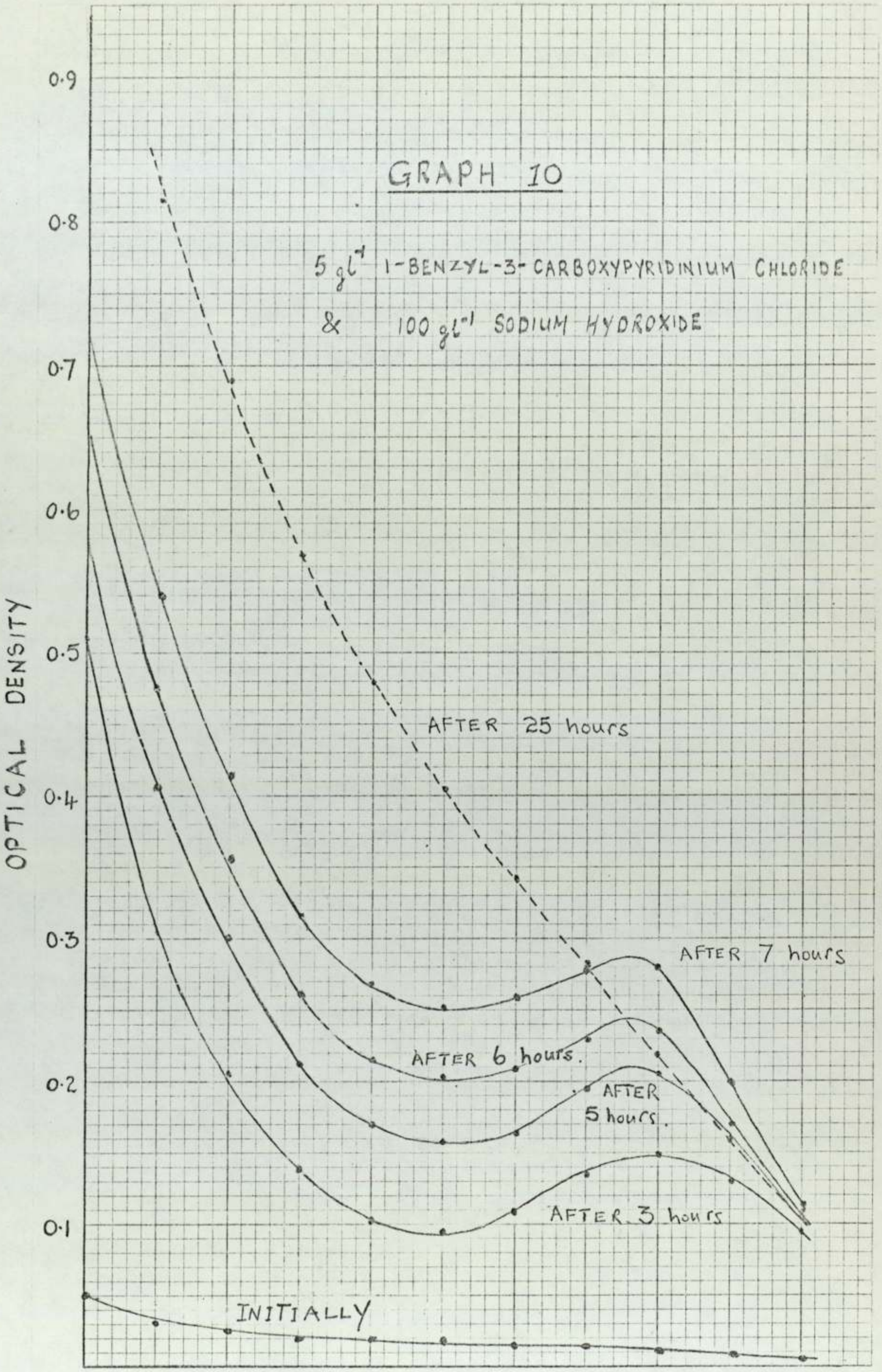
The rate of production of this maximum appeared to be much slower than from 1-benzyl-3-carboxypyridinium chloride. This was confirmed by comparison of the rate of production of the maximum at 360 nm., obtained from 1.0 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride with the results obtained from 10.0 and 4.0 gl^{-1} of 1-propyl-3-carboxypyridinium bromide, as shown in graph 8.

Graph 9, illustrates the inert behaviour of 5.0 gl^{-1} of 1-benzyl-4-carboxypyridinium chloride dissolved in 100 gl^{-1} of sodium hydroxide solution. 5.0 gl^{-1} of nicotinic acid also exhibits identical behaviour, with no possibility of a maximum at about 360 nm.

Extra Experiments with 1-Benzyl-3-carboxypyridinium Chloride

Graph 10, illustrates the growth of a maximum at about 575 nm., produed when 5.0 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride was dissolved in 100 gl^{-1} of sodium hydroxide.

The growth of the maximum at about 360 nm., obtained with 0.2 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride and 100 gl^{-1} sodium hydroxide, is the same in the absence or presence of 10 gl^{-1} of Zn^{2+} ions, as can be seen from Appendix (xii).


GRAPH 10
5 gl⁻¹ 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE
& 100 gl⁻¹ SODIUM HYDROXIDE
OPTICAL DENSITY
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
AFTER 25 hours
AFTER 7 hours
AFTER 6 hours.
AFTER 5 hours.
AFTER 3 hours
INITIALLY
500
510
520
530
540
550
560
570
580
590
600
WAVELENGTH IN NANOMETRES

Results of the Combined Plating and U.V. Experiments

Table 3, shows the optical density measurements obtained at a wavelength of 360 nm., initially and then after 24 and 170 hours, for 0.05 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride, 0.5 gl^{-1} of 1-propyl-3-carboxypyridinium bromide and 1.0 gl^{-1} of nicotinic acid.

Table 3

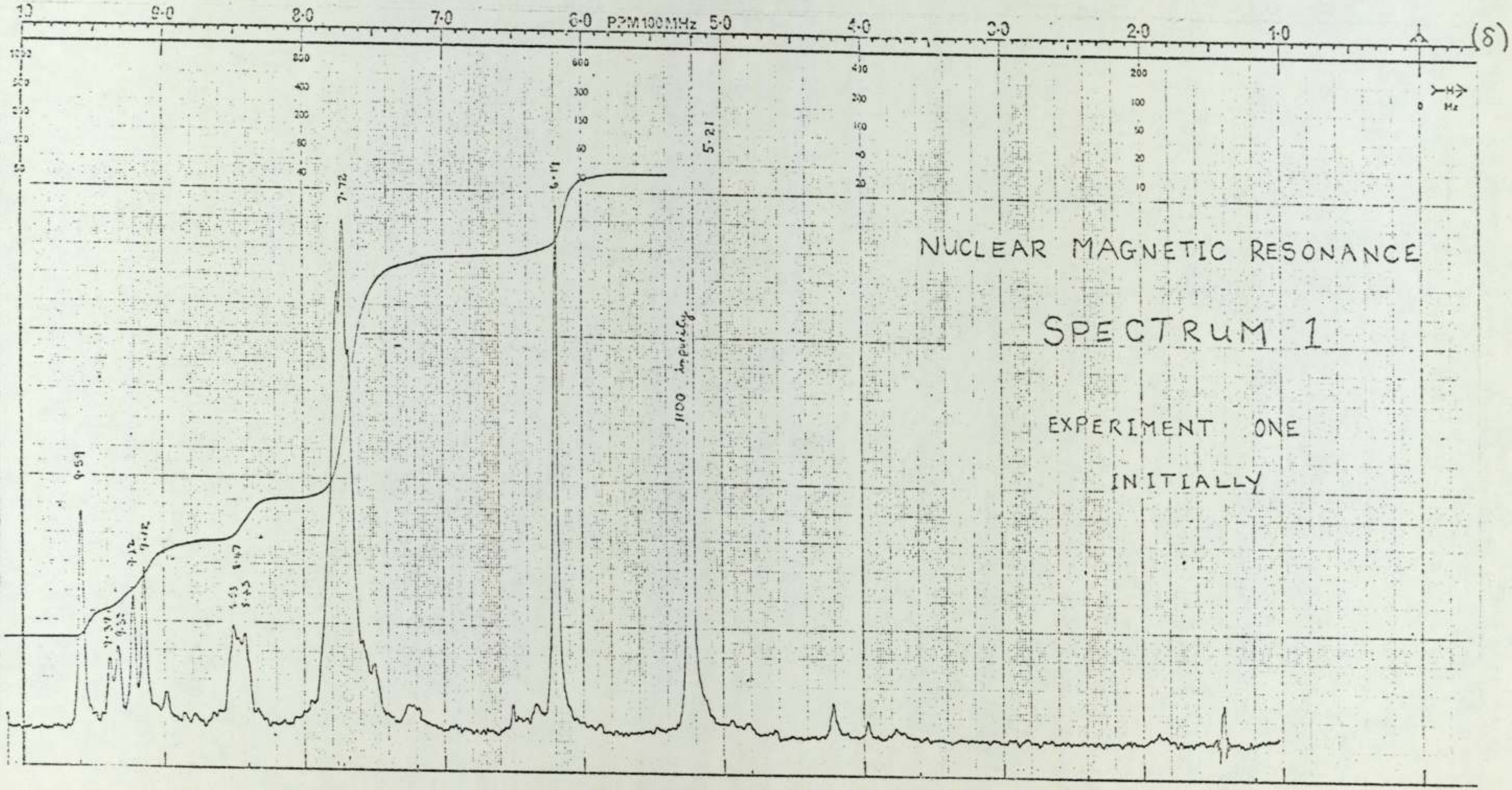
Time (hours)	0.05 gl^{-1} 1-benzyl 3-carboxy pyridinium chloride	0.5 gl^{-1} 1-propyl 3-carboxy pyridinium bromide	1.0 gl^{-1} nicotinic acid
zero	0.022	0.018	0.015
24	0.063	0.051	0.015
170	0.098	0.086	0.016

The most obvious point of interest are the very low optical density values obtained. This is a direct result of the concentrations of pyridine derivative used. The more normal concentration of 0.5 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride, would have produced optical density readings of above 2.0, the brightness of the plated deposit being so intense that any improvement would be very difficult to detect.

The plated Hull cell panels, initially showed only a slight improvement over that obtained from the base, containing 4 gl^{-1} of Polymin G35. The results of the nicotinic acid being identical to that from the base, with the two quaternary pyridinium compounds showing a slight improvement, but still possessing a hazy appearance.

After 24 hours the nicotinic acid gave a Hull cell panel, with no improvement on that obtained initially. The two quaternary compounds showed a definite improvement in brightness, the 1-propyl-3-carboxypyridinium bromide producing the best plate. In both cases the hazy appearance was beginning to disappear, particularly in the low current density (right hand side) areas of the Hull cell panels.

After 170 hours, the nicotinic acid still gave no signs of improvement, over the results obtained initially. The Hull cell panels from the electrolyte containing the two quaternary pyridinium compounds, showed further increase in brightness. The 1-benzyl-3-carboxypyridinium chloride producing a Hull cell panel with the brightest high current density (left hand side) area. In both cases the haze had almost been eliminated.

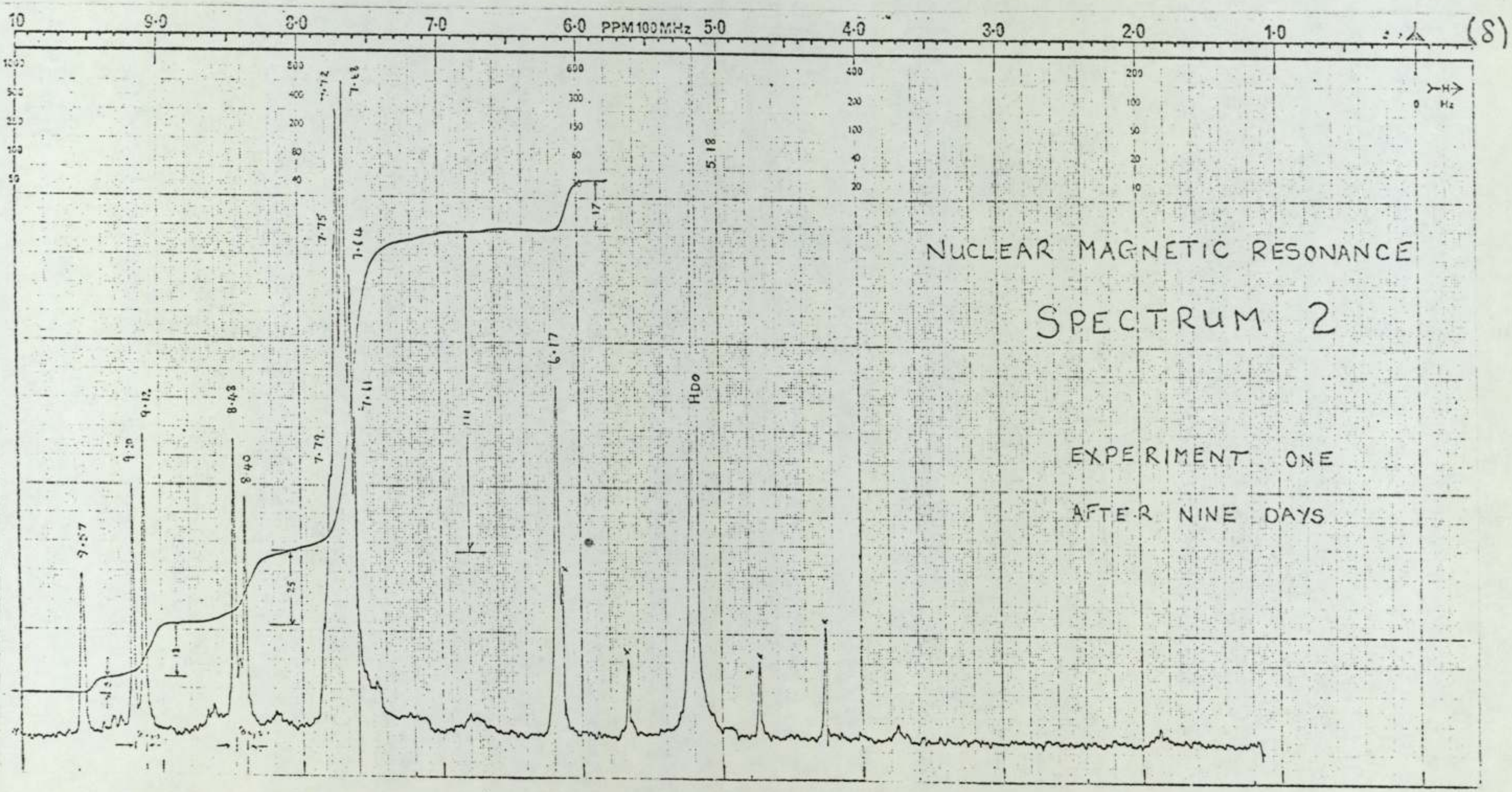


NUCLEAR MAGNETIC RESONANCE

SPECTRUM 1

EXPERIMENT ONE

INITIALLY



NUCLEAR MAGNETIC RESONANCE

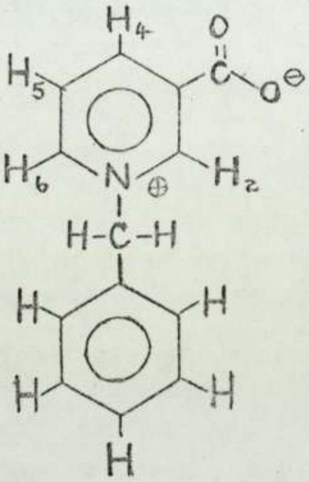
SPECTRUM 2

EXPERIMENT ONE

AFTER NINE DAYS

Results of the Nuclear Magnetic Resonance Experiments

Spectrum (I), recorded initially, is consistent with that expected for the betaine of 1-benzyl-3-carboxypyridinium chloride, the structure of which is drawn below.



The spectrum (with structural assignments) was as follows:

singlet 9.59 (H2)
doublet 9.39 and 9.35 (H6)
doublet 9.22 and 9.12 (H4)
complex 8.53, 8.47 and 8.43 (H5)
singlet (with structure) 7.72 (benzene ring)
singlet 6.19 (methylene linkage)

The integration agreed with the number of protons postulated.

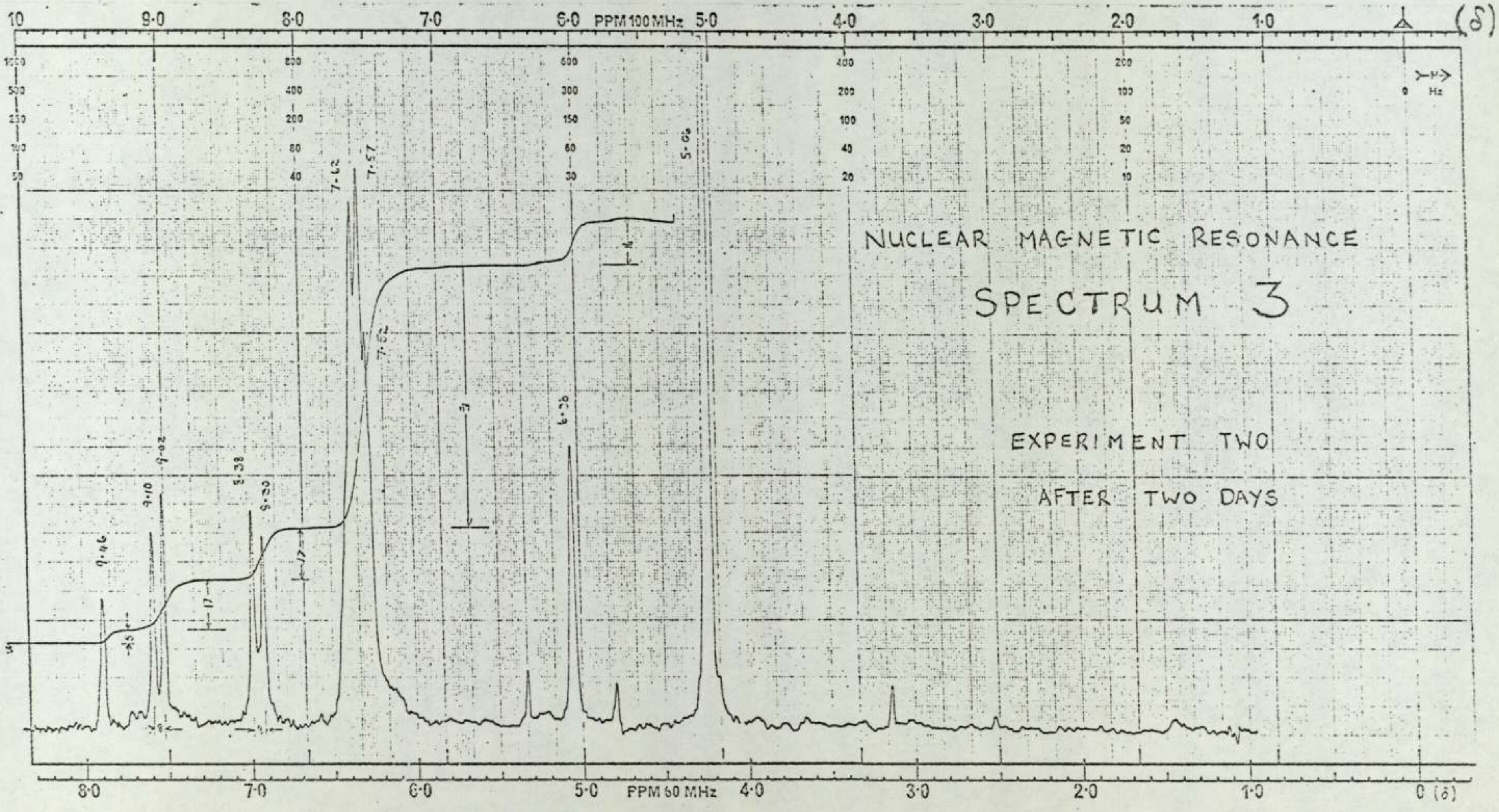
The above assignments were made on the basis of the work of Dubb et al[21], on 1-methyl-3-carbamoylpyridinium iodide and Caughley and Schellenberg[22], on 1-benzyl-3-carbamoyl pyridinium chloride.

The only area of doubt is the assignment of resonances to H6 and H4, but both sets of workers favour the above assignments.

After nine days the Spectrum 2, had altered and now exhibited;

singlet 9.57 (H2)
doublet 9.20 and 9.12 (H4) J = 8 cycles per second
doublet 8.48 and 8.40 (H5) J = 8 cycles per second
complex 7.79, 7.75, 7.72, 7.68, 7.64 and 7.61 (benzene ring)
singlet 6.17 (methylene linkage)

The resonances formerly assigned to H6 (at 9.39 and 9.33)

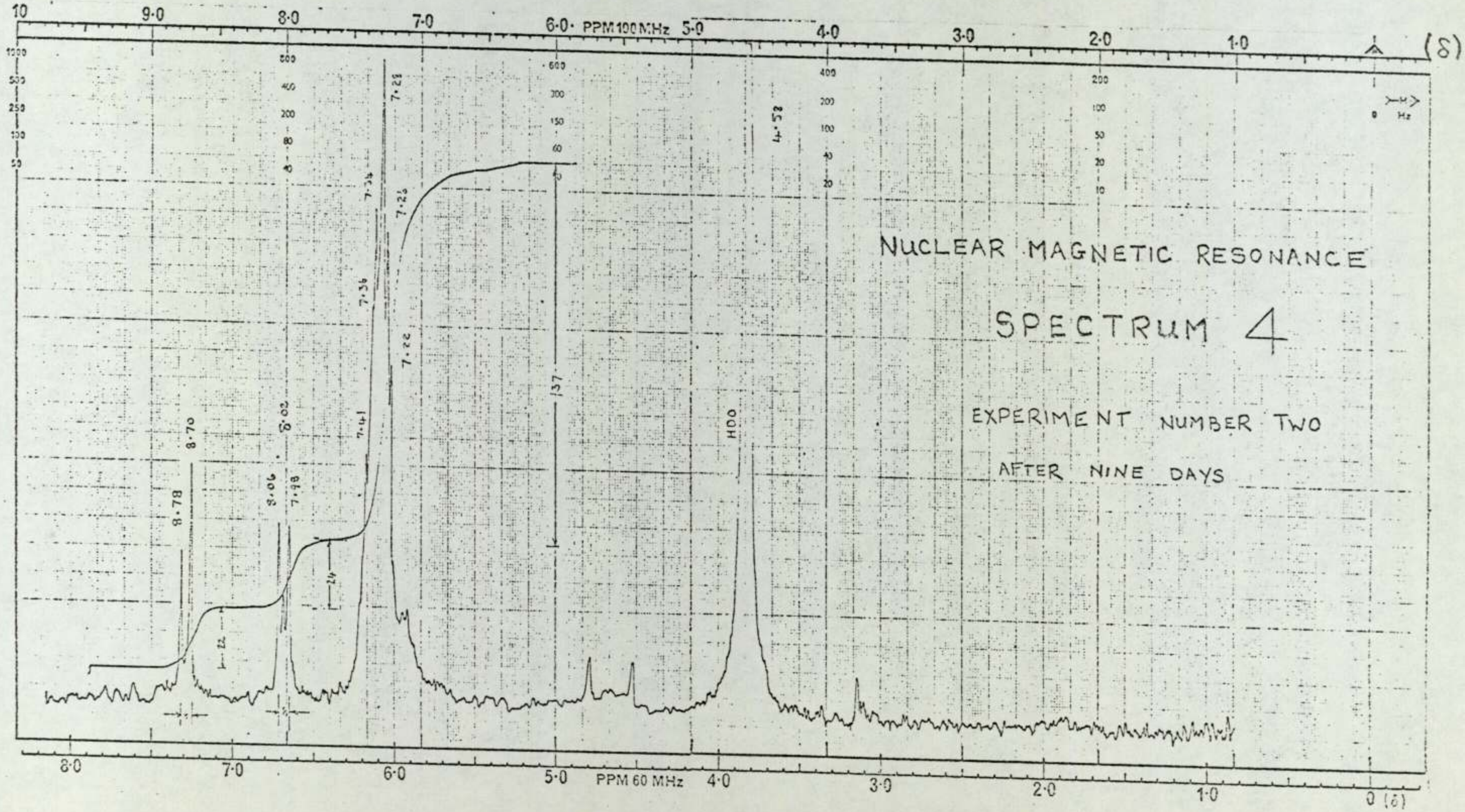


NUCLEAR MAGNETIC RESONANCE

SPECTRUM 3

EXPERIMENT TWO

AFTER TWO DAYS

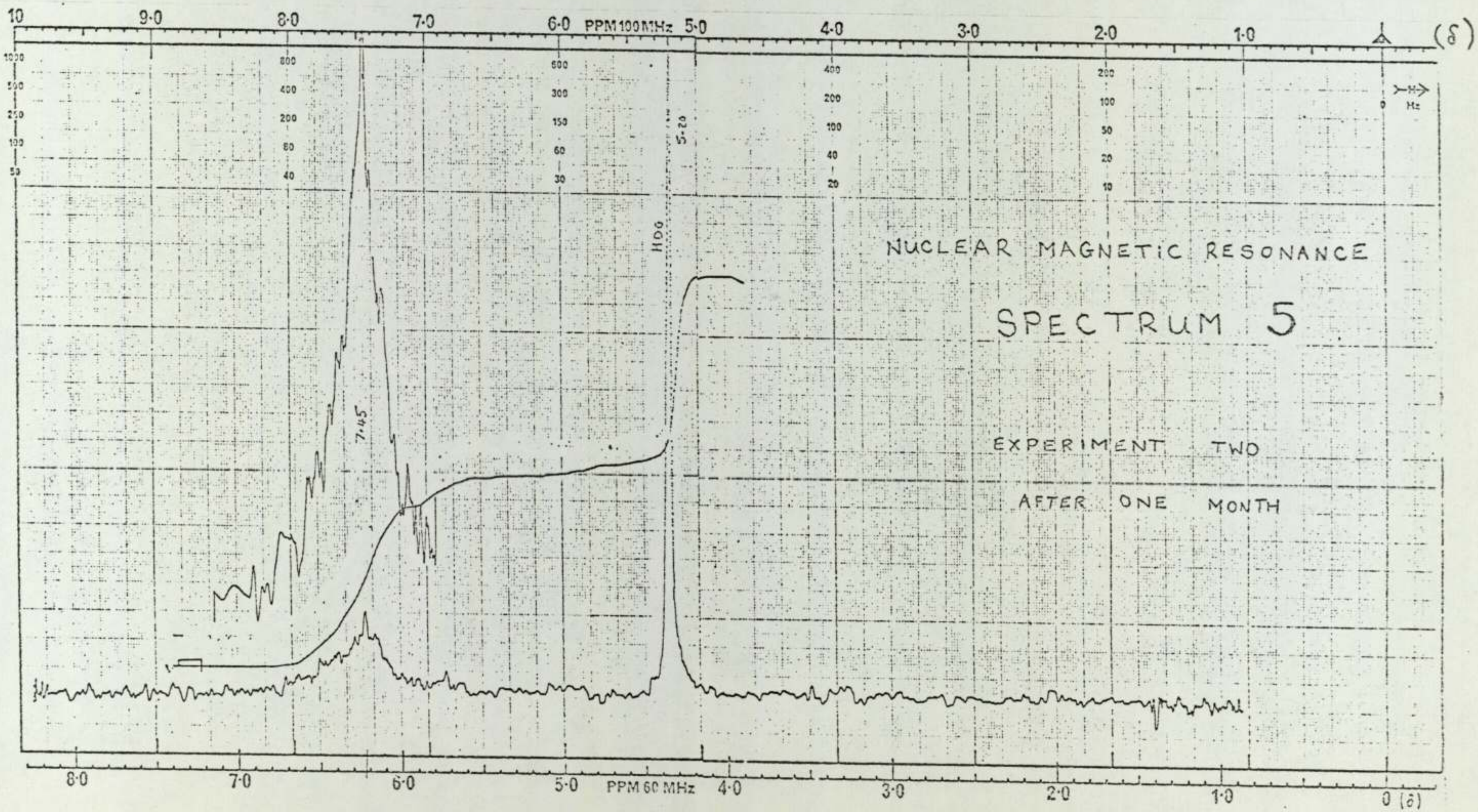


NUCLEAR MAGNETIC RESONANCE

SPECTRUM 4

EXPERIMENT NUMBER TWO

AFTER NINE DAYS



NUCLEAR MAGNETIC RESONANCE

SPECTRUM 5

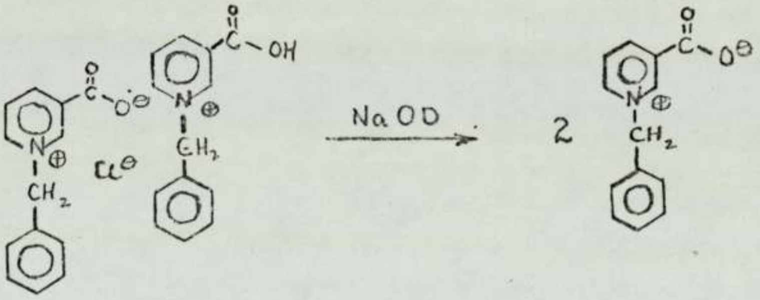
EXPERIMENT TWO

AFTER ONE MONTH

had vanished, indicating the removal of this proton. The separation of the resonances at 9.20 and 9.12, and between those at 8.48 and 8.40, was the same (8 cycles per second). It is plausible to presume that the protons responsible are undergoing coupling interactions of a strong nature, and so are probably adjacent to each other.

The coupling (J) of 8 cycles per second, can also be observed in the initial spectrum (1), but the picture is complicated by further coupling with the proton at position 6, which is split by an interaction of 6 cycles per second. This is presumably due to an interaction with the proton at the 5 position, which can now be identified as a doublet of doublets.

No evidence is available for the existance of any ring opened products, since these would have resonances between the HDO resonance (5.18) and the TMS resonance (zero).



1.0 grams (0.00208 mole) of 1-benzyl-3-carboxypyridinium chloride, gives 0.886 grams (0.004 mole) of the betaine. In the first experiment 0.4 cm^3 of 52% NaOD solution gives 0.208 grams (0.005 mole) of NaOD. In the second experiment 2.0 cm^3 of 52% NaOD solution, gives 1.04 grams (0.025 mole) of NaOD.

The second N.M.R. experiment gave an initial spectrum identical to that obtained previously.

After the extra NaOD was added and the mixture left for two days, the Spectrum 3 was as follows;

singlet 9.46 (H2)
doublet 9.10 and 9.02 (H4) separation = 8 cycles per second
doublet 8.38 and 8.30 (H5) separation = 8 cycles per second
complex 7.62, 7.57 and 7.52 (benzene ring)
singlet 6.06 (methylene linkage)

All the resonances occur at similar relative positions to those in Spectrum 2, but at a value of 0.1 lower.

The separation of the doublets is the same value as in Spectrum 2, indicating the same interactions are present, suggesting the protons are again adjacent.

The integration suggests that the proton at the 2-position, has been partially deuterated, since its intensity is only one third of the expected intensity. If the doublets are assumed to arise from only one proton each, the complex presumed due to the benzene ring, approximates to five protons as expected. However, the resonance due to the methylene group, integrates to only one proton, suggesting partial deuteration.

After nine days the Spectrum 4, exhibited;

doublet 8.78 and 8.70 separation = 8 cycles per second
triplet 8.06, 8.02 and 7.98 separation = 8 cycles per second of outter two resonances
complex 7.41, 7.36, 7.34, 7.28. 7.26 and 7.22

Assuming the resonances correspond to those in Spectrum 3, they are all low by a value of 0.32 .
The resonances due to the 2-position proton and the methylene linkage have disappeared.

After one month the Spectrum 5, exhibited only one feature, a complex pyrimidal shaped resonance at 7.45, presumably due to the presence of a benzene ring.

DISCUSSION

The complex nature of the discussion, could lead to confusion, and so the following summary is intended to act as a guide.

The discussion begins with a brief review of the results, particularly those concerned with the production of the maximum at approximately 360 nm. Reference is then made to the literature, and other workers ideas on pseudo base formation and the position of hydroxide ion attack described. Work on the ring opening of pyridine compounds is then outlined, and the possibility of this being an explaination for the maximum observed at approximately 575 nm., postulated.

The calculated orders of reaction for hydroxide ion and 1-benzyl-3-carboxypyridinium chloride concentration are then outlined, and the formation of a bimolecular ether as a logical explaination advanced. The literature evidence for the existance of bimolecular ethers is then reviewed and this leads to the introduction of betaines. This leads in turn to the hypothesis, that this type of compound can explain the nuclear magnetic resonance results is then detailed.

Finally, support for the arguments presented is given by a review of a relevant patent.

Discussion

Alkaline cyanide and none-cyanide electrolytes containing 1-benzyl-3-carboxypyridinium chloride, acquire a pronounced yellow tinge after working for some time. This observation is explained by the growth of a maximum at about 360 nm., which is produced in the presence of hydroxide ions, and does not seem to be influenced in any way by the zinc ions present. The growth of a maximum at about 360 nm., is also observed for 1-propyl-3-carboxypyridinium bromide in the presence of hydroxide ions, but the rate of production of the maximum appears to be slower, under identical conditions, than for 1-benzyl-3-carboxypyridinium chloride. 1-benzyl-4-carboxy pyridinium chloride, nicotinic acid and homarine hydrocloride, do not give a similar maximum with hydroxide ions.

The production of the maximum at about 360nm., appears to have a correlation with the brightening ability of the pyridine derivatives. 1-benzyl-3-carboxypyridinium chloride in alkaline cyanide electrolytes gives zinc deposits with better brightness, than those obtained using 1-propyl-3-carboxy pyridinium bromide, while 1-benzyl-4-carboxypyridinium chloride, nicotinic acid and homarine hydrochloride have no brightening action at all. The same observations are true for the alkaline none-cyanide zincate electrolyte, except for homarine hydrochloride, which appears to have some brightening action in this electrolyte.

In commercial plating, it is a commonly observed fact that plating baths, produce their best results after an initial "working in" period. The improvement in the brightness of electrodeposited zinc plate, correlated with an increase in the optical density at 360 nm., for both 1-benzyl-3-carboxy pyridinium chloride and 1-propyl-3-carboxypyridinium bromide separately, gives further substance to this obervation.

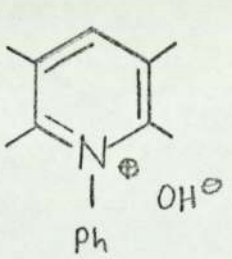
A plausible explaination of the results, is that the maxima at about 360 nm., are due to new chemical species which are the brightening agents, and not to the compounds originally added to the plating electrolytes. The best results are not obtained initially, but the new species appear to build up to an optimum concentration, with time.

The structure and mechanism of formation of the new species, is consequently of great importance, before any further conclusions can be reached, about the mechanism of brightening action.

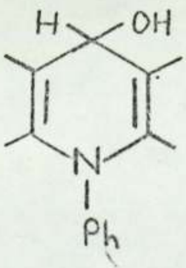
It is known from the literature that treatment of 1-substituted pyridinium salts and related compounds, with hydroxide ions yield, easily dissociated pseudo-bases, in which the hydroxide ion has become bound covalently to one of the carbon atoms of the heterocyclic ring[23]. The action of hydroxide ions on pyridinium salts, have been known for some time, being first reported in 1881[24].

Pseudo-bases have been studied in other heterocyclic ring systems, such as quinoline, isoquinoline and acridine, particularly the latter, the pseudo-bases of which can readily be isolated in a pure form.[25] The reason being, that because pseudo-base formation results in a loss of aromatic character, the effect on stability is not so pronounced in multi-ring systems, which still retain the stabilising effects of the unreacted rings.

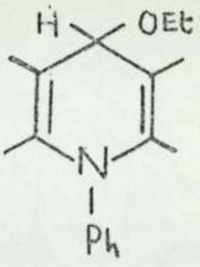
The pseudo base obtained by treating an aqueous solution of N-phenylacridinium iodide with sodium hydroxide, when crystallised from ethanol or even treated with cold ethanol, forms the O-ethyl ether (i).



quaternary ammonium hydroxide



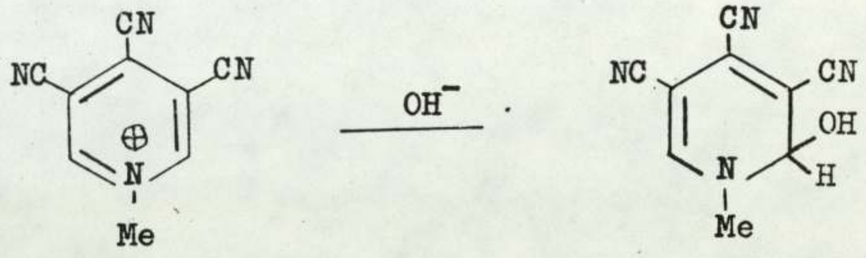
pseudo base



(i)

pseudo base ethyl ether (i)

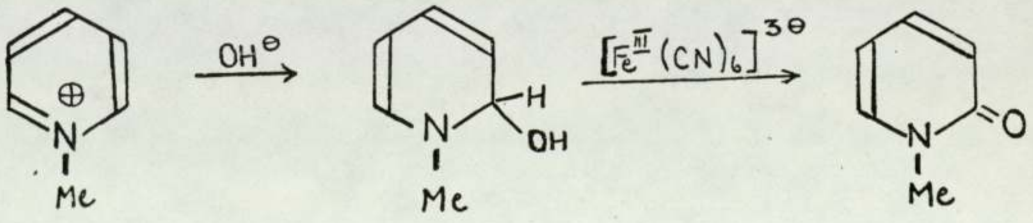
Recently[26] a pyridinium pseudo-base (ii) has been isolated, from the reaction of hydroxide ions and 1-methyl-2,3,4-tricyanopyridine.



(ii)

The classical work on the nature of the pseudo-bases formed from pyridine derivatives, has been deduced from indirect evidence, a brief review of which now follows.

The electrical conductivity of a solution containing 1-methylpyridinium and hydroxide ions, shows 1-methylpyridinium hydroxide to be a strong completely dissociated base. The conductivity does not decrease with time and so it follows that the equilibrium between the quaternary hydroxide and the pseudo-base must lie overwhelmingly towards the former.[27] The addition of potassium hexacyanoferrate(III), results in the oxidation of the pseudo-base and 1-methylpyrid-2-one may be isolated.[28] The formation of 1-methylpyrid-2-one is attributed to the continuous removal of the pseudo-base, which is assumed to be present in a very small concentration.[29]

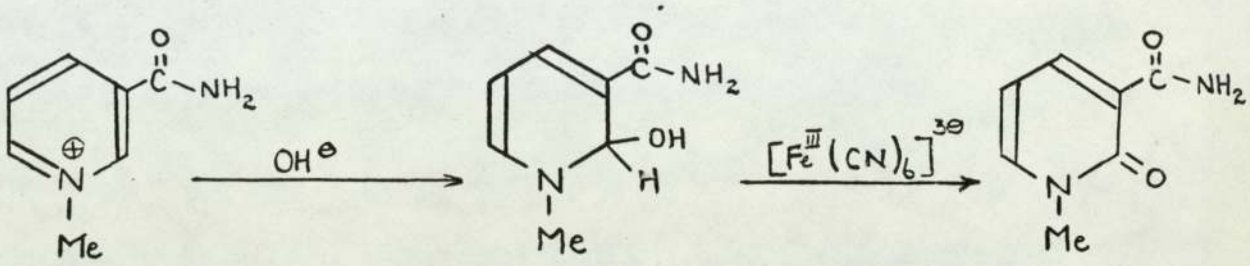


1-methylpyridinium hydroxide

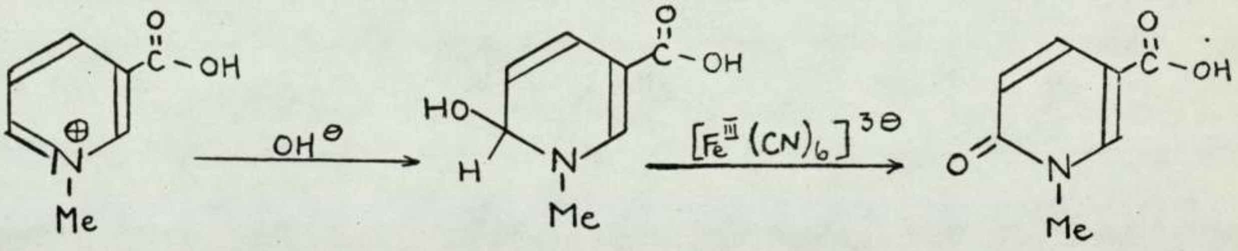
pseudo base

1-methylpyrid-2-one

Bradlow and VanderWerf[30], have used this, the Decker reaction (the oxidation of 1-substituted pyridinium derivatives with alkaline hexacyanoferrate(III)), to show that 1-methyl-3-carbamoylpyridinium iodide was converted to 1-methylpyrid-2-one-3-carboxamide, while 1-methyl-3-carboxy pyridinium sulphate was converted to 1-methylpyrid-2-one-5-carboxylic acid. Thus, implying 1-methyl-3-carbamoylpyridinium ions undergo attack at the 2-position, while 1-methyl-3-carboxy pyridinium ions are attacked at the 6-position.



1-methyl-2-pyridone
-3-carboxamide

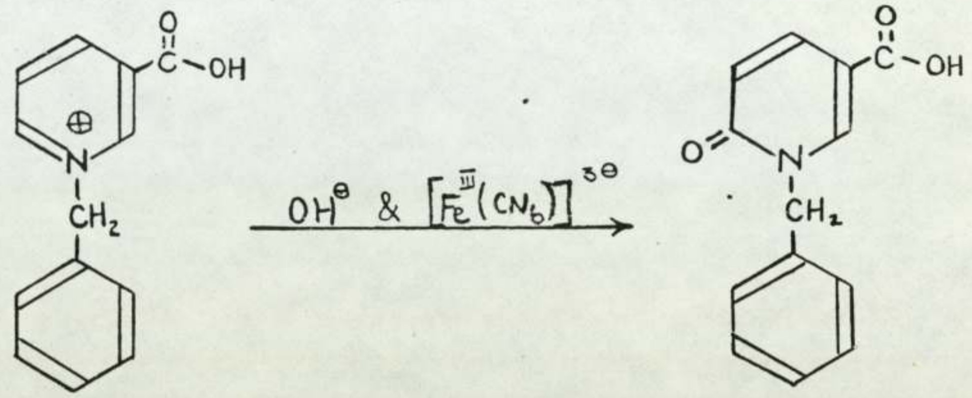


1-methyl-2-pyridone
-5-carboxylic acid

A consideration of the above reaction mechanism suggests that the orientation of the pseudo-base, could be the factor which determines the position at which oxidation occurs.

Another possible reason for attack at the 6-position, of 1-methyl-3-carboxypyridinium ions, is because electrostatic interaction is possible between the oxygen atoms of the carboxylate ion (formed in basic solution) and the hydrogen atom of the hydroxide group in the 2-position, but not of course with that at the 6-position. A further factor could be the possibility that the ionic charge of the carboxylate group would tend to block pseudo base formation at the 2-position, because of its electrostatic repulsion on the approaching hydroxide ion.

1-benzyl-3-carboxypyridinium chloride when oxidised with alkaline hexacyanoferrate(III), gives 1-benzyl-5-carboxy-2-pyridone.[31]



An ethanolic solution of 1-benzyl-5-carboxy-2-pyridone, showed absorption maxima at 260 nm., (ϵ 15,700) and 299-308 nm.,(ϵ 4,799).

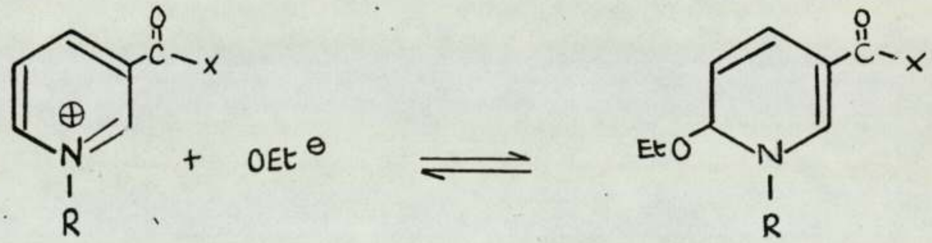
Anderson and Berkelhammer[32], qualitatively investigated the effect of base on the ultra-violet spectrums of solutions of a number of quaternary pyridinium halides in ethanol.

TABLE 4

Compound	λ_{max}(nm) in ethanol	λ_{max}(nm) in basic ethanol
1-benzyl-3-carbamoyl pyridinium chloride	266	359, 318
1-propyl-3-carbamoyl pyridinium bromide	266	259, 315
1-benzyl-3-carboxymethyl pyridinium chloride	264	258, 316
1-propyl-3-carboxymethyl pyridinium bromide	265	265, 314
1-benzyl-3-acetyl pyridinium chloride	264	271, 323
1-benzylpyridinium chloride	259	259

One drop (about 0.04 cm^3), of 3 molar aqueous sodium hydroxide solution was added to the ethanolic solution of the pyridinium compound in a 1 cm Cary cell. The results are shown in Table 4, the spectra of all the compounds with a carbonyl-containing substituent in the 3-position, underwent similar changes in basic solution. The original spectrum was reproduced in all cases upon acidification. 1-benzylpyridinium chloride, alone among the compounds investigated, displayed essentially identical spectra in neutral, basic and acidic ethanol.

A reasonable explaination of the spectral changes in basic solution is that some basic species, undoubtedly ethoxide ion, has added to the pyridinium ring to form a compound characterised by the absorption at 314-325 nm. The shorter wavelength absorption present in basic solution is probably the slightly displaced pyridinium absorption. Thus, an equilibrium of the following type is suggested;

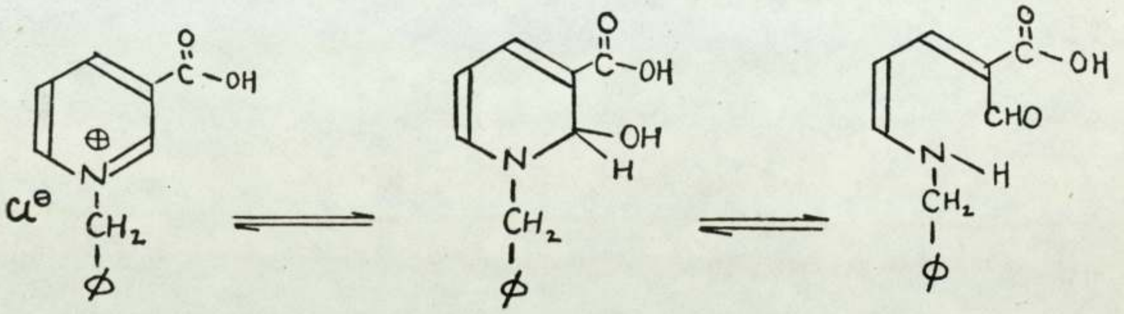


As the solution was made more basic the ratio of the long wavelength absorption intensity to that of the short wavelength absorption increased, representing a shift of the equilibrium to the right. Similar spectral changes were found for 1-benzyl-3-carbamoylpyridinium chloride and 1-benzyl-3-acetyl pyridinium chloride in water, although the solutions had to be considerably more basic in order to give a ratio of intensities comparable in magnitude to those obtained in ethanol; that is, the higher dielectric constant of water results in a displacement of the equilibrium in favour of the ions (substituted pyridinium and hydroxide) at the expense of the covalently bonded pseudo base.

Addition at the 6-position was favoured, since the chromaphore which would be formed following addition at the 2-position, would contain a nitrogen atom conjugated through two double bonds to a carbonyl group and so would be expected to absorb at a considerably higher wavelengths.[33]

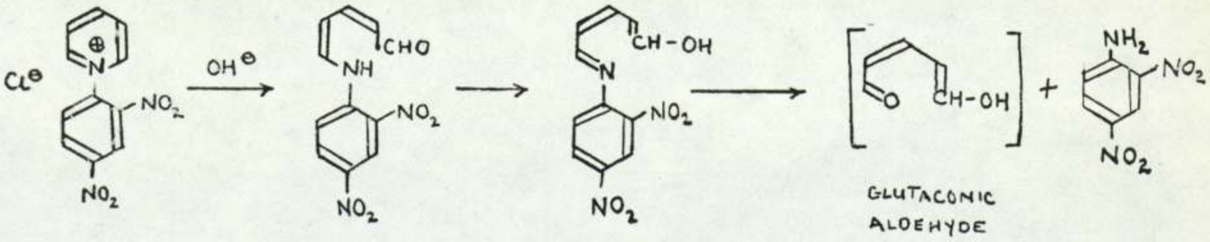
The observation that the spectrum of 1-benzylpyridinium chloride was unchanged in basic ethanol, is in agreement with the conductivity studies of Hantzsch and Kalb[23], who found no evidence of pseudo base formation by the quaternary salts of pyridine. Apparently the presence of a substituent capable of imparting resonance stabilisation to the pseudo-base by conjugation with the ring nitrogen, through one of the double bonds, causes a significant increase in the stability of the pseudo-base relative to the quaternary salt.

Recently, Gadamer's[34] views have been widely accepted. He postulated for these compounds a tautomeric system of three components, in which the quaternary ammonium hydroxide, the pseudo-base (or carbinolamine)[35], and the open chain amino aldehyde[36], all exist in a mobile equilibrium.



However, a critical examination of the enormous amount of experimental material, that has accumulated over more than 80 years, leads to the conclusion that the three tautomeric forms postulated by Gadamer, have not been proven in one case. The so called evidence is based on chemical reactions[37], which are non-compelling, or on physical constants that have been interpreted in a biased manner.[38] For the simultaneous existance of both forms of the ring-chain prototropic system, i.e., the carbinolamine and amino aldehyde, evidence is available only for one single case.[39]

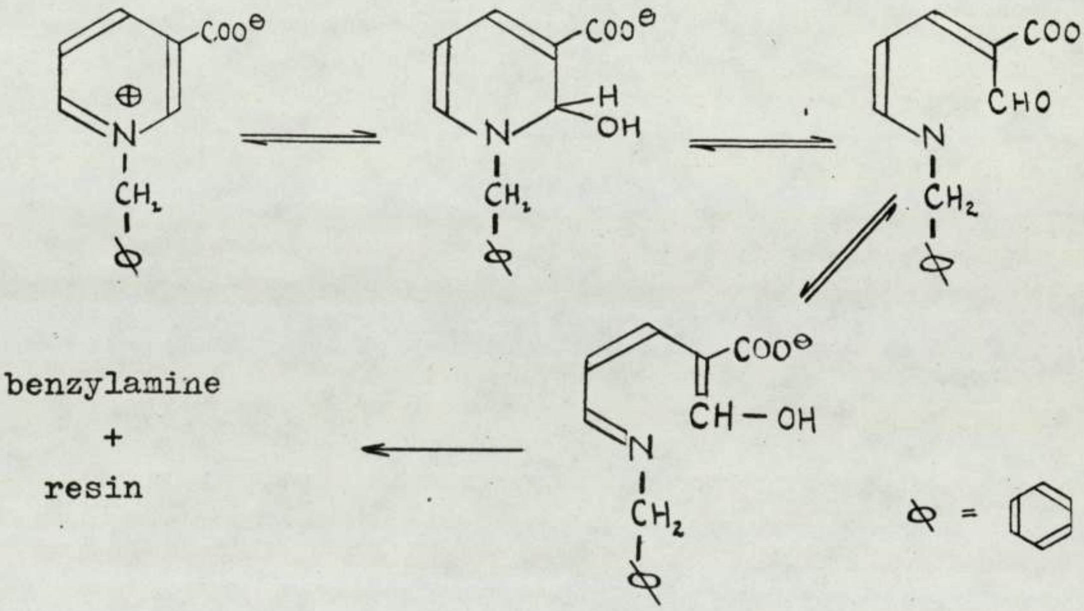
Considerable evidence[40] exists to suggest that the pyridinium ring can be opened by alkali. Zinke[41] found 1-(2,4-dinitrophenyl)pyridinium chloride, reacts with aromatic amines and with alkali to give deep red products. The reaction proceeds by way of the amino-aldehyde postulated by Gadamer, and in the case of alkali results in the ultimate production of glutaconic aldehyde and 2,4-dinitroaniline.



These ring opening reactions could explain the reason for the transient maximum observed at about 575 nm., which was produced when 5 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride was dissolved in 100 gl^{-1} of sodium hydroxide solution.

Apart from the work of Zinke, described above, no relevant reference could be found in the literature.

The position of the absorption maximum at 575 nm.(approx.), suggests that the species responsible, must possess extensive conjugation, with the transient nature reflecting the reactive nature, giving credibility to the relevance of the following reaction scheme.



No attempt was made to isolate the final products of hydroxide attack on 1-benzyl-3-carboxypyridinium chloride, but after standing for three months, no 1-benzyl-3-carboxy pyridinium chloride could be recovered.

Kolyer[18] found that 1-benzyl-3-carbamoylpyridinium chloride, when refluxed with sodium hydroxide for one hour, yielded ammonia (54%), carbon dioxide (12%) and benzylamine (14%)

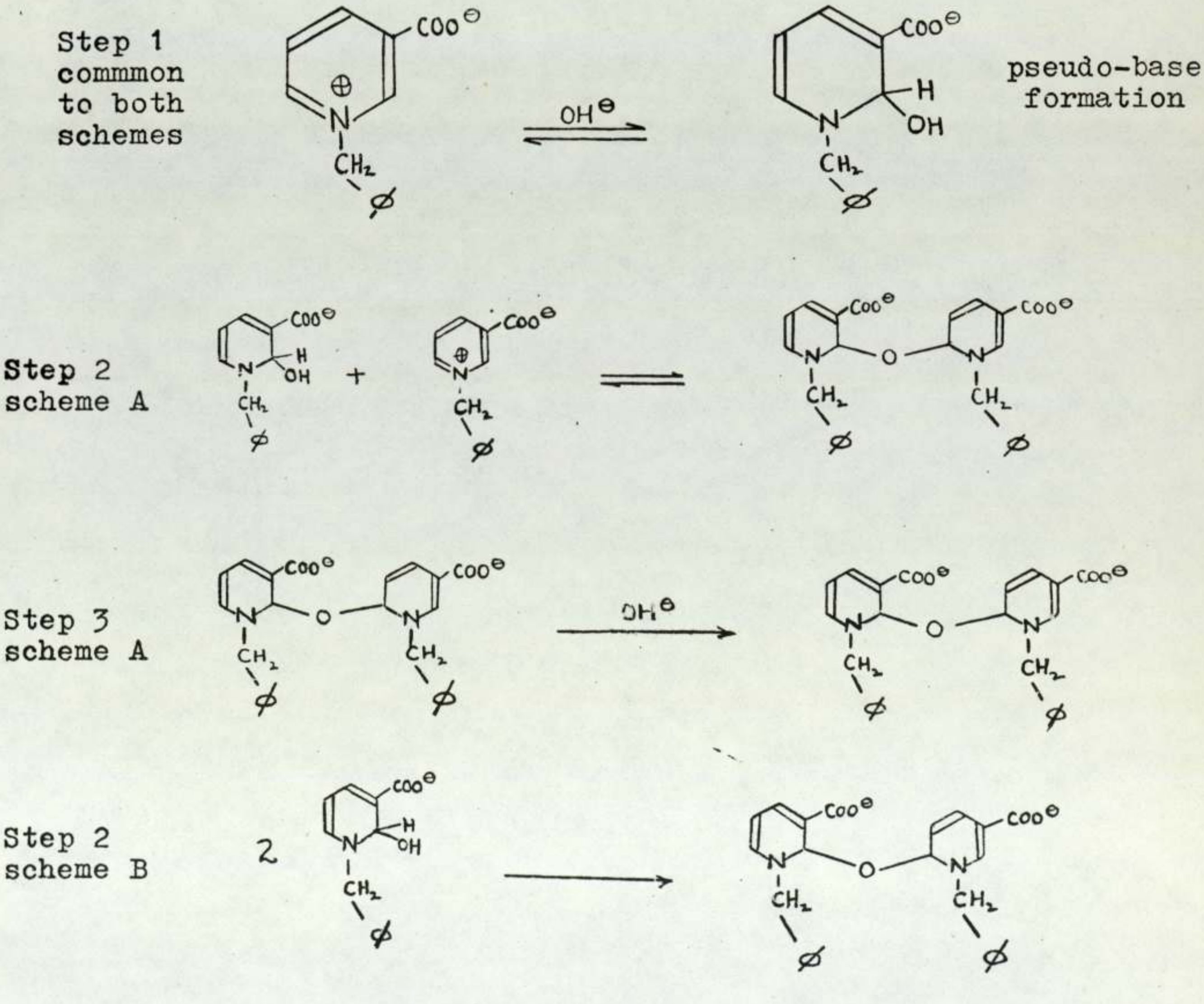
The results of the log-log plots of initial rate against concentration for sodium hydroxide and 1-benzyl-3-carboxy pyridinium chloride, indicate that the reaction appears to be second order, with respect to both species. The rate equation may be expressed in the form;

$$\text{Rate} = k[\text{OH}^-]^2\ [\text{1-benzyl-3-carboxypyridinium chloride}]^2$$

where k is a constant

In other heterocyclic systems[42] pseudo bases are known to form bimolecular pseudo-base ethers.

In an analogous manner, to the pyrazinium system studied by Aston[43], the system under investigation could be forming a bimolecular ether, and conform to one of the following schemes, which both obey the observed rate law.



Both schemes involve the reaction of two hydroxide ions and two 1-benzyl-3-carboxypyridinium chloride ions, so conforming to the observed rate law.

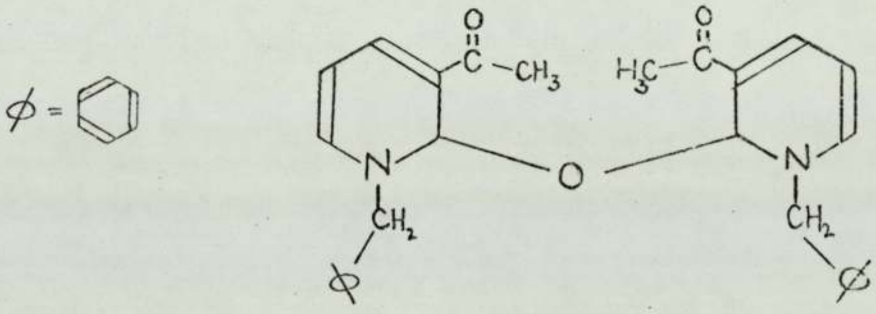
Scheme B, is the most simple involving the condensation of two pseudo-base molecules, with the formation of the bimolecular ether and a molecule of water. Some doubt is cast upon the validity of this mechanism, by the literature references outlined earlier in this discussion which suggests that the pseudo-base is only present in small concentration, so making the chance of collision and reaction remote.

Consequently, the reaction of the pseudo-base with the pyridinium quaternary and subsequent reaction with hydroxide to produce the bimolecular ether and a water molecule, is a more plausible scheme (A).

The mixing of concentrated solutions (20 - 50% by weight) of sodium hydroxide and 1-benzyl-3-carboxypyridinium chloride, results in a yellow oily precipitate, but this could not be isolated since it quickly dissolved. The precipitate was assumed to be the bimolecular ether, but no evidence is available to confirm this hypothesis.

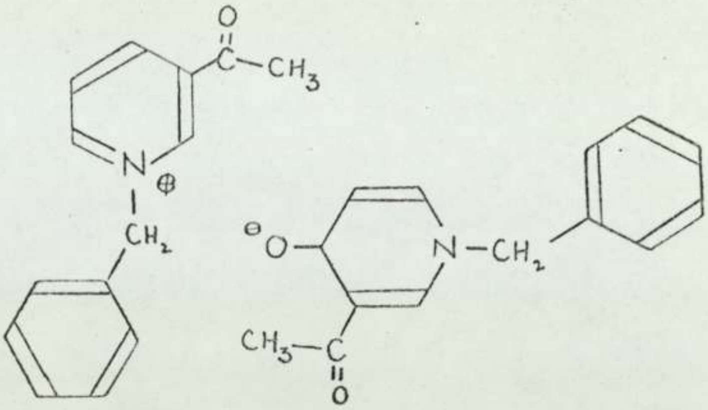
Anderson[17] and Berkelhammer achieved the first isolation of a bimolecular pseudo-base ether in the pyridine series, by the reaction of 1-benzyl-3-carboxypyridinium chloride with aqueous sodium hydroxide. A lemon yellow solid was obtained which darkened at room temperature, but was stable in the refrigerator. All efforts at recrystallisation failed, usually resulting in the recovery of an oil. When a solution of the yellow solid was treated with hydrochloric acid, a quantitative yield of 1-benzyl-3-acetylpyridinium chloride was realised.

The method of formation of the yellow solid and its behaviour in acid, suggested the possibility of it being a pseudo-base. Elemental analysis of the dried crude product eliminated this possibility, pointing instead to a bimolecular ether of a pseudo-base, such as:



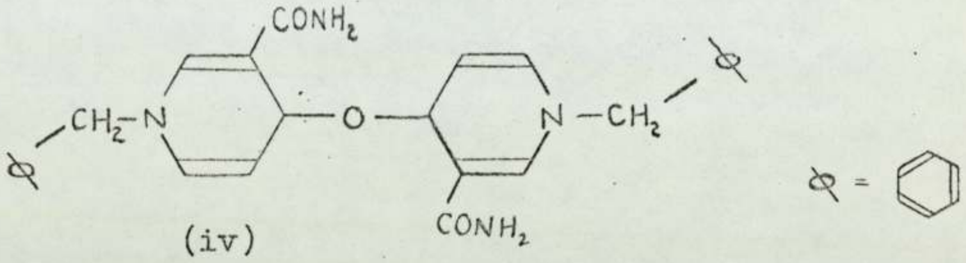
The ether oxygen is represented as joining the 2-positions of the two rings in the bimolecular ether, solely on the basis of a similarity of the ultra-violet spectrum (λ_{max} 278, 351 nm in dioxane) with that of a compound reported by Stein and Stiassny[32], to be either a 1,2- or a 1,6-dihydro model compound. If the ethoxide addition, with its shorter wavelength maxima, takes place at the 6-position, as postulated earlier, this leaves the 2-position for the oxygen bridge in the bimolecular ether. Another possibility is that the oxygen joins the 4-positions of the rings, which would account for the 351 nm maximum, and that the ether is in equilibrium with the pyridinium alcoholate, (iii) which would be expected to show pyridinium adsorption in the vicinity of 265 nm.

pyridinium
alcoholate
(iii)



The actual position of the short wavelength absorption, at 278 nm., would seem to be rather high for a pyridinium ion, however; and the low dielectric constant of dioxane would not be expected to favour such ionisation. When the ultra-violet spectrum of the bimolecular ether was recorded using ethanol as solvent, the initial spectrum, λ_{max} 270, 362 nm., was replaced within two minutes of preparing the solution by the spectrum of the ethoxide addition compound, λ_{max} 270, 323 nm.

The only other reported isolation of a bimolecular pseudo-base ether in the pyridine series was by Dittmer and Kolyer[44], who obtained from the action of aqueous sodium hydroxide on 1-benzyl-3-carbamoylpyridinium chloride, a product formulated as:

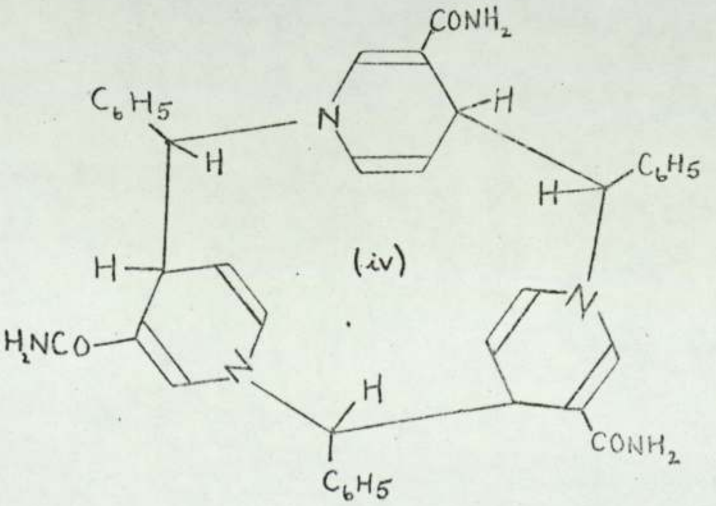


(iv)

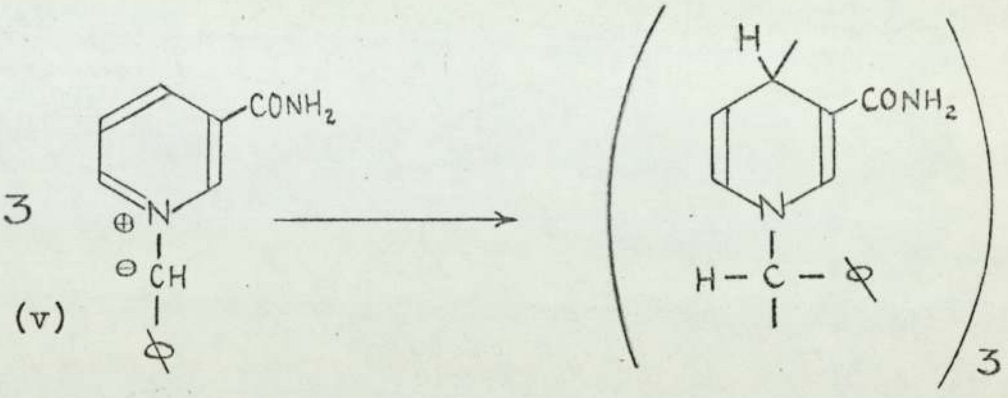
Similarly the bimolecular ethers of 3-carbamoyl-1-(2,6-dichlorobenzylpyridinium bromide, 3-carbamoyl-1-(p-fluorobenzyl) pyridinium chloride and 3-carbamoyl-1-(p-nitrobenzyl)pyridinium chloride, were also reported.

The bimolecular ether is formulated as possessing a 1,4-dihydro structure, on the basis of it exhibiting only one ultra-violet maximum at 330 - 335 nm., in none polar solvents (benzene, ether). A 1,6-isomer would be expected to have two maxima, because of cross conjugation in the exited states, and a 1,2-isomer would be expected to have a maximum at a longer wavelength.[45]

When the bimolecular ether (iv) illustrated above, is dissolved in ethanol a white solid precipitates, which has been characterised to be a cyclic trimer $(C_{13}H_{12}N_2O)_3$, with the structure opposite (iv), on the basis of infra-red, ultra-violet and nuclear magnetic resonance results.

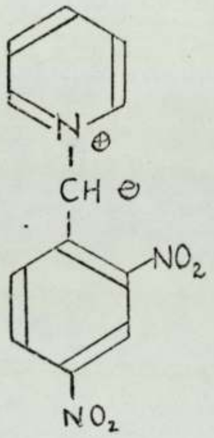


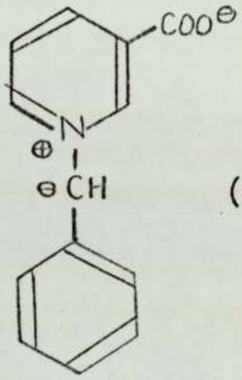
A possible explaination for the formation of the cyclic trimer, is initial production of the betaine (v), which then forms the trimer.



Similar betaines are known and the betaine illustrated below (vi) has been prepared by Krohnke[46], but was rather unstable.

(vi)





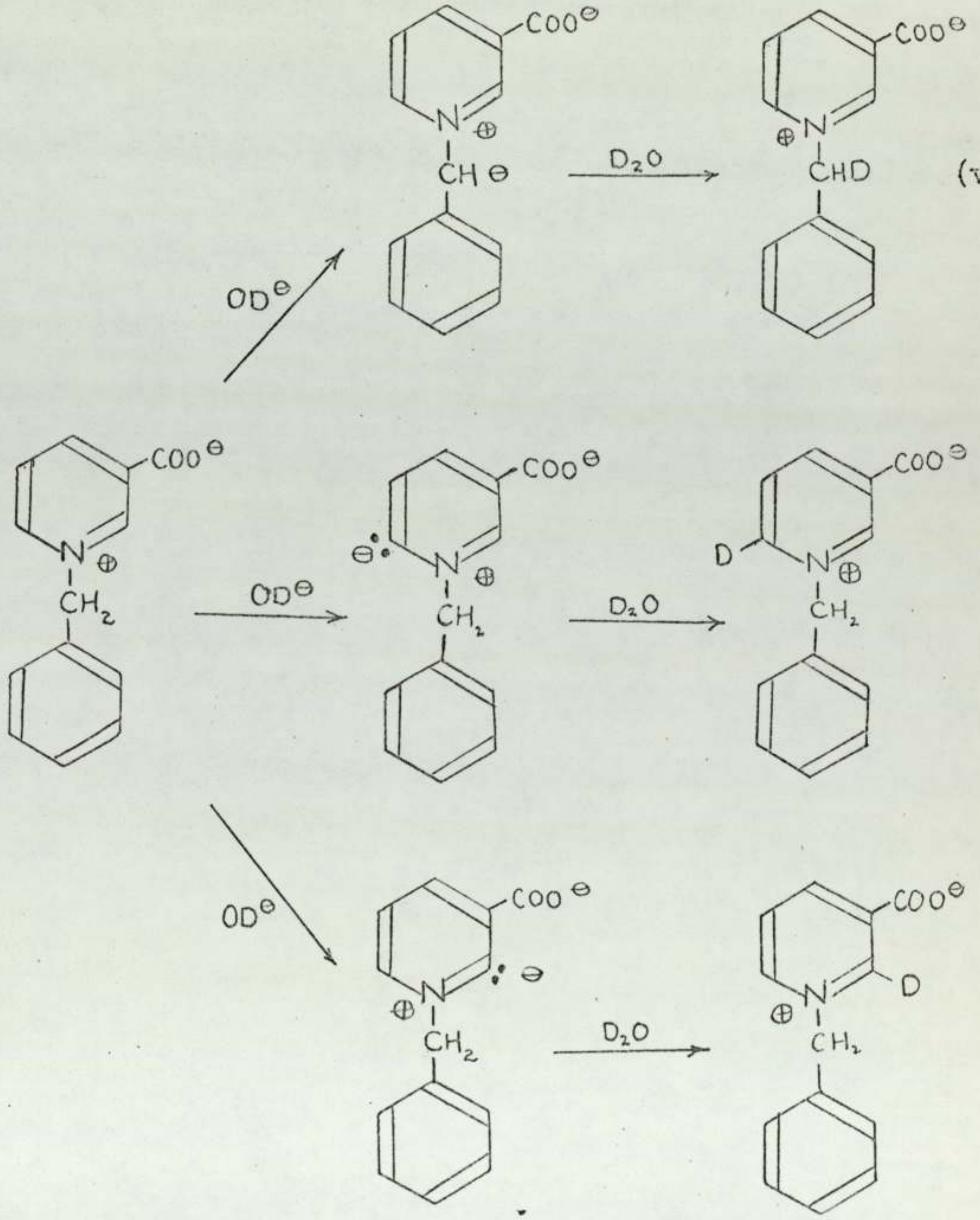
(vii)

The betaine (vii) from 1-benzyl-3-carboxypyridinium chloride, thus appears feasible and could be another possible explaination for the transient maximum at 575 nm., observed when 5 gl^{-1} of 1-benzyl-3-carboxypyridinium chloride was dissolved in 100 gl^{-1} of sodium hydroxide solution.

The results of the nuclear magnetic resonance experiments suggest that a betaine of this type could exist, since the spectrum after nine days appears to indicate the presence of only one methylene proton, and a second experiment with more deutoxide ions showed that after nine days, no evidence of methylene proton resonances.

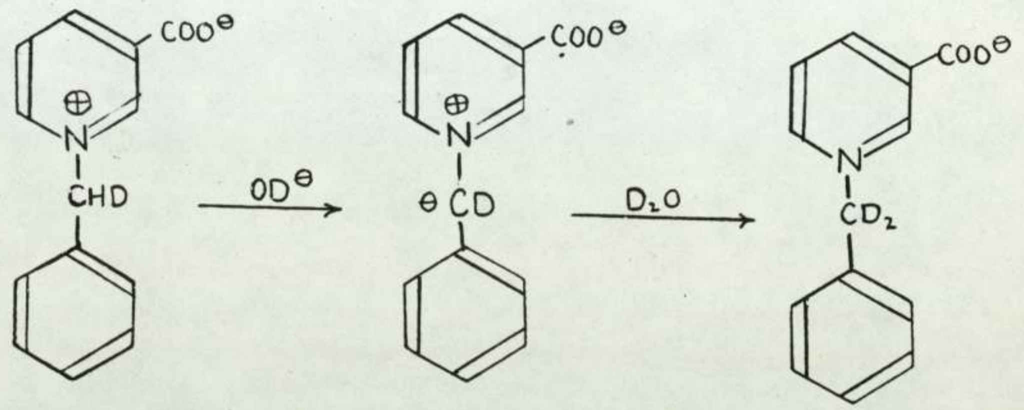
The ring protons also appear to be easily removed, the resonance due to the proton in the 6-position disappearing entirely after nine days, and the resonance due to the proton in the 2-position exhibited only one third the area expected. After nine days with extra sodium deutroxide, the spectrum revealed the complete exchange of the 2-position proton.

The betaine produced probably undergoes exchange with deuterium oxide (D_2O), yielding the appropriate deuterio compounds, in accordance with the following scheme:

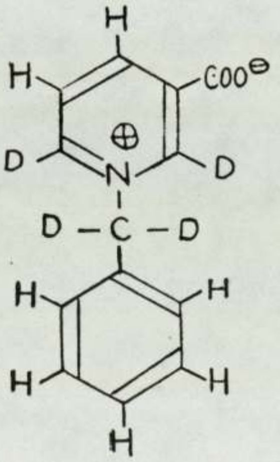


(viii)

The betaine (viii), can react further, as follows;



Nuclear magnetic resonance spectrum 4, shows that after nine days, the compound present is probably;



The betaines shown above could possibly give rise to the transient maximum at about 575 nm., observed when 5 gl^{-1} 1-benzyl-3-carboxypyridinium chloride was dissolved in 100 gl^{-1} of sodium hydroxide solution

The difference in concentrations of the solutions used for the nuclear magnetic resonance and ultra-violet experiments, makes any correlation of results between these two techniques dubious.

CONCLUSION

The quaternary pyridinium derivatives which have a brightening action on electroplated zinc, give rise to a maximum at about 360 nm., in the presence of hydroxide ions. The rate of growth of this maximum appears to correlate with increasing brightening action.

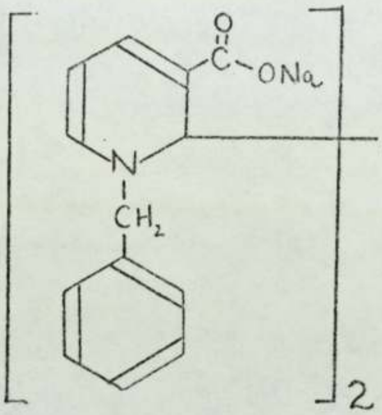
Evidence regarding the nature of the species producing the maximum, for the reaction between 1-benzyl-3-carboxylpyridinium and hydroxide ions, was obtained from the order of reaction, calculated from log-log plots of initial rates against varying concentrations of the above ions. Since, the reaction was found to be second order with respect to both hydroxide and 1-benzyl-3-carboxypyridinium ions, the most likely species was a bimolecular ether formed from an intermediate pseudo-base.

Since, pyridinium derivatives with carboxylate groups in the 2- and 4-positions of the pyridine ring possess no brightening ability, it may be tentitively postulated that substitution in the 3-position of the pyridine ring is a necessary prerequisite for a compound to be a brightener. The nature of the quaternising group is also important, because propyl quaternised pyridine-3-carboxylate has inferior brightening ability compared to the benzyl quaternised pyridine-3-carboxylate.

No useful information about the structure of the bimolecular ether, could be obtained from the nuclear magnetic resonance spectra, but this technique did give some interesting results regarding the labile nature of the protons attached to the pyridine ring.

The results have been further emphasised by the recent publication of three United States patents 3 755 097, 3 781 296 and 3 928 365. These patents disclose the preparative details for a complex mixture of di(1-benzyl-3-carboxy-1,2-dihydropyridyl-2) ethers, for use as brightening addition agents in alkaline cyanide zinc electroplating baths and also as sequestrants and stabilizers for plastics and rubbers.

The first example of United States patent 3 755 097, illustrates the preparation of a composition containing the sodium salt of di(1-benzyl-3-carboxy-1,2-dihydropyridyl-2) ether, with the structure shown below, and which may also contain the corresponding isomers, where the ether linkage is attached to the dihydropyridine ring, at the 4-position forming a 1,4-dihydro pyridyl-4-ether and at the 6-position forming a 1,6-dihydro pyridyl-6-ether.



The preparative instructions given are as follows; into a one litre three necked flask equipped with a dropping funnel, stirrer and thermometer, there was added 20 grams (0.08 mole) of 1-benzyl-3-carboxypyridinium chloride in 400 cm^3 of water. The resultant solution was heated to 45^{o}C., in order to dissolve the pyridinium salt. After cooling to 30^{o}C., 6 grams (0.16 mole) of sodium hydroxide dissolved in 114 cm^3 of water was added to the reaction mixture, over a 30 minute period. After addition of the sodium hydroxide, the reaction mixture was agitated at room temperature for one hour, whereupon the solution changed from colourless to orange-red, indicating the completion of the reaction. The solution contains 15.6% by weight, of the desired ether derivatives.

A small portion of the solid reaction product was then isolated by distillation of the aqueous layer, followed by extraction with methanol. When subjected to infra-red, nuclear magnetic resonance and elemental analysis, the above structure was confirmed for at least one component of the solid. The only evidence offered however, was that nitrogen found was 5.3% and nitrogen calculated was 5.7%.

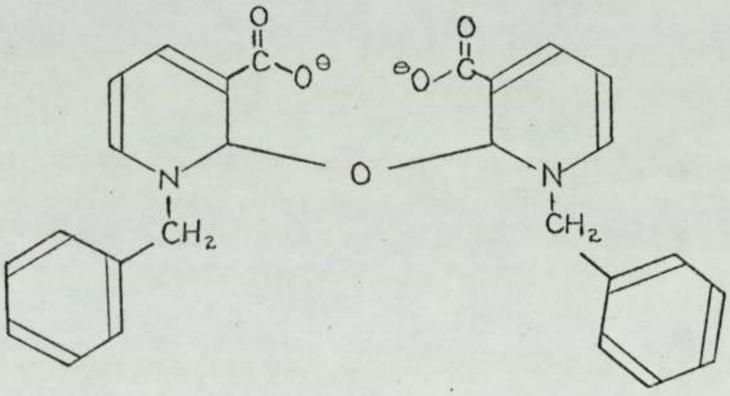
PART TWO

PREPARATION AND PROPERTIES OF MODEL COMPOUNDS

PART TWO

INTRODUCTION

We were unsuccessful with attempts made to isolate the product of hydroxide ion attack on 1-benzyl-3-carboxypyridinium chloride, which we postulate as the bimolecular ether illustrated below, which is believed to be the active brightening agent in alkaline zinc plating electrolytes.



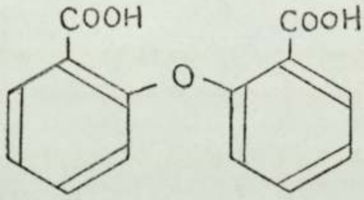
It was, therefore, decided to investigate the co-ordination chemistry of such a species by using model compounds, in the hope that any information gained from this approach could then be applied to elucidate the mechanism of the brightening action of the actual system under investigation.

The model compounds chosen were as follows;

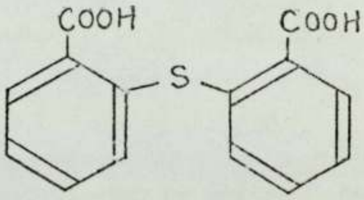
3,3'-Oxydipropionic acid $HOOC.CH_2.CH_2.O.CH_2.CH_2.COOH$

3,3'-Thiodipropionic acid $HOOC.CH_2.CH_2.S.CH_2.CH_2.COOH$

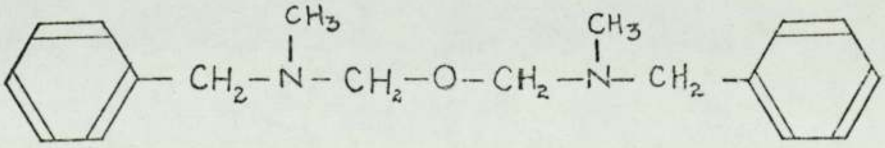
2,2'-Oxydibenzoic acid



2,2'-Thiodibenzoic acid



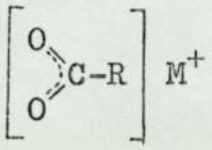
An attempt was also made to prepare a model compound with the structure;



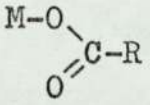
but the attempted preparative procedure proved unsuccessful.

Co-ordination Complexes of Carboxylic Acids

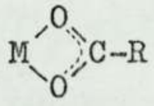
Compounds of carboxylic acid derivatives can be structurally divided into four main groups.



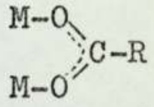
(I)



(II)

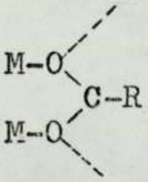


(III)



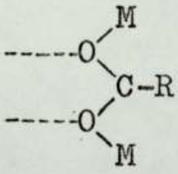
(IV)

Type (IV) can exhibit three structures depending on the bond formed between the metal and the oxygen of the carboxylate anion.



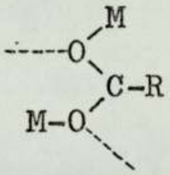
syn-syn

(IVa)



anti-anti

(IVb)



syn-anti

(IVc)

An example of type (I) co-ordination is shown by sodium formate $[Na^{\oplus}(HCOO)^{\ominus}]$, the ionic nature of which is readily confirmed by X-ray analysis.[47]

The equivalence of the two C-O bonds (1.27 A) in sodium formate, contrasts markedly with the situation in lithium acetate dihydrate $[Li(OOCCH_3)_2.2H_2O]$, which exhibits type (II) co-ordination. In this compound the acetate functions as a unidentate ligand, the bond length in the C-O-M unit is 1.33 Å, while that of the free carbonyl portion is 1.22 Å.

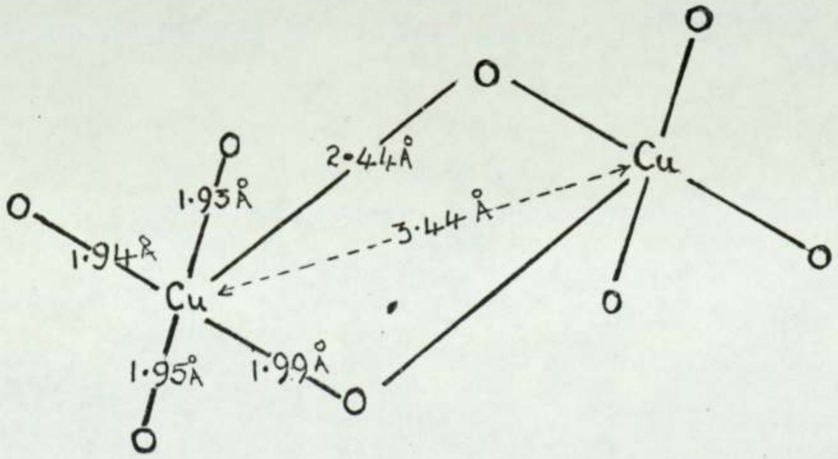
Another example of type (II) co-ordination is given by cobalt(II) diacetate tetrahydrate $[Co(OOCCH_3)_2.4H_2O]$.[49]

Type (II) bonding is best described as monodentrate co-ordination, where each carboxylate group uses only one of the two available oxygen atoms to form a bond to the metal.

Lowry and French[50] were the first to postulate that the acetate group could function as a bidentate chelate and form a four membered ring, as illustrated above for type (III) co-ordination. There are, however, few confirmed examples of the acetate ion chelating to a metal atom. In the case of the zinc complex[51], $Zn(OOCCH_3)_2.2H_2O$ and the uranyl complex[52], $Na\left[UO_2(OOCCH_3)_3\right]$, this has been confirmed by X-ray crystallography. This mode of attachment to a metal is the least favoured and although there are examples scattered around inorganic chemistry, chelate formation is more the exception than the rule.

The intricate chemistry of copper (II) formate complexes provides examples of carboxylate systems of the (IVb) and (IVc) types, which have the syn-anti and anti-anti structures respectively and so exclude any possibility of metal to metal bond formation.

In the royal blue, anhydrous copper (II) formate[53], $Cu(OOCH)_2$, the anti-syn configuration of the ligand results in a closest approach of copper atoms of 3.44 Å. The tetragonal-pyrimidal co-ordination around each copper atom requires a "sharing" of one of the oxygen atoms and this is reflected in the bond lengths, as illustrated below.



In the case of the tetrahydrated copper (II) formate,[54] $Cu(OOCH)_2.4H_2O$, which has the anti-anti configuration, the closest approach of the metal atoms is 5.80 A.

There are a large number of complexes, particularly within the transition series, which have a bridged acetate cage structures, and it has been observed that such structures appear to be favoured by metals which have, in octahedral stereochemistry, one unpaired electron in the e_g orbitals.[55] These complexes have a type (IVa) structure, with a syn-syn configuration and so the possibility exists for the postulation of metal to metal interactions or even metal to metal bonding in some cases.[56]

The reason that this distinction between direct bonding and loose coupling of spins is needed, is that acetic acid exists as a hydrogen bonded dimer. Consequently, these dimeric complexes may be regarded as simple metal replacement of the hydrogen atoms and in many instances, e.g. copper (II) acetate $[Cu(OOCCH_3)_2.H_2O]_2$, the fact that the metal atoms are "adjacent" is simply a condition demanded by the bridged acetate ligand. When, however, the metal to metal distance is short enough to cause a distortion from the hydrogen-bonded dimer dimensions, then obviously metal to metal bonding has to be considered.

Another example of type (IVa) co-ordination, is given by the dimer of chromium (II) acetate, $[Cr(OOCCH_3)_2.H_2O]_2$.[57]

Interpretation of the Infra-red Spectra of Carboxylate Complexes

The best approach to this topic is a consideration of the work of Curtis[58], who assumed that the acetate ion is able to co-ordinate in a variety of ways, as a unidentate ligand, as a chelate (symmetrical or asymmetrical) and as a bridging group in polymeric species. From a comparison of the infra-red spectra of the acetate ion in compounds of known structure, Curtis has declared it possible to distinguish between the various types of acetate co-ordination on the basis of their infra-red spectra.

Infra-red Spectrum of the Acetate Ion

The acetate ion has two strong bands in the infra-red, associated with the stretching of the carboxy-group. For sodium acetate these bands occur at 1578 and 1414 cm^{-1} (with a separation of 164 cm^{-1})[59], while for acetate esters the bands correspond to $\nu(C=O)$ at 1740 cm^{-1} and $\nu(C-O)$ at 1240 cm^{-1} (with a separation of 500 cm^{-1}).[60]

In aqueous solutions the sodium acetate carboxy-band values are 1556 and 1413 cm^{-1},[59] indicating that hydrogen -bonding to the acetate ion causes a decrease in the asymmetrical stretching frequency of the carbonyl group.

Unidentate Co-ordination

For unidentate co-ordination of the acetate ion to a bivalent metal ion, values close to those of ionic acetate, but shifted slightly towards the covalent ester values, would be expected.

Nickel acetate tetrahydrate has a structure with the nickel in pseudo-octahedral co-ordination to one oxygen of ea each of the acetate ions and the oxygen atoms of the four water molecules.[49] The carboxy-bands are at 1520 and 1413 cm^{-1} (a separation of 107 cm^{-1}), the asymmetrical stretching frequency of the carbonyl group has shifted compared to that obtained for sodium acetate. This is considered to be a consequence of hydrogen-bonding by the acetate ion, the structure having strong intramolecular hydrogen-bonding between the none co-ordinated carboxy-oxygen atoms and a water molecule (2.59 Å), as well as intermolecular hydrogen-bonding between each of the carboxy-oxygen atoms and water molecules co-ordinated to other nickel ions.

Symmetrical Bidentate Co-ordination

Bisacetobisaquozinc (II), [zinc acetate dihydrate , $Zn(H_2O)_2(OOCCH_3)_2$], is known to have a pseudo-octahedral structure with two co-ordinated water molecules and both acetate ions acting as symmetrical chelates.[51] The observed carboxy stretching frequencies are 1550 and 1430 cm^{-1} (a separation of 120 cm^{-1}).

Asymmetrical Bidentate Co-ordination

Bisacetatobisthioureazinc(II), $Zn(tu)_2(OOCCH_3)_2$, has a structure with the thiourea ligands co-ordinated by the sulphur atoms, and with the acetate ions co-ordinated with one long and one short bond.[61] The carboxy stretching frequencies are 1577 and 1425 cm^{-1} (a separation of 152 cm^{-1}), intermediate between the symmetrical bidentate value and the expected value for unidentate co-ordination (similar to those for nickel(II) probably with slightly decreased carboxy stretching frequencies separation

Bridging Acetato-groups

A number of compounds have structures with acetate ions functioning as bridging groups. The reported spectra of dimeric $Cu(OOCCH_3)_2(H_2O)_2$[62] and tetrameric $Zn_4O(OOCCH_3)_6$[63] with symmetrical bridging acetate groups have asymmetrical stretching carbonyl frequencies above 1600 cm^{-1}, higher than compounds with other types of acetate ion co-ordination.[64]

In $CaCu(OOCCH_3)_4.6H_2O$ each acetate ion is acting as an asymmetric chelate to the copper atom, with the more distant oxygen atom also bridging to the calcium atom[65], and this compound has carboxy-stretching frequencies higher than $Zn(tu)_2(OOCCH_3)_2$, which is an asymmetrical chelate but has no bridging. It has previously been suggested that a sharp well defined carbonyl asymmetrical stretching frequency at 1595 to 1600 cm^{-1}, is indicative of bridging carboxy groups.[66]

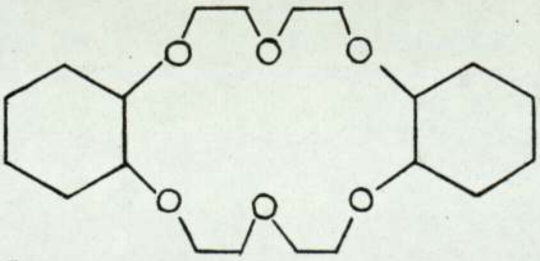
Co-ordination of Ethers and Thioethers.

Ethers can form complexes with a wide variety of elements, illustrating the co-ordinating ability of the ether linkages. Probably the best known of the ether co-ordination complexes are those formed with magnesium, the Grignard reagent.

The donor properties of sulphur are quite different from those of oxygen. In general, they are somewhat more restricted as regards the nature of the acceptor atom, but in some types of compound, the bonds are exceptionally strong. The thioethers form much more stable compounds than the corresponding oxy oxyethers. Pfeiffer[67] has pointed out that the thioethers, show a strong tendency to unite, with salts of such metals as nickel, copper and zinc, but more especially with those of platinum and palladium.

Co-ordinating ability decreases in the series water, alcohol and ether, but increases in the series hydrogen sulphide, mercaptans and thioethers.

Interest has recently been aroused concerning the co-ordinating ability of the ether linkage by the discovery of numerous and often very stable crystalline solvates of the alkali metals and alkaline earth metals (Groups I & II) and in particular Na, K, Li, Rb and Cs, with a wide variety of macrocyclic polyethers. Ethers with from 3 to 20 oxygen atoms have been synthesised, and an example is 2,5,8,15,18, 21-hexaoxatricyclo 20.4.0.0 hexacosane, usually abbreviated to cyclohexyl-18-crown-6, the structure of which is shown below.



In distilled water the equilibrium constants of the complexes formed are in the order; $K^+ > Rb^+ > Cs^+$, $Na^+ > Li^+$.

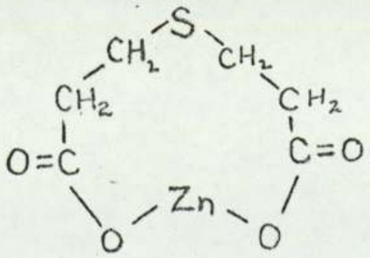
The polyether complexes have been used as models for naturally occurring compounds, that are involved in the transport of alkali and alkaline earth metal ions across membranes and for the very high selectivities towards Na^+ and K^+ or Ca^{2+} and Mg^{2+} shown by natural systems.

A search of the literature revealed, that of the four model compounds, for only one 3,3'-thiodipropionic acid had any attempt been made to study the co-ordinating ability.[68] This work mainly concerns the use of potentiometric titrations and has indicated[69], that 1:1 chelates are formed (comprising 6 membered rings) with the stability order $Cu > Pb > Cd > Zn > Ni > Co$.

Rossotti et al[70] have found that copper (II) ions in the presence of 3,3'-thiodipropionate ions, produce small amounts of the protonated complex BHA^+ in equilibrium with the mononuclear species $BA_n^{(2n-2)-}$, where $n \leq 2$. No attempt was made to isolate and identify any solid complexes but this possibility existed, and can be illustrated by the following extract.[71] "Good results were obtained for the thiodipropionate system, in spite of limitations imposed by the low solubility of the copper complex."

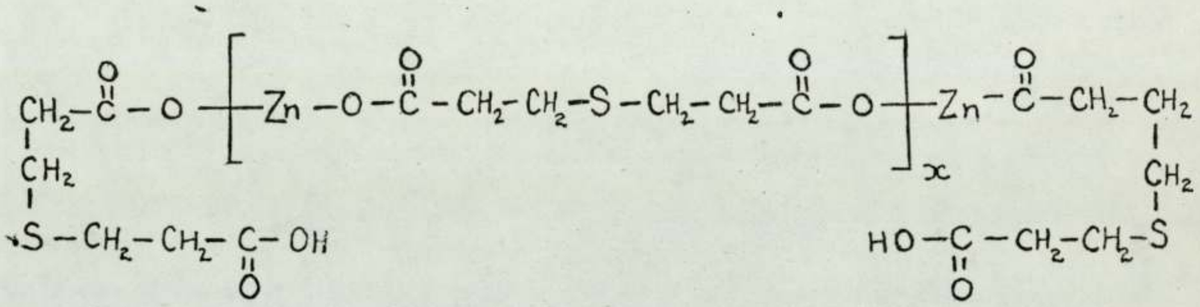
The zinc complexes of 3,3'-thiodipropionic acid are mentioned in United States patent 3 697 488, where they are used as superior catalysts for the production of high molecular weight episulphide polymers, which can be vulcanised into rubber.

The monomeric zinc complex of 3,3'-thiodipropionic acid is given, in the above patent, the structure;



No method is given for the preparation of this compound and no information other than the structure opposite.

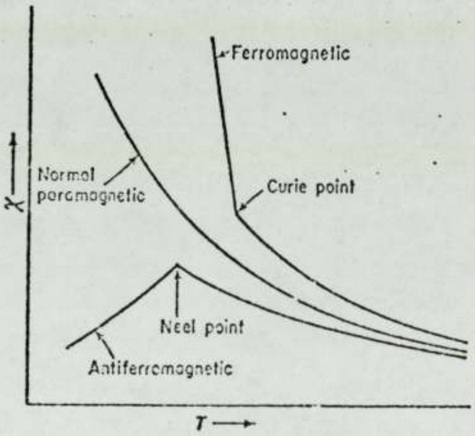
The polymeric form of the zinc complex of 3,3'-thiodipropionic acid, can be prepared according to the patent, by the dropwise addition of a solution of 3,3'-thiodipropionic acid to a dialkyl zinc compound (such as diethyl zinc) in an inert liquid medium under reflux, followed by digestion at a temperature of 25 to 75°C., for about 1 to 3 hours. The above procedure is said to produce a mixture comprising 20% monomeric and 80% of a linear polymeric form which may be represented by the formula;



where x has values of 1 to 20.

Magnetic Susceptibility

The idealised form of behaviour for the magnetic susceptibility of a paramagnetic material with temperature is the Curie law; $\chi = C/T$, with C the Curie constant. The majority of paramagnetic substances, however, obey a simple modification of the Curie law, the Curie - Weiss law; $\chi = C/T + \theta$, where θ is an empirical quantity and is a measure of the deviation from the ideal. These equations assume that the individual paramagnetic ions in a compound act independently of each other. When the paramagnetic centres in a substance are allowed to influence each other, effects of two associated types arise, namely ferromagnetism and antiferromagnetism. A plot of magnetic susceptibility (χ) against temperature (T), produce a characteristic curve, as can be seen below.



It can be seen that for a compound exhibiting ferromagnetism, there is a discontinuity at some temperature, T_c, called the Curie temperature. Above the Curie temperature the substance exhibits simple paramagnetism, while below T_c the susceptibility varies in a different way with temperature, (and is also field dependent).

Antiferromagnetic materials also have a characteristic temperature, T_n, called the Néel temperature. Above T_n the substance exhibits simple paramagnetism, but below T_n the susceptibility drops with decreasing temperature.

The peculiar behaviour of ferromagnetic and antiferromagnetic substances below their Curie or Néel points, arise due to interionic interactions, which have magnitudes comparable to the thermal energies at the Curie or Néel temperature and so become progressively greater than the thermal energies as the temperature is further lowered. The effect that neighbouring magnetic dipoles have upon each other is that they tend to align their neighbours to point either in the same direction or in an opposite direction to that in which they themselves point.

In the case of antiferromagnetism, the moments of the ions in the lattice tend to align themselves so as to cancel one another out. Thus, above the Néel temperature thermal agitation prevents very effective alignment, and the interactions are manifest only in the form of a Weiss constant. However, below the Néel temperature, this antiparallel alignment becomes effective and the susceptibility is diminished.

If the orbital angular momentum is neglected and the spin angular momenta of two neighbouring ions are taken to be $\vec{S}_1$ and $\vec{S}_2$. Then the interaction between the two neighbouring ions give rise to two energy levels one in which $\vec{S}_1$ and $\vec{S}_2$ are in the same direction and the other with them in opposing directions. This interaction is described formally as spin-spin coupling between the ions of the form $\Delta E = J.\vec{S}_1.\vec{S}_2$ where J is known as the exchange coupling constant or the exchange integral. If J is positive, the level corresponding to aligned spins, lies lowest, and if J is negative that with anti-aligned spins.

An interaction with J positive gives rise to the phenomenon of ferromagnetism, but since the conditions are very stringent, ferromagnetism only occurs for a limited range of substances.

The condition that J be negative is met much more frequently and results in antiferromagnetic behaviour. From now on attention will be restricted to antiferromagnetic behaviour. Two types may be distinguished; intermolecular where the interactions extend throughout the crystal, and intramolecular where the interactions are confined within the molecule.

Intermolecular Antiferromagnetism

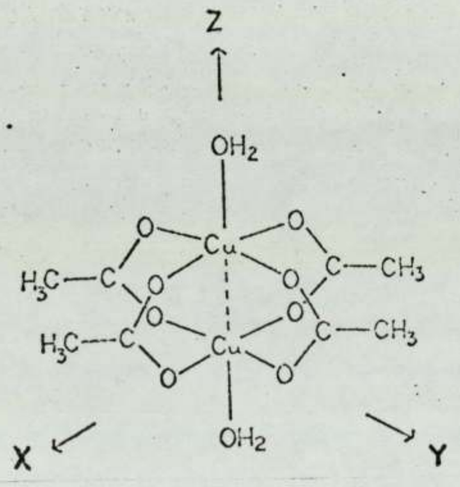
In most co-ordination compounds the shell of ligands surrounding the metal ion is sufficient to ensure that the individual paramagnetic ions in a compound act independently of each other. However, in some substances the magnetic dilution may well not be adequate and each paramagnetic ion now interacts with several neighbours and each of these again with its set of neighbours and so on throughout the crystal. For such sets of interactions to be possible, in simple salts, it is usually necessary for crystals to be of cubic symmetry, or nearly so. Body-centred and face-centred, cubic and spinel arrangements are suitable and the metal oxides, simple halides and some complex halides form the compounds of greatest importance, showing intermolecular antiferromagnetism. Here, a metal ion is commonly surrounded by an octahedron or tetrahedron of halogen or oxygen ions, which share corners, edges or faces. Since the direct spin-spin coupling by overlap of metal orbitals falls off very rapidly as the distance between the metal ions exceeds the combined radii of the ions, it is not surprising to find that the coupling takes place by bridging through an intervening oxygen or halogen atom, forming structures such as M-O-M, rather than by direct exchange.

This circumstance gives rise to the rather surprising fact that coupling is often strongest between next-nearest neighbours rather than nearest ones. This phenomenon is referred to as "superexchange".

Intramolecular Antiferromagnetism

In this type of antiferromagnetism the interaction takes place within a single molecule. The simplest system that can be formulated is that where two ions of spin $\frac{1}{2}$ interact with each other, but with no other paramagnetic centres in the substance. The lowest level is then that with total spin 0 (i.e. $\frac{1}{2} - \frac{1}{2}$), a singlet and at a distance J higher lies a triplet level, with total spin 1 (i.e. $\frac{1}{2} + \frac{1}{2}$).

An example of such a simple system is found in copper (II) acetate monohydrate, which consists of a binuclear molecule $Cu_2(CH_3COO)_4.2H_2O$, in which copper (II) ions are bridged in pairs by four acetate groups, with two water molecules occupying the terminal positions[62], as can be seen in the diagram below.



The copper (II) ion is 0.22 Å, out of the plane of the four oxygen atoms. One interesting feature of this sixfold co-ordinated copper complex is the close approach of 2.64 Å., between the two copper (II) ions, which is only slightly greater than 2.56 Å., the interatomic distance in metallic copper.

The magnetic susceptibility of this compound passes through a maximum at about 270 K., and decrease rapidly as the temperature is lowered, not obeying the Curie-Weiss law.[72]

Figgis and Martin[73] made exact measurement of the temperature variation of the susceptibility and deduce an expression which partially explained this behaviour.

An expression for the molar susceptibility can be readily obtained from Van Vleck's[74] basic formula:

$$\chi_m = \frac{N \sum_{nm} \left\{ \frac{(E_{nm}^{(1)})^2}{kT} - 2E_{nm}^{(2)} \right\} \exp(-E_n^{(0)}/kT)}{\sum_n g_n \exp(E_n^{(0)}/kT} \quad \ldots 1$$

Where $E^{(0)}$ denotes the energy levels under no applied field and $E_{nm}^{(1)}$ and $E_{nm}^{(2)}$ denote coefficients of the first and second order Zeeman displacements of levels, defined by the relation;

$$E_{nm} = E^{(0)} + E_{nm}^{(1)} H + E_{nm}^{(2)} H^2 \quad \ldots 2$$

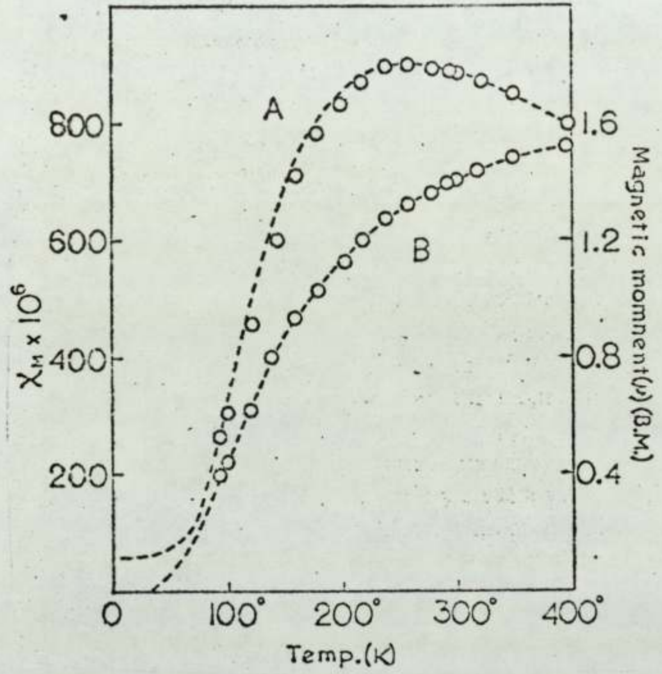
The magnetic field removes the spin degeneracy of g_n of level n and these sublevels are specified by the magnetic quantum number m. Terms in H^2 do not change the separation of the four orbital levels but introduce a temperature independent term $N\alpha$ into the susceptibility which is not affected by the relative distribution of Cu^{2+} ions between the singlet and triplet state.

To the first order of magnetic field;

$$\chi_m = \frac{2g^2N\beta^2}{3kT} \cdot \frac{1}{1 + \frac{1}{3}\exp(J/kT)} + N\alpha \quad \ldots 3$$

Where g is the magnetic field splitting factor which is 2, if the magnetic moment arises from spin only, but since it is not possible to neglect entirely the influence of orbital contributions to the moment of the cupric ion, and this is allowed for in the case ofcopper (II) acetate, by employing the factor $g = 2.2$.

In the case of copper (II) acetate, J is about 300 cm^{-1}, so at room temperature ($kT \doteq 200\ cm^{-1}$), the upper state is appreciably occupied and results in a room temperature moment of 1.4 B.M./Cu atom. At low temperatures, only the singlet state is occupied and the moment drops to zero, apart from the $N\alpha$ contribution (which is the temperature independent paramagnetism of one mole of copper (II) ions).



The diagram opposite shows a plot of the magnetic susceptibilities and magnetic moments of copper (II) acetate monohydrate, at various temperatures.
------- indicates the theoretical curve obtained obtained by using equation 3, and the symbol o being experimental values obtained for: curve A, the magnetic susceptibilities and curve B, the magnetic moments.

It follows from equation 3, that $\chi_m = N\alpha$ when $T = 0$, and rises to a maximum value at $T_n \triangleq 5/8\ J$ (J in ^{o}K, or 5/8 J/k when J is in cm^{-1}), so that the exchange energy can be derived directly from the temperature at the maximum, or Néel point; i.e. $J = 5/8\ k/T_n$ (J in cm^{-1}).

At temperatures well above J it can be shown that the effect of the interaction on this system of two interacting spins of $\frac{1}{2}$ is to cause the susceptibility to obey a Curie-Weiss law, with $\theta = \frac{1}{4}J$ (J in ^{o}K), and $T_n = 5/2\,\theta = 5/8\ J$. In the case of copper (II) acetate, T_n is 270^{o}K and θ is 108^{o}K.

The general form of intramolecular antiferromagnetism follows in broad outline that of the copper (II) acetate example of two interacting spins of $\frac{1}{2}$. There is always a maximum in the susceptibility versus temperature curve, and the behaviour at temperatures much greater than J is of the Curie-Weiss form. However, as the number of ions in the group and the spin on each of them increases, so the Neel point becomes ill defined and it is necessary to go to temperatures very large indeed compared to J to find Curie-Weiss law behaviour. T_n and θ are given by different functions of J to those given above, for the various spin systems which may be encountered.

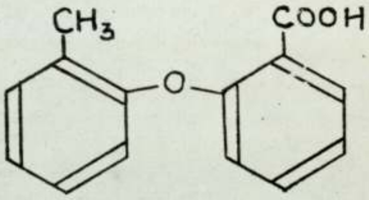
PREPARATION OF THE MODEL COMPOUNDS

AND THE COMPLEXES OBTAINED FROM THEM.

Preparation of 2,2'-Oxydibenzoic Acid

This material was prepared by a minor modification of the method published by Anschutz and Clasen[75] in 1922, which involves the initial preparation of o-tolylsalicylic acid[76] $HOOC.C_6H_4.O.[2]C_6H_4[1]CH_3$ and its subsequent oxidation with potassium permanganate. The modifications made, involved increasing the scale by a factor of ten and the use of a new purification procedure for the crude product.

Preparation of o-Tolylsalicylic Acid



50g (0.26 mole) of the potassium salt of o-chlorobenzoic acid was added with stirring to a solution containing 67 cm^3 (70g , 0.65 mole) o-cresol and 15g (0.29 mole) of sodium methoxide and 1g of copper bronze. The mixture was then heated, with stirring. Reaction became apparent at about 150°C., and the source of heat was removed, the heat of reaction taking the temperature finally to about 230°C., with the production of a deep violet colour. After cooling the reaction mixture was dissolved in 500 cm^3 of distilled water and all the insoluble material filtered off. The filtrate was then extracted with five 30 cm^3 portions of diethyl ether. The aqueous layer was then treated with activated charcoal to remove the faint pink colour which persisted and the white solid precipitated on addition of conc., hydrochloric acid was filtered off. This material was recrystallised twice from boiling water giving 54g (93%) of o-tolylsalicylic acid, which was identified by the determination of its melting point and equivalent weight, the latter being obtained from a titration with 0.1N sodium hydroxide solution to a phenolphthalein end point.

Conversion of o-Tolylsalicylic Acid to 2,2'-Oxydibenzoic Acid

45.6g (0.2 mole) of o-tolylsalicylic acid was dissolved in a solution containing 11.2g (0.2 mole) of potassium hydroxide dissolved in 400 cm^3 of distilled water. A solution containing 71.1g (0.45 mole) of potassium permanganate dissolved in one litre of distilled water was then added dropwise over a period of 8 hours, with continuous stirring. The temperature was then raised to 50°C., for two hours, with stirring. After cooling sodium bisulphite was slowly added until the permanganate colour had been removed. The precipitate was then filtered off and washed twice with 100 cm^3 of hot distilled water. The washings and filtrate were then combined and acidified with concentrated hydrochloric acid. The white precipitate was recrystallised twice from boiling distilled water and dried over P_4O_{10} in vacuo.

The yield was 44.3g (86%) of 2,2'-oxydibenzoic acid with m.pt., 229-230°C. (230°C.[75]), identified by infra-red and nuclear magnetic resonance spectra and equivalent weight, the latter being determined by titration with 0.1N sodium hydroxide solution to a phenolphthalein end point.

Preparation of 2,2'-Thiodibenzoic Acid

This material was first prepared by Meyer[77] in 1910, who reacted the potassium salts of thiosalicylic acid and o-chlorobenzoic acid in aqueous media at 135-140°C., using an autoclave. The method used comprised of an increase in scale and the use of an inert solvent.

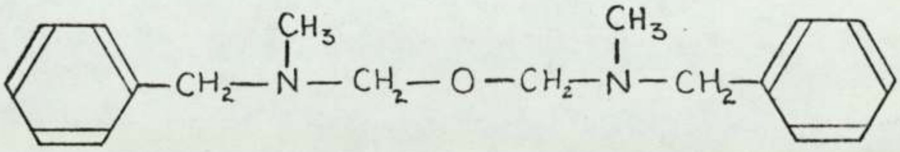
30.8g (0.2 mole) of thiosalicylic acid (o-mercaptobenzoic acid) and 31.3g (0.2 mole) of 2-chlorobenzoic acid (o-chloro benzoic acid), were suspended in 150 cm^3 of ethyl cellosolve and 55.3g (0.4 mole) of potassium carbonate was slowly added with vigorous stirring. 1g of copper bronze was then added and the mixture refluxed for 10 hours. After cooling the solution was diluted to one litre with distilled water and then filtered. The filtrate was treated with charcoal and after this had been removed, acidified with concentrated hydrochloric acid. The white precipitate was recrystallised twice from acetic acid. A yield of 42.8g (78%) of 2,2'-thiodibenzoic acid with melting point 229-230°C. (229-230°C.[77]), was obtained. The infra-red and nuclear magnetic resonance spectra were obtained, and also the equivalent weight by titration with 0.1N sodium hydroxide solution to a phenolphthalein end point.

Preparation of 3,3'-Oxydipropionic Acid

This material was prepared by a modification of the general method proposed by Christian and Hixon[78] in 1948, and involved the acid hydrolysis of di(2-cyanoethyl)ether (also called 2,2'-dicyanodiethylether and β,β'-oxydipropionitrile)

31.0g (0.2 mole) of di(2-cyanoethyl)ether and 100 cm^3 (1.0 mole approx.) of concentrated hydrochloric acid were mixed in a 250 cm^3 round bottomed flask equipped with a reflux condenser, and heated at 70-80°C., for four hours and then at 100°C., for 30 minutes. The mixture was then evaporated to dryness in vacuo and extracted with warm acetone. Evaporation of the acetone solution under reduced pressure gave a syrup which could not be induced to crystallise. The syrup was then distilled under reduced pressure, the main component boiling at 190-195°C. (approx., 1-2mm Hg). The material was recrystallised from an ethyl acetate-petroleum ether (100 - 120°C.,) mixture, and yielded 22.0g (54%) of 3,3'-oxydipropionic acid, with melting point 60-61°C. (lit., 60-61°C.[74]), identified by infra-red and nuclear magnetic resonance spectra, and the equivalent weight was obtained by titrating against 0.1N sodium hydroxide solution to a phenolphthalein end point.

Attempted Preparation of 1,1'-Dibenzyl-1,1'-dimethyl-2-oxa ethandiamine Bis(1-benzylmethylaminomethylene)ether



This material was intended to be prepared in the form of the dihydrochloride by the following procedure:

70.5g (0.58 mole) of 1-benzylmethylamine was dropped slowly into 25 cm^3 (0.29 mole) of bis(chloromethyl)ether dissolved in 200 cm^3 of dry methanol, contained in a 500 cm^3 round bottomed flask equipped with a reflux condenser and magnetic stirring. After the addition of the amine was complete (about 2 hours), the mixture was refluxed for 2 hours. On cooling a white precipitate was formed, which was filtered off. One litre of freshly distilled acetone, was then added and more of the precipitate obtained. The two precipitates were combined, after infra-red spectroscopy had confirmed them to be the same material, and recrystallised twice from acetone.

Since bis(chloromethyl)ether is a human carcinogen, utmost care was taken when handling this material and throughout the above procedure, all waste being refluxed for 5 hours with 20% sodium hydroxide solution before disposal.

Due to the failure to prepare the desired material and the dangers involved, no further attempts were made to prepare this compound, and all further investigation of this type of model compound abandoned.

Preparation of the Zinc, Cobalt, Copper and Iron Complexes of 2,2'-Oxydibenzoic acid

36.15g (0.14 mole) of 2,2'-oxydibenzoic acid, was dissolved in 300 cm^3 of distilled water, containing 15.7g (0.28 mole) of potassium hydroxide and the pH adjusted to 7.0 with 1% potassium hydroxide solution. Finally the solution was diluted accurately to 350 cm^3 with distilled water.

i) Zinc Complex

To a 50 cm^3 aliquot of the ligand stock solution was added, with vigorous stirring, 7.4g (0.02 mole) of zinc perchlorate hexahydrate, dissolved in 50 cm^3 of distilled water. A white precipitate formed immediately and this was filtered off, washed with distilled water, methanol and diethyl ether, then dried in vacuo over P_4O_{10}.

ii) Cobalt Complex

To a 50 cm^3 aliquot of the ligand stock solution was added, with vigorous stirring, 5.8g (0.02 mole) of cobalt (II) nitrate hexahydrate, dissolved in 50 cm^3 of distilled water. No precipitate was formed initially, but after 24 hours large violet crystals had formed. These were filtered off, washed with methanol and diethyl ether, and divided into two equal portions. One portion was placed in a desiccator, over sodium hydroxide, and after one week still retained their original colour. The second portion was dried over P_4O_{10} in vacuo, and after two days had changed to a blue colour, but retained their original crystalline form.

iii) Copper Complex

To a 50 cm^3 aliquot of the ligand stock solution was added with vigorous stirring, 7.4g (0.02 mole) of copper(II) perchlorate hexahydrate dissolved in 50 cm^3 of distilled water. A pale blue precipitate formed immediately and was filtered, washed with distilled water, methanol and diethyl ether, then divided into two portions. One portion was dried in a desiccator over NaOH, and after one week retained its original colour. The second portion was dried in vacuo over P_4O_{10}, and after two days had changed to a green colour.

iv) Iron (II) and (III) Complexes

Iron (III) Complex

To two separate 50 cm^3 aliquots of the ligand stock solution was added with vigorous stirring;

a) 9.6g (0.02 mole) of ammonium iron (III) sulphate, $(NH_4)_2SO_4FeSO_4.6H_2O$,

and

b) 9.2g (0.02 mole) of iron (III) perchlorate hexahydrate,

both dissolved in 50 cm^3 of distilled water. The material from both iron (III) sources was identical, an immediately formed mustard precipitate. This was filtered, washed with distilled water, methanol and diethyl ether and dried over P_4O_{10} in vacuo.

Iron (II) Complexes

A 50 cm^3 aliquot of the ligand stock solution, was transferred to a 250 cm^3 round bottomed flask equipped with a reflux condenser and a nitrogen bubbler. 50 cm^3 of distilled water was introduced and the solution heated to boiling, while bubbling through a continuous stream of nitrogen. The solution was allowed to cool slowly, with a stream of nitrogen being passed continuously. A solution containing 7.8g (0.02 mole) of ammonium iron (II) sulphate, $(NH_4)_2SO_4FeSO_4.6H_2O$, in 50 cm^3 of distilled water, was prepared in a 250 cm^3 round bottomed flask equipped with a reflux condenser and a nitrogen bubbler. The solution was heated to boiling and then cooled, while continuously bubbling a strem of nitrogen, to remove all dissolved air. The nitrogen bubblers and condensers of both preparations were removed, the solutions mixed and the flask stoppered. The green solution was left for two days, at the end of which green crystals had been formed. These crystals were filtered, washed with methanol and diethyl ether and divided into two equal portions.

a) The first portion was dried over NaOH, and after one week still retained their original green colour, although there was some very slight "yellowing".

b) The second portion was dried in vacuo over concentrated sulphuric acid, and after two days had changed to a dark brown colour with a metallic golden sheen on one face.

c) The third portion was placed in an oven and dried at 105°C., for 5 hours. This portion also changed to the dark brown form with the golden sheen, and proved on later examination to be identical with that obtained by procedure (b) above.

Preparation of the Zinc and Copper Complexes of 2,2'-Thiodibenzoic Acid

10.96g (0.04 mole) of 2,2'-thiodibenzoic acid was dissolved and adjusted to pH 7, with about 3.2g of "Aristar" sodium hydroxide, in 100 cm^3 of distilled water.

i) Zinc Complex

To a 50 cm^3 aliquot of the ligand stock solution, was added with vigorous stirring, 7.45g (0.02 mole) of zinc perchlorate hexahydrate, dissolved in 20 cm^3 of distilled water. A white precipitate was slowly formed.

ii) Copper Complex

To a 50 cm^3 aliquot of the ligand stock solution, was added slowly with vigorous stirring, 7.4g (0.02 mole) of copper (II) perchlorate hexahydrate, dissolved in 20 cm^3 of distilled water. A pale green precipitate formed immediately but changed in a short time on standing, to a darker blue-green colour.

The precipitates were filtered, washed with distilled water, methanol and diethyl ether and dried in vacuo over P_4O_{10}.

Preparation of the Zinc and Copper Complexes of 3,3'-Oxydipropionic Acid

6.48g (0.04 mole) of 3,3'-oxydipropionic acid was dissolved in 10 cm^3 of distilled water and the pH adjusted to 7 with about 3.2g (0.08 mole) of "Aristar" sodium hydroxide dissolved in 10 cm^3 of distilled water.

i) Zinc Complex

7.45g (0.02 mole) of zinc perchlorate hexahydrate, was dissolved in 10 cm^3 of distilled water, and mixed with 10 cm^3 of the ligand stock solution.

ii) Copper complex

7.4g (0.02 mole) of copper (II) perchlorate hexahydrate, was dissolved in 10 cm^3 of distilled water, and then mixed with 10 cm^3 of the ligand stock solution.

No precititates formed initially, but on standing in sealed containers, precipitates appeared in both solutions. After two weeks these precipitates were filtered, washed with diethyl ether and dried in vacuo over P_4O_{10}.

Preparation of the Zinc and Copper Complexes of 3,3'-Thiodipropionic Acid

17.8g (0.1 mole) of 3,3'-thiodipropionic acid was dissolved in 100 cm^3 of distilled water with the aid of about 8.0g (0.2 mole) of "Aristar" sodium hydroxide, and the solution adjusted to pH 7.

i) Zinc Complex

To a 50 cm^3 aliquot of the ligand stock solution, was added with vigorous stirring, 18.6g (0.05 mole) of zinc perchlorate hexahydrate dissolved in 50 cm^3 of distilled water. A white precipitate was formed immediately.

ii) Copper Complex

To a 50 cm^3 aliquot of the ligand stock solution, was added with vigorous stirring, 18.5g (0.05 mole) of copper (II) perchlorate hexahydrate dissolved in 50 cm^3 of distilled water. A green precipitate formed immediately.

The precipitates were filtered, washed with distilled water, methanol and diethyl ether and dried in vacuo over P_4O_{10}.

Equipment Information

The elemental analysis for carbon, hydrogen and nitrogen were obtained using a Hewlett-Packard 185 C,H & N analyser.

The nuclear magnetic resonance spectra, were obtained using a Perkin-Elmer R14, with deuterated dimethylsulphoxide as solvent and tetramethylsilane as internal standard.

The infra-red spectra were obtained using a Pye-Unicam SP 1000 (3,800 to 625 cm^{-1} with a separation at 2,000 cm^{-1}), or a Perkin-Elmer 457 (4,000 to 250 cm^{-1}).

The diffuse reflectance spectra were obtained using a Pye-Unicam SP 800, fitted with the standard accessory.

The metal analysis was mainly determined using a Pye-Unicam SP 90 or Perkin-Elmer 322, Atomic Absorption Spectrophotometers. The copper content of the appropriate complexes was also determined from a titration of the iodine liberated from potassium iodide, in acid conditions, with standardised sodium thiosulphate solution.[79] The complex being destroyed by fuming down to dryness with concentrated nitric acid, as described in the reference.

The magnetic susceptibility measurements at different field strengths, were determined on a standard Gouy balance, at different magnet currents. Although the current does not appear to be directly proportional to the field strength, especially at high currents, the procedure was adequate for the information obtained. If ferromagnetic behaviour had been encountered, then more accurate data could have beem obtained by determining the magnetic field strength produced by a given current using a Hall probe.

The magnetic susceptibility measurements at different temperatures, were obtained using a Gouy balance (Newport Instruments), the sample cavity of which could be cooled to liquid nitrogen temperatures.

The Mossbauer data was obtained by P. Gillespie using equipment described in the Ph.D., thesis of M. Fernandopulle.[80]

Problems Encountered During Sulphur Analysis

An attempt was made to determine the sulphur content of the metal complexes prepared from 2,2'-thiodibenzoic acid and 3,3'-thiodipropionic acid, using the oxygen flask method.[81] This involves the oxidation of sulphur to sulphate ions, using gaseous oxygen, and subsequent titration of the sulphate produced with 0.02 molar barium perchlorate solution, using Thorin* as indicator.

* 2-(2-hydroxy-3,6-disulpho-1-naphthylazo)phenyl arsonic acid, sodium salt.

Satisfactory results were obtained for 2,2'-thiodibenzoic acid and 3,3'-thiodipropionic acid, but no results could be obtained for the copper (II) complexes and only low results for the zinc complexes.

When no sulphur could be found in the copper (II) - 2,2'-thiodibenzoic acid complex, it was thought initially that the sulphur may have been eliminated during the preparation of the complex, some change having occurred because of the colour change, from pale apple green to blue-green, observed during preparation.

Consequently, the complex was destroyed using a solution containing sodium hydroxide and ethylenediaminetetraacetic acid. A white solid was precipitated with concentrated hydrochloric acid, isolated by filtration, recrystallised from water and dried in vacuo over P_4O_{10}, for several days. The melting point, infra-red spectrum and elemental analysis (which gave the correct sulphur determination), confirmed the material to be 2,2'-thiodibenzoic acid.

The conclusion inferred from these results was that the oxygen flask method for the determination of sulphur, does no not work in the presence of copper (II) ions and is inhibited to a lesser extent by zinc ions.

Recourse to the literature[82], confirms that other workers have indicated that this procedure is sensitive to cationic interference. The use of an ion exchange resin to remove interfering cations, could rectify this difficulty.

Problem Encountered During the Measurement of the Magnetic Susceptibilities of Complexes at Low Temperatures

During the measurement of the magnetic susceptibilities with temperature, an interesting problem was encountered. As the temperature was lowered, the weight of the Gouy tube plus sample decreased, i.e., it suffered a weight loss.

At first it was thought that this effect was due to the stream of nitrogen, used continuously to flush the sample cavity. Experiments using different nitrogen flow rates, still gave the same weight losses and so this possible cause was eliminated.

A plausible explanation can be provided by considering the increase in the density of the nitrogen as the temperature is lowered. From the ideal gas equation PV = nRT, and fact that the density of nitrogen at $0^{o}C.$, at standard atmospheric pressure is 1.2507 grams per litre. It can be calculated that 1 cm^3 of nitrogen at $T^{o}K.$, will weigh; $\frac{1.2507 \times 273.15}{1000 \times T}$ grams.

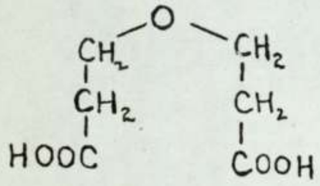
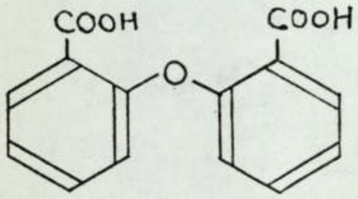
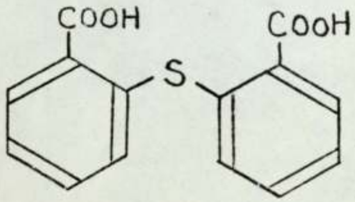
The Avagadro hypothesis states that the upthrust produced is equal to the volume of gas displaced, consequently, as the density of the gas increases so must the resultant upthrust.

This approach applied to the results obtained is illustrated in Table 5, the best fit being obtained when the volume displaced is assumed to be 2.6 cm^3, which appears to be a good approximation for the tubes external volume.

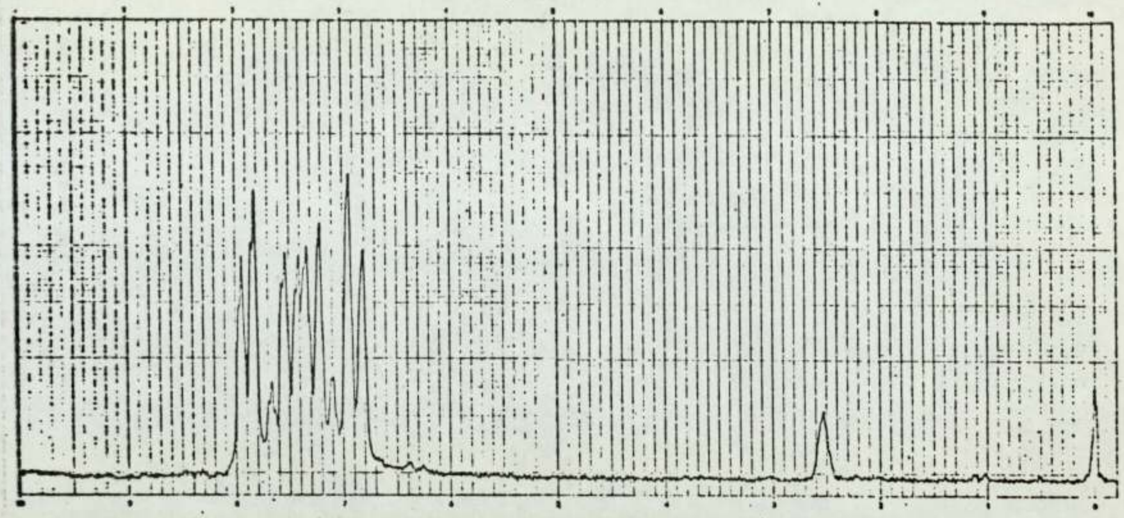
TABLE 5, WEIGHT LOSS DURING LOWERING OF TEMPERATURE

TEMPERATURE IN °K	WEIGHT OF GOUY TUBE (+SAMPLE) IN GRAMS	WEIGHT LOSS IN GRAMS ($\times 10^4$)	UPTHRUST ($\times 2·6$) IN GRAMS ($\times 10^4$)	UPTHRUST PER CM^3 OF NITROGEN IN GRAMS ($\times 10^4$)	WEIGHT OF ONE CM^3 OF NITROGEN IN GRAMS ($\times 10^3$)
273·15	7·5457				1·2507
263·15	7·5456	1·0	1·2	0·47$_5$	1·298
243·15	7·5451$_5$	5·5	4·0	1·54	1·405
223·15	7·5448$_5$	8·5	7·3	2·80	1·531
203·15	7·5445	12·0	11·2	4·31	1·682
183·15	7·5440	17·0	16·0	6·15	1·866
163·15	7·5435$_5$	21·5	21·9	8·44	2·095
143·15	7·5428	29·0	29·6	11·37	2·388
123·15	7·5416$_5$	40·5	39·7	15·25	2·776
103·15	7·5402$_5$	54·5	53·7	20·64	3·315

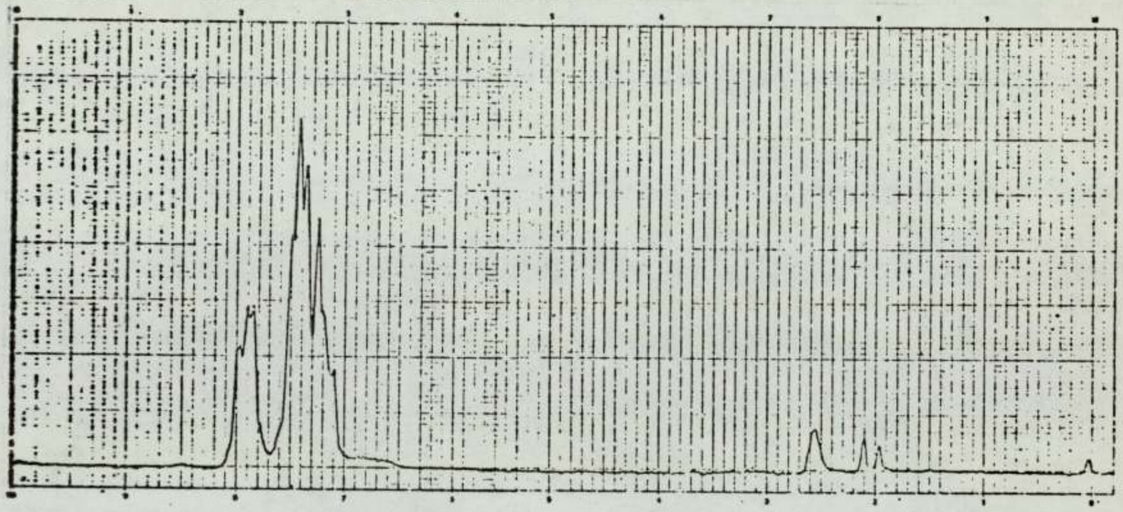
ANALYTICAL RESULTS FOR MODEL COMPOUNDS

COMPOUND	ELEMENTAL ANALYSIS			EQUIVALENT WEIGHT		MELTING POINT °C		STRUCTURE
	ELEMENT	FOUND	CALCULATED	FOUND	CALCULATED	FOUND	LITERATURE	
3,3′-OXY DIPROPIONIC ACID	C	44·40% 44·77%	44·4%	83 85	81	60-61	60-61	
	H	6·29% 6·34%	6·2%					
2,2′-OXY DIBENZOIC ACID	C	65·08% 64·77%	65·12%	127 129	129	229 to 230 (dec)	229 to 230 (dec)	
	H	3·40% 3·77%	3·90%					
2,2′-THIO DIBENZOIC ACID	C	60·52% 60·72%	61·3%	135 139	137	229 to 230 (dec)	229 to 230 (dec)	
	H	3·73% 3·62%	3·68%					
	S	11·58%	11·69%					

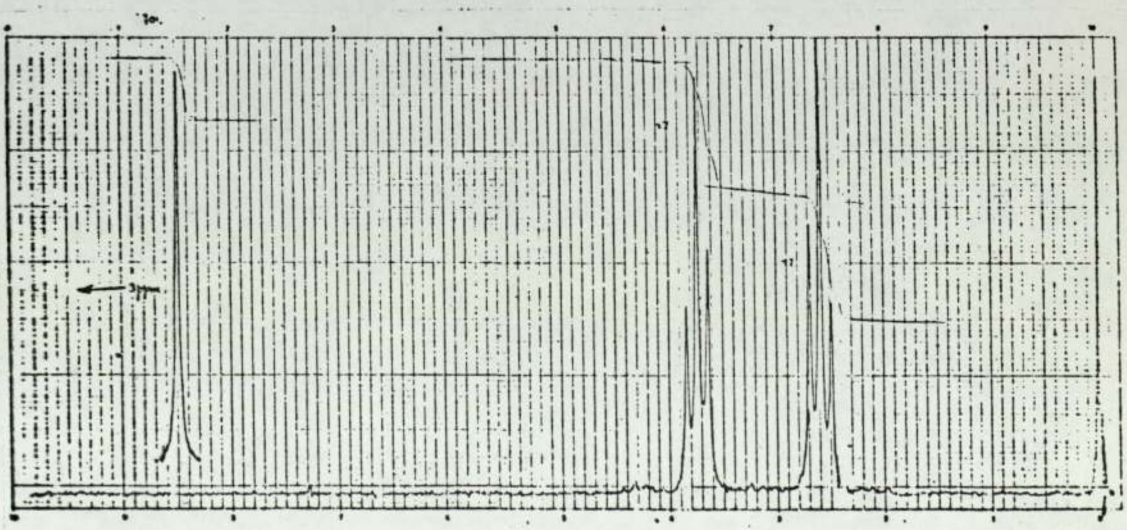
NUCLEAR MAGNETIC RESONANCE SPECTRA



2,2'-OXYDIBENZOIC ACID



2,2'-THIODIBENZOIC ACID



3,3'-OXYDIPROPIONIC ACID

RESULTS AND DISCUSSION

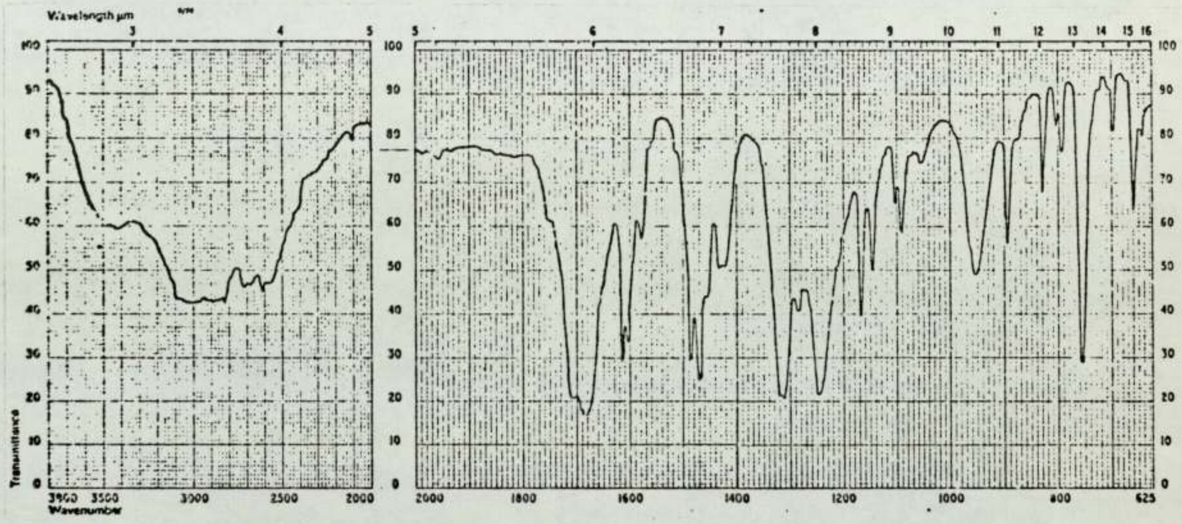
The zinc and copper complexes of 3,3'-thiodipropionic acid were the most accessible, due to the availability of the ligand. However, because the main objective of this work was to model the behaviour of the bimolecular ether, postulated in part one, which entails essentially a study of the co-ordinating ability of the ether linkage in carboxylate complexes, to evaluate the possibility that the bimolecular ether could be acting as a terdentate ligand, little attention was given initially to the zinc and copper complexes of 3,3'-thiodipropionic acid.

Initially, interest centred on 3,3'-oxydipropionic acid and 2,2'-oxydibenzoic acid, but despite both having appeared in the literature, information regarding their preparation, particularly the former, was vague. The preparation of 2,2'-oxydibenzoic acid proved easiest, great difficulty being encountered in the isolation of 3,3'-oxydipropionic acid, due to the formation, presumably by hydrolysis, of large amounts of hydroxypropionic acid.

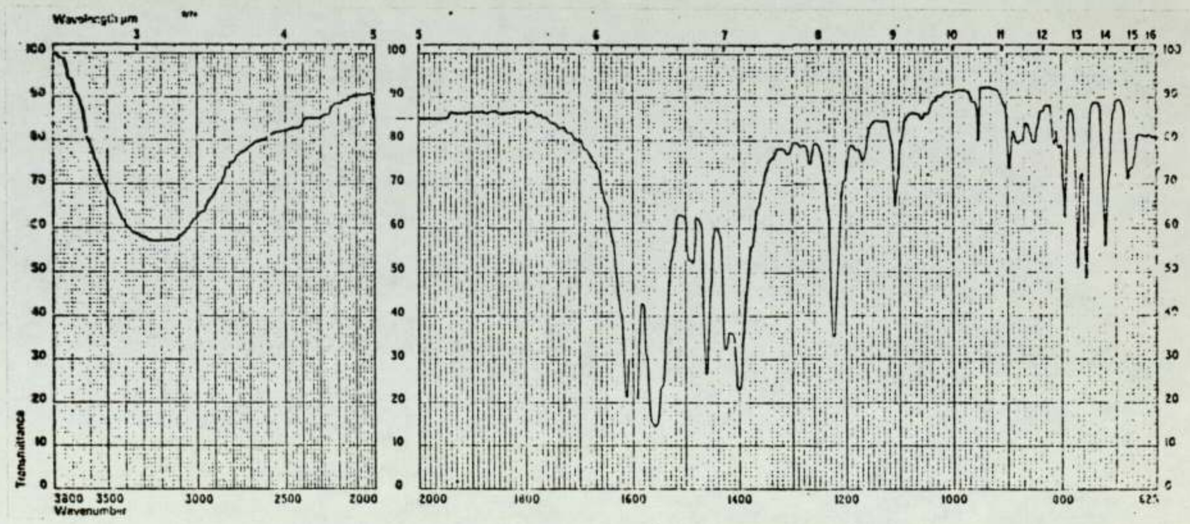
TABLE 6, RESULTS OF ELEMENTAL ANALYSIS FOR ZINC COMPLEX OF 2,2'-OXYDIBENZOATE

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L $\cdot\frac{1}{2}H_2O$	M·L $\cdot H_2O$	M·L $\cdot 1\frac{1}{2}H_2O$	M·L $\cdot 2H_2O$	M·L $\cdot H_2O \cdot OH$	M·O·L $\cdot H_2O$
ZINC	18·6, 19·4	20·33	19·37	19·31	19·78	19·25	18·75	18·28	18·33	18·39
CARBON	48·45, 48·31	52·29	49·81	49·66	50·86	49·51	48·23	47·02	47·15	47·29
HYDROGEN	3·00, 3·12	2·51	2·39	2·68	2·74	2·97	3·18	3·38	3·11	2·83

INFRA-RED SPECTRA



2,2'-OXYDIBENZOIC ACID



ZINC COMPLEX OF 2,2'-OXYDIBENZOATE

Complexes of 2,2'-Oxydibenzoic Acid

Zinc Complex of 2,2'-Oxydibenzoic Acid

The elemental analysis of this complex was consistent with a zinc to ligand ratio of one to one, and also one and a half water molecules, i.e. $Zn.L.1\frac{1}{2}H_2O$. Table 6, shows that other formulas are also possible, involving hydroxyl and oxa bridges, but it is doubtful that even if more accurate analytical data was available it would be possible to give an unequivocal assignment, because of the small variation in the composition of these complexes.

The infra-red spectrum of the zinc complex (page 117), gives more information regarding the composition, but it still does not resolve the problem.

The broad, medium intensity absorption at 3,000 - 3,500 cm^{-1}, suggests the presence of an hydroxyl group, but weak interaction of some kind must be postulated, to account for the displacement from the usual position at 3,500 - 3,650 cm^{-1}.

The sharp, strong well resolved doublet at 1595 - 1610 cm^{-1}, could possibly be due to the asymmetric carbonyl stretching frequency of the carboxylate, but is more probably arises from the ligand, since a similar feature is observed in the spectrum of the free ligand. The broad, strong absorption (possibly a poorly resolved doublet) at 1560 cm^{-1} (with shoulder at 1545 cm^{-1}), is a better candidate for the asymmetric carbonyl stretching frequency, which is assigned to the strong, poorly resolved doublet at 1680 and 1710 cm^{-1}, in the spectrum of the free ligand.

If the sharp, strong absorption at 1400 cm^{-1}, can be assigned to the symmetric carbonyl stretching frequency (assumed to be the sharp, strong absoption at 1315 cm^{-1}, in the free ligand), this would give a separation of 160 cm^{-1}, between the asymmetrical and symmetrical carbonyl stretching frequencies.

This separation is too large for unidentate (about 100 cm^{-1}) or symmetrical bidentate (about 120 cm^{-1}) behaviour, but fits the separation postulated for asymmetrical bidentate co-ordination (about 150 cm^{-1}). The possibility of the carboxylate group bridging between two metal atoms may be neglected, since the asymmetric carbonyl stretching frequency is rather low, because for bridging it should be at 1600 cm^{-1} or above.

The sharp, strong absorption at 1425 cm^{-1}, is most probably due to the ligand but the possibility also exists that it may be due to a symmetrical carbonyl stretching frequency with would give a separation of 135 cm^{-1} (when coupled with the absorption at 1560 cm^{-1}) or 120 cm^{-1} (when coupled with the shoulder of this absorption at 1545 cm^{-1}).

The prominent absorption (strong, sharp), at 1225 cm^{-1}, possibly related to the strong, broader absorption at 1245 cm^{-1} in the free acid, may be due to the C-O stretching vibration of the ether linkage, but is more probably C-O stretching vibrations or OH deformation vibrations of a water molecule or hydroxyl group.

One noticeable absence in the spectrum of the zinc complex, when it is compared with the spectrum obtained for the free ligand, is the broad, medium intensity absorption at 955 cm^{-1}, which is most probably caused by hydroxyl out of plane deformations.

The region 625 - 900 cm^{-1}, is very different when comparing the spectrum of the free ligand with that of the zinc complex. The dominant feature of the free ligand, namely a sharp, strong absorption at 755 cm^{-1}, in the zinc complex, has either been reduced in intensity or split into the doublet at 755 and 770 cm^{-1}.

TABLE 7, RESULTS OF ELEMENTAL ANALYSIS FOR BLUE COBALT COMPLEX OF 2,2'-OXYDIBENZOATE

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L $\cdot\frac{1}{2}H_2O$	M·L $\cdot H_2O$	M·L $\cdot 1\frac{1}{2}H_2O$	M·L $\cdot 2H_2O$	M·L $\cdot H_2O\cdot OH$	M·O·L $\cdot H_2O$
COBALT	17·4, 18·3	18·70	17·80	17·74	18·18	17·69	17·22	16·78	16·83	16·88
CARBON	48·61, 51·64	53·36	50·78	50·63	51·88	50·47	49·14	47·88	48·02	48·16
HYDROGEN	2·45, 2·96	2·56	2·44	2·73	2·80	3·03	3·24	3·44	3·17	2·89

TABLE 8, RESULTS OF ELEMENTAL ANALYSIS FOR GREEN COPPER COMPLEX OF 2,2'-OXYDIBENZOATE

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L $\cdot\frac{1}{2}H_2O$	M·L $\cdot H_2O$	M·L $\cdot 1\frac{1}{2}H_2O$	M·L $\cdot 2H_2O$	M·L $\cdot H_2O\cdot OH$	M·O·L $\cdot H_2O$
COPPER	18·2, 18·9	19·87	18·93	18·87	19·33	18·81	18·32	17·86	17·96	17·96
CARBON	49·23, 49·73	52·59	50·08	49·93	51·15	49·78	48·49	47·26	47·53	47·53
HYDROGEN	2·98, 2·94	2·52	2·40	2·69	2·76	2·98	3·20	3·40	3·13	2·85

Cobalt and Copper Complexes of 2,2'-Oxydibenzoic Acid

The cobalt and copper complexes of 2,2'-oxydibenzoic acid were then prepared, in the hope that the diffuse reflectance spectra, together with magnetic susceptibility measurements, elemental analysis and infra-red spectra, would be of assistance in establishing the structure of these complexes.

The cobalt complex crystallised from solution in the form of purple prisms, which on drying over P_4O_{10} in vacuo, retained their original form but changed colour to blue.

The copper complex (like the zinc complex), precipitated immediately as a blue powder, which turned green on drying over P_4O_{10} in vacuo.

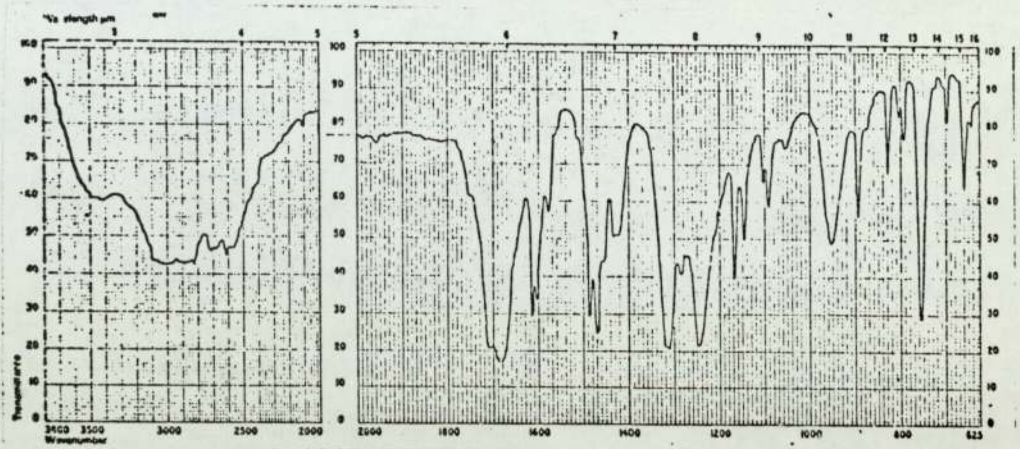
Elemental analysis of the cobalt complex, indicates a metal to ligand ratio of one to one, with the presence of one molecule of water.

Elemental analysis of the copper complex, gave a metal to ligand ratio of one to one, with the presence of one molecule of water.

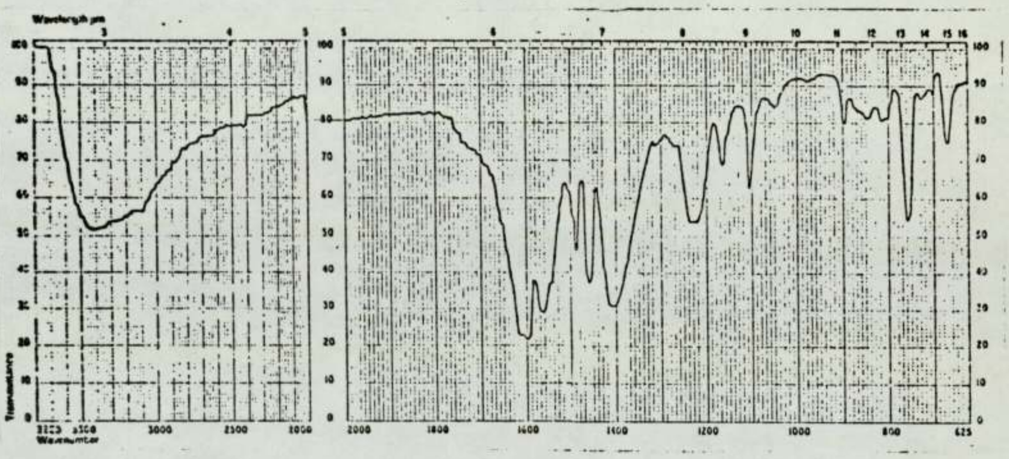
The complexes may thus be written, $M.L.H_2O$, where M = cobalt or copper and L = 2,2'-oxydibenzoate.

Elemental analysis of the purple cobalt complex and the blue copper complex, indicated about two molecules of water to be present, but the results depended on the method of desiccation.

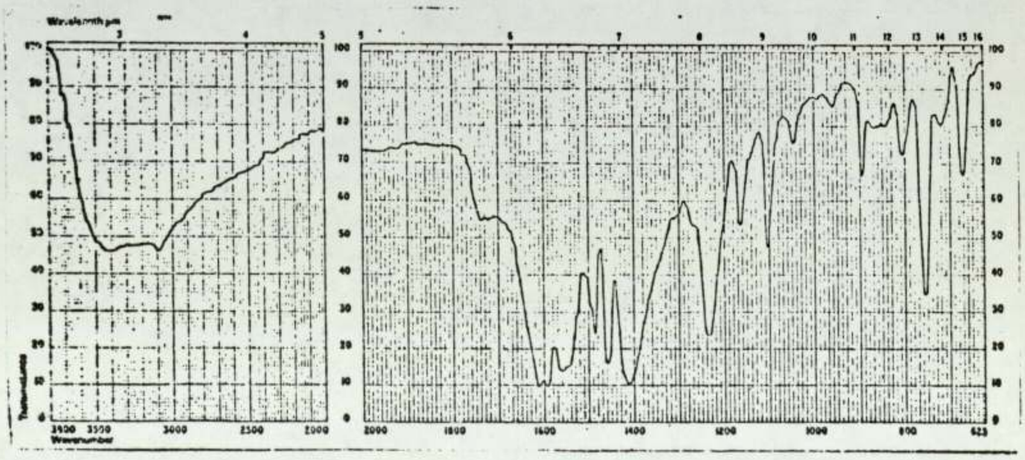
INFRA-RED SPECTRA



2,2'-OXYDIBENZOIC ACID



BLUE COBALT (II) COMPLEX OF 2,2'-OXYDIBENZOATE



GREEN COPPER (II) COMPLEX OF 2,2'-OXYDIBENZOATE

The infra-red spectra of the cobalt and copper complexes are very similar, but differ in many respects from the infra-red spectrum obtained for the zinc complex. The overall impression being that the spectrum obtained from the zinc complex, contains more absorptions and these absorptions are sharper.

The region 2,000 - 3,800 cm^{-1} is identical in the spectra of the cobalt and copper complexes, but is different to that observed in the spectrum of the zinc complex. The dominant feature is a strong, broad absorption in the cetntre of this region, with two sharper absorptions superimposed upon it, the absorption at 3,100 cm^{-1} is most probably due to the aromatic C-H stretch of the ligand, while the broader absorption at about 3,400 cm^{-1} is probably a O-H stretching frequency.

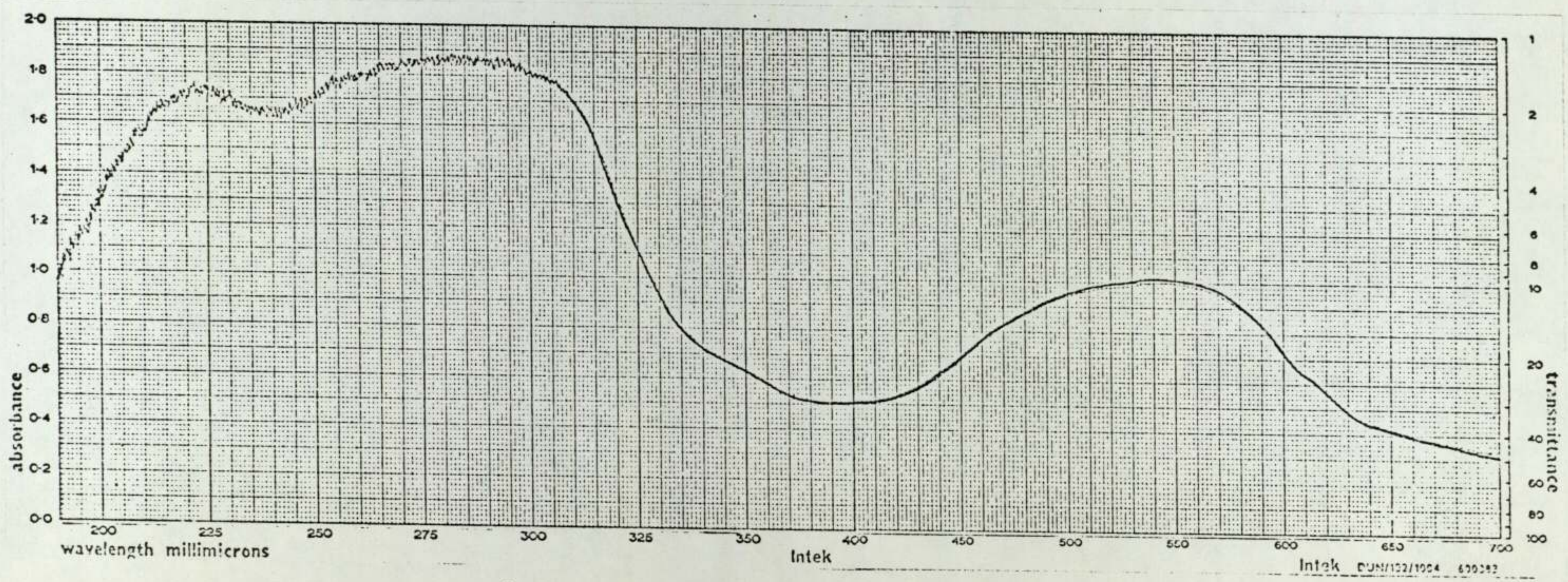
Assuming the doublet at 1590 and 1610 cm^{-1} in the spectra of the cobalt and copper complexes to be due to the ligand, as postulated earlier for the zinc complex. The asymmetrical carbonyl stretching frequency is most probably the sharp, strong absorption (with shoulder) at 1565 cm^{-1} in the spectrum of the cobalt complex and the broad, strong absorption (probably a porly resolved doublet) at 1545 and 1560 cm^{-1} in the spectrum of the copper complex.

The symmetrical carbonyl stretching frequency is most probably represented by the strong, broad absorption found in both spectra. Thus, the separation is 155 cm^{-1} (or 135 cm^{-1} for shoulder) for the cobalt complex and 135 & 150 cm^{-1} for the copper complex, indicating that the carboxylate groups are most probably involved in bidentate asymmetric co-ordination.

A broad, fairly intense absorption occurs at 1235 cm^{-1} in the specrum of the copper complex, while a less intense absorption at 1220 - 1240 cm^{-1} is found in the spectrum of the cobalt complex. This is almost the same value as a similar absorption found in the spectrum of the zinc complex at 1225 cm^{-1}, and as postulated earlier may arise from the C-O stretching of the ether linkage but is more probably C-O stretching of the carboxylate group or O-H deformation.

The absorption at 955 cm^{-1} observed in the spectrum of the free acid is again absent in both spectrum, but both exhibit a single absorption at 755 cm^{-1} which is only slightly less intense than the absorption in the free acid. The spectrum in the region 625 - 900 cm^{-1} is very similar to that obtained for the free acid.

DIFFUSE REFLECTANCE SPECTRUM OF THE BLUE COBALT (II) COMPLEX OF 2,2'-OXYDIBENZOATE



Diffuse Reflectance Spectra of the Cobalt and Copper Complexes

Cobalt Complex

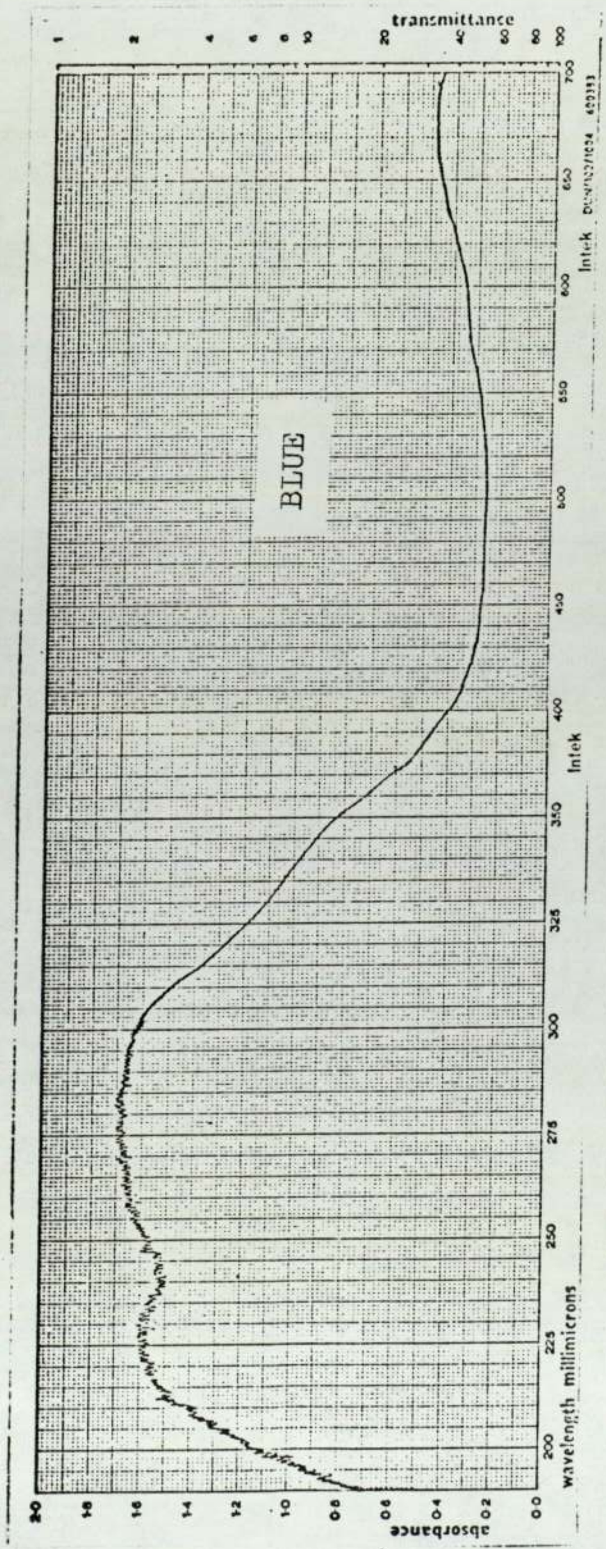
The colour change, from purple to blue, observed when the cobalt complex was dried over P_4O_{10} in vacuo, could be of importance. In many cobalt compounds, the octahedral complexes are typically pale red or purple, while the tetrahedral complexes are usually an intense blue colour.

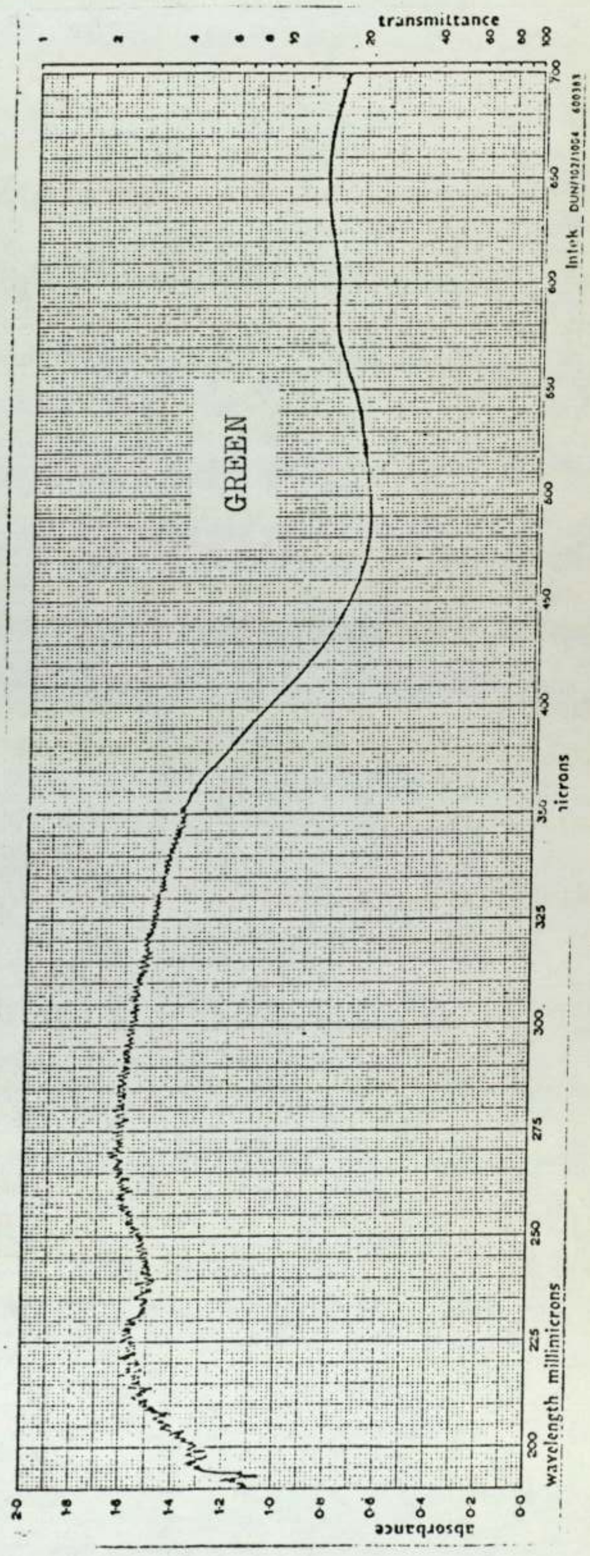
The dominant feature of the visible region of the diffuse reflectance sprctrum of the cobalt complex, is a broad absorption at about 625 nm (16,000 cm^{-1}). This is more typical of tetrahedral co-ordination (about 650 nm in the case of $[CoCl_4]^{2-}$) than octahedral co-ordination (about 525 nm in the case of $[Co(H_2O)_6]^{2+}$). This absorption is not symmetric and the possibility of another absorption at about 460 nm is indicated, and the presence of a shoulder on the long wavelength side of the 625 nm absorption, indicates the possibility of a further absorption at about 610 nm. The transitions in the visible spectra for both the octahedral and tetradehral cases, especially the tetrahedral case, generally have complex envelopes because a number of transitions to doublet exited states occur in the same region and these aquire some intensity by means of spin-orbit coupling.

The absorption at about 225 nm, the plateau from 250 to 300 nm (presumably derived from absorptions at about 260 and 300 nm) and the shoulder (due to an absorption at about 350 nm) are most logically assigned to ligand transitions.

DIFFUSE REFLECTANCE SPECTRA

COPPER (II) COMPLEXES OF 2,2'-OXYDIBENZOATE

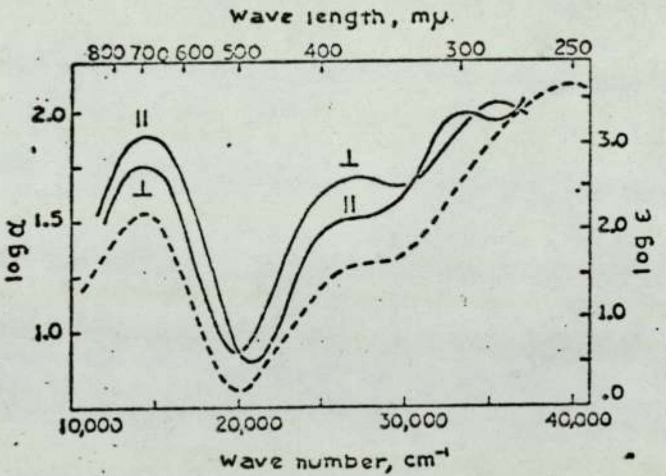




Copper Complex

In the visible region, the diffuse reflectance spectra of the copper complexes exhibit two absorptions of low intensity at about 575 - 580 (17,390 - 17,240 cm^{-1}) and 650 nm (15,385 cm^{-1}), in both the blue and green forms. The latter absorption is more intense in the spectrum of the blue form and may be at 670 nm.

The spectrum obtained for copper (II) acetate monohydrate is illustrated below, and it can be seen that it exhibits an absorption 700 nm.



Absorption spectra of copper(II) acetate monohydrate in the crystalline state (left scale, ———): || absorption with the light polarized in the complex plane, ⊥ absorption with the light polarized along copper–copper linkage. Absorption in ethanol (right scale, - - - - -).

Virtually all complexes of copper (II) are blue or green, the exception being generally caused by strong ultra-violet bands (charge transfer), tailing off into the blue end of the visible spectrum and thus causing the substances to appear red or brown. The blue or green colours arise from absorption bands in the 600 to 900 nm., region of the spectrum. The envelopes of these bands are generally unsymmetrical, seeming to encompass several overlapping transitions, but definitive resolution into the proper number of sub-bands with correct locations is difficult.

Table 9, Results for the Purple Cobalt (II) Complex of 2,2'-Oxydibenzoate

χ MAGNETIC SUSCEPTIBILITY AT CURRENT (IN AMPÉRES)												χ_m	χ'_m	μ.
5	5½	6	6½	7	7½	8	8½	9	9½	10	AVERAGE			
												× 351·2	+ 161·4	T = 292·15 °K
25·88	25·71	25·91	25·79	25·72	25·76	25·89	25·79	25·70	25·80	25·70	25·79	9056	9217	4·66
26·08	26·06	26·21	26·01	25·91	25·93	25·97	25·99	25·91	25·94	25·94	26·00	9129	9290	4·68

Table 10, Results for the Blue Cobalt (II) Complex of 2,2'-Oxydibenzoate

MAGNETIC SUSCEPTIBILITY AT CURRENT (IN AMPÈRES)												χ_m	χ'_m	μ.
5	5½	6	6½	7	7½	8	8½	9	9½	10	AVERAGE			
												× 333·2	+ 148·4	T = 292·15 °K
29·95	29·98	29·79	29·93	29·82	29·93	29·63	29·67	29·55	29·84	29·99	29·83	9938	10,099	4·88
30·49	30·33	30·69	30·53	30·36	30·42	30·50	30·49	30·29	30·45	30·37	30·45	10,145	10,306	4·93
30·20	30·10	30·18	30·16	30·15	30·16	30·20	30·08	30·04	30·13	29·92	30·12	10,036	10,197	4·90
29·15	28·87	29·03	28·85	28·86	28·97	28·90	28·80	28·79	28·92	28·73	28·90	9629	9790	4·80

Table 11, Results for the Blue (top) and Green (bottom) Copper (II) Complexes of 2,2'-Oxydibenzoate

MAGNETIC SUSCEPTIBILITY AT CURRENT (IN AMPÉRES)												χ_m	χ'_m	μ.
5	5½	6	6½	7	7½	8	8½	9	9½	10	AVERAGE			
											χ			
2·38	2·28	2·30	2·32	2·30	2·29	2·29	2·29	2·27	2·32	2·30	2·30	χ. 337·8 777	χ_m + 148·4 925	1·48
2·26	2·24	2·26	2·22	2·26	2·26	2·28	2·26	2·28	2·28	2·30	2·26	χ. 337·8 763	χ_m + 148·4 912	1·47
2·82	2·81	2·78	2·75	2·76	2·72	2·75	2·73	2·73	2·74	2·74	2·76	χ. 335·8 982	χ_m + 161·4 1143	1·64
2·96	2·87	2·85	2·83	2·91	2·90	2·88	2·86	2·87	2·87	2·88	2·88	χ. 335·8 1025	χ_m + 161·4 1186	1·67

Magnetic Susceptibility Measurements

It can be seen from Table 9, that the magnetic susceptibility measurements for the purple cobalt (II) complex with 2,2'-oxydibenzoate, at different magnetic field strengths, are relatively constant. The effective magnetic moment, calculated from these two sets of results, was 4.67 Bohr magnetons on average.

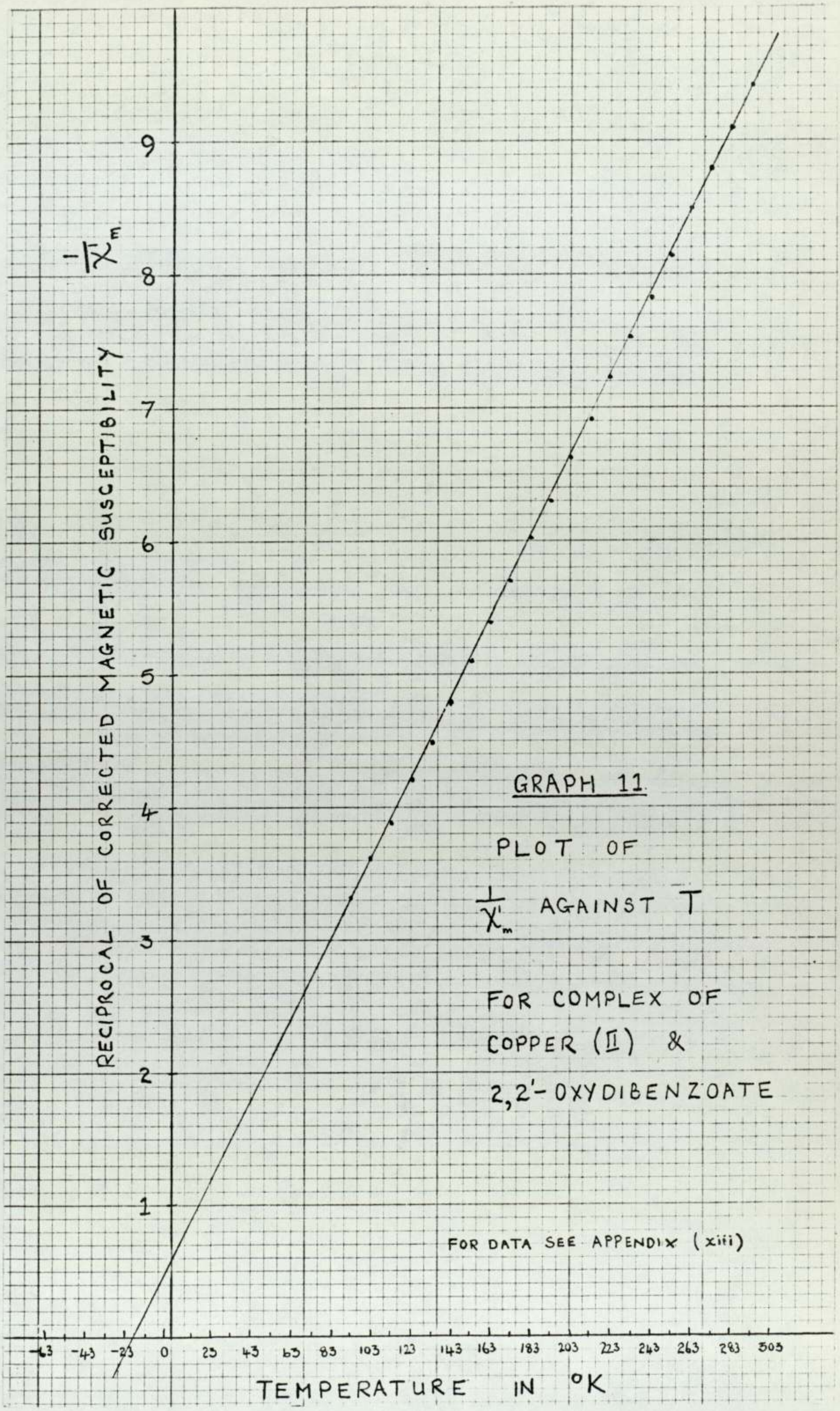
The magnetic susceptibility measurements at different magnetic field strengths for the blue cobalt (II) complex with 2,2'-oxydibenzoate, were also constant. The effective magnetic moments calculated from these results being 4.88, 4.93, 4.90, 4.80 Bohr magnetons, giving an average value of 4.88 Bohr magnetons.

For cobalt (II) complexes, containing three unpaired electrons in the spin-free situation, the experimental magnetic moment are usually in the range 4.30 - 5.0 Bohr magnetons (3.88 Bohr magnetons in theory). While for the one unpaired electron of the spin-paired situation, the experimental magnetic moments are around 1.8 Bohr magnetons (1.73 Bohr magnetons in theory).

The effective magnetic moments for both the purple and blue complexes, are in the range usually associated with three unpaired electrons, with no spin pairing. The effective magnetic magnetic moment for the purple complex is slightly lower than for the blue complex, indicating a different environment for the cobalt atoms.

From Table 11, it can be seen that the magnetic susceptibility measurements of the blue and green copper (II) complexes of 2,2'-oxydibenzoate, are independent of the magnetic field used.

The effective magnetic moments calculated from this data, give average values of 1.47_5 Bohr magnetons for the blue

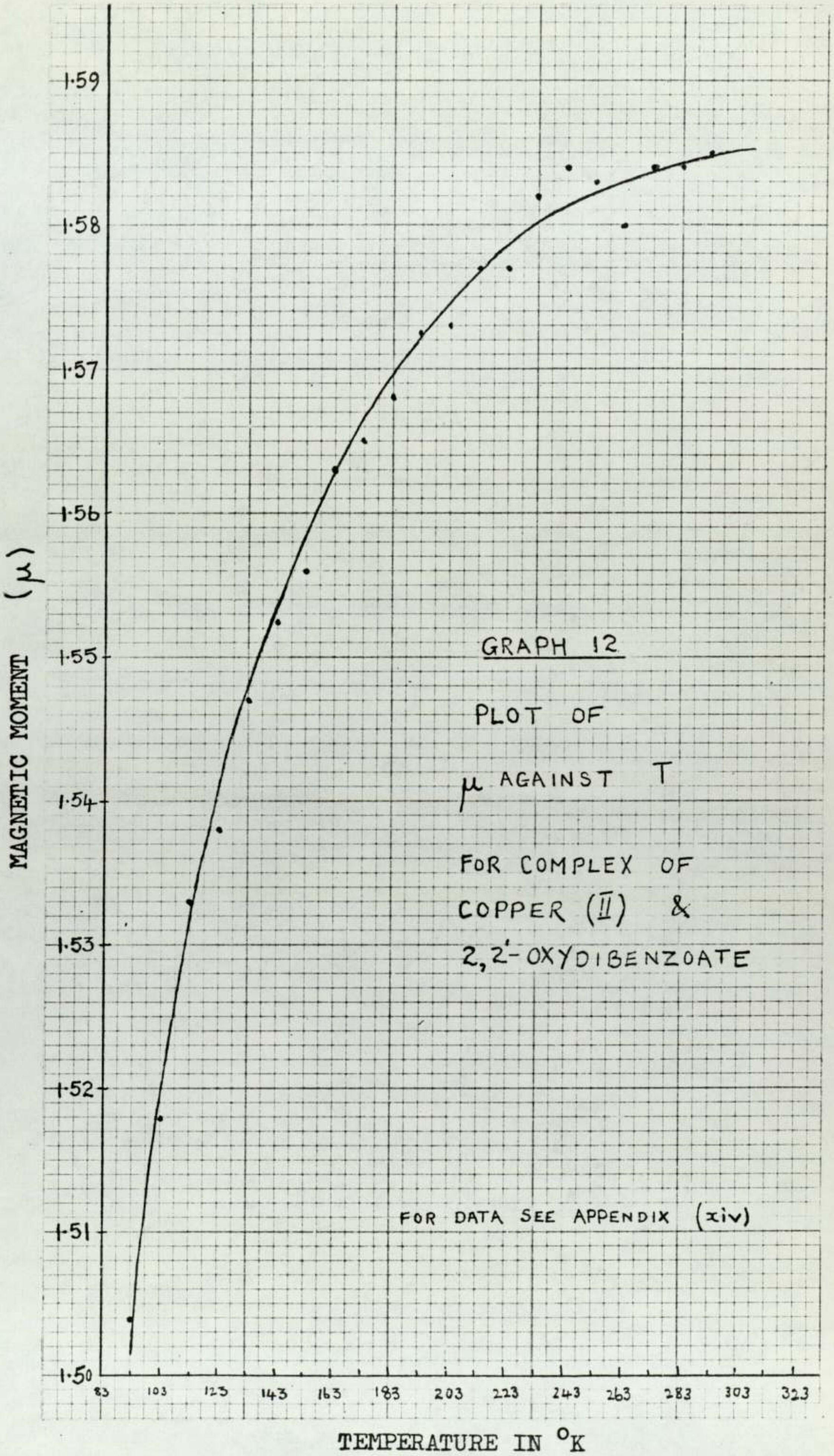


GRAPH 11

PLOT OF $\frac{1}{\chi'_m}$ AGAINST T

FOR COMPLEX OF COPPER (II) & 2,2'-OXYDIBENZOATE

FOR DATA SEE APPENDIX (xiii)


GRAPH 12
PLOT OF
μ AGAINST T
FOR COMPLEX OF
COPPER (II) &
2,2'-OXYDIBENZOATE
FOR DATA SEE APPENDIX (xiv)
MAGNETIC MOMENT (μ)
1·50
1·51
1·52
1·53
1·54
1·55
1·56
1·57
1·58
1·59
83
103
123
143
163
183
203
223
243
263
283
303
323
TEMPERATURE IN °K

complex, and 1.65_5 Bohr magnetons for the green complex.

The expected magnetic moment, for a single electron, would be in the range 1.70 - 2.0 Bohr magnetons, and so both results are lower than would be expected, with the green complex only differing by a slight extent.

The magnetic susceptibility of the green complex, was measured at 10°C., intervals down to -180°C. A plot of the reciprocal of the diamagnetic corrected, molar susceptibility against temperature was constructed (see graph 11). This gave a straight line which intersected the temperature axis at about -20°K., at zero susceptibility. This behaviour obeys the Curie-Weiss law, i.e. $\chi'_m = \frac{C}{T + \theta}$

giving a θ value of 20°K. The θ value being a measure of the deviation from ideal behaviour, on which the Curie law is based. From the small value θ, it is evident that this deviation is not very large. The magnetic moments calculated from the measured susceptibilities are not constant, but (as can seen from graph 12) fall from about 1.58 Bohr magnetons at room temperature to about 1.50 Bohr magnetons at 90°K. This indicates that some spin-spin coupling is occuring and it is of the antiferromagnetic type, since the magnetic susceptibilities are field independent and the falling magnetic moments indicate that the spins are aligning antiparallel and so tending to cancel one another out.

The magnetic susceptibility measurements and diffuse reflectance spectra, far from elucidating the situation, have complicated it still further. The iron (II) and iron (III) complexes were prepared, in the hope that Mössbauer data could give more information and so determine the structure of these compounds.

Table 12, Results of the Elemental Analysis for the Iron (III) Complex of 2,2'-Oxydibenzoate

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L $\cdot\frac{1}{2}H_2O$	M·L $\cdot H_2O$	M·L $\cdot 1\frac{1}{2}H_2O$	M·L $\cdot 2H_2O$	M·L $\cdot H_2O\cdot OH$	M·O·L $\cdot H_2O$
IRON	16·4, 16·9	17·90	17·02	16·97	17·39	16·92	16·47	16·04	16·09	16·14
CARBON	50·68, 50·54	53·89	51·26	51·10	52·37	50·94	49·59	48·31	48·45	48·59
HYDROGEN	2·73, 2·61	2·58	2·46	2·76	2·83	3·05	3·27	3·48	3·19	2·91

Table 13, Results of the Elemental Analysis for the Brown (with Golden sheen) Iron Complex obtained on drying the Green Iron (II) Complex of 2,2'-Oxydibenzoate

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L $\cdot\frac{1}{2}H_2O$	M·L $\cdot H_2O$	M·L $\cdot 1\frac{1}{2}H_2O$	M·L $\cdot 2H_2O$	M·L $\cdot H_2O\cdot OH$	M·O·L $\cdot H_2O$
IRON	15·9 , 15·7	17·90	17·02	16·97	17·39	16·92	16·47	16·04	16·09	16·14
CARBON	48·45, 48·77	53·89	51·26	51·10	52·37	50·94	49·59	48·31	48·45	48·59
HYDROGEN	2·78 , 2·80	2·58	2·46	2·76	2·83	3·05	3·27	3·48	3·19	2·91

Iron Complexes of 2,2'-Oxydibenzoic Acid

The iron (III) complex (like the zinc and copper), precipitated immediately, and gave a mustard coloured powder on drying over P_4O_{10} in vacuo.

The iron (II) complex slowly deposited as green crystals, which changed to a dark brown colour with a golden sheen on one facet, on drying over P_4O_{10} in vacuo. The metallic sheen seemed to indicate the presence of metal-metal interaction, either direct or more probably by means of a bridging atom or molecule.

Elemental analysis of the iron (III) complex (see Table 12), confirmed a metal to ligand ratio of one to one, with the probability of an hydroxyl or oxa linkage present. The presence of an hydroxyl molecule or an oxa linkage, being necessary to maintain electrical neutrality.

Elemental analysis of the brown crystals with the golden sheen obtained from the green iron (II) complex, confirmed a metal to ligand ratio of one to one and the presence of either a water molecule, an hydroxyl molecule or an oxa linkage, as can be seen from Table 13.

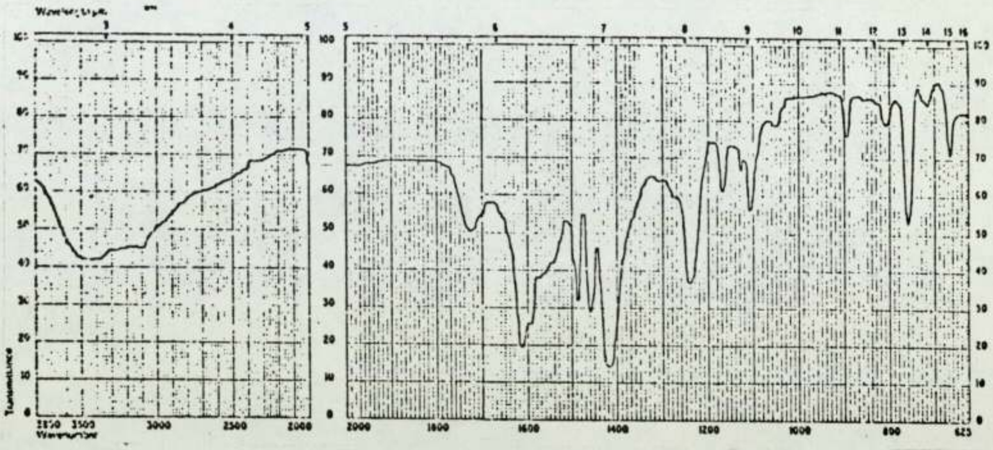
Infra-red Spectra

The infra-red spectrum of the iron (III) complex is less complex than either of the iron (II) spectra.

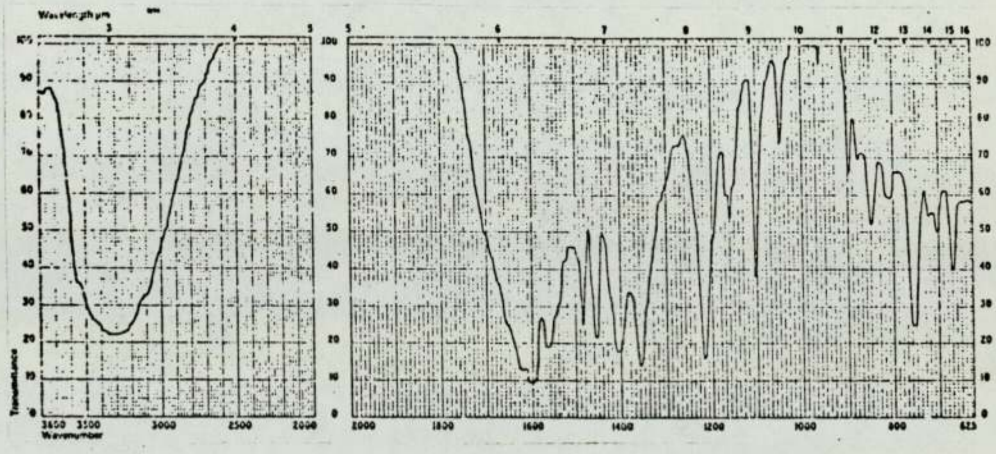
Iron (III) Complex

The broad, medium intensity absorption from 3100 to 3500 cm^{-1}, probably arises from the superimposition of two or more absorptions, the region around 3100 cm^{-1} most probably arising from the C-H stretching of the ligand and the region around 3500 cm^{-1} suggests the presence of an hydroxyl group,

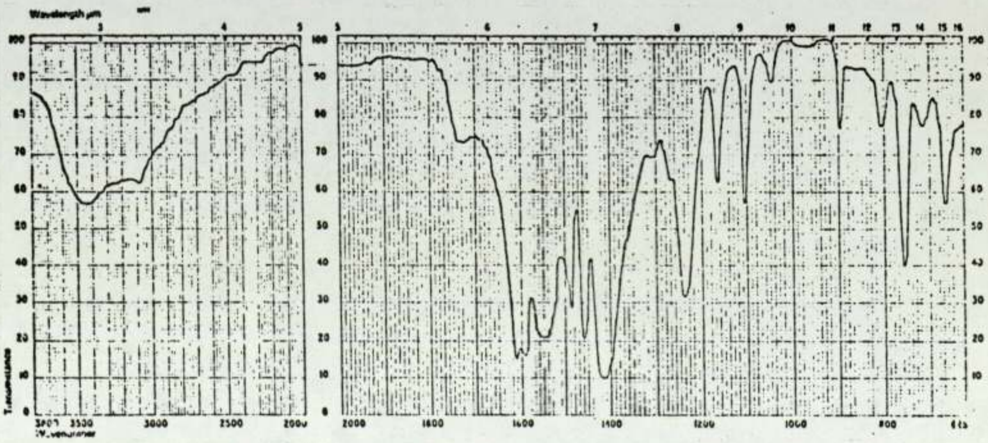
INFRA-RED SPECTRA



IRON (III) COMPLEX OF 2,2'-OXYDIBENZOATE



GREEN IRON (II) COMPLEX OF 2,2'-OXYDIBENZOATE



BROWN (WITH GOLDEN SHEEN) IRON COMPLEX
OF 2,2'-OXYDIBENZOATE

but weak interactions, typical of hydrogen bonding, must be postulated to account for the displacement from the usual position at 3500 - 3650 cm^{-1}.

The broad, weak absorption at 1720 - 1680 cm^{-1}, is most probably due to O-H deformations, but it is also possible that it could arise from the C=0 vibrations of an unco-ordinated carboxylate group. This feature is not present in the zinc, cobalt or copper, complex spectra, but does correspond to a similar absorption in the spectrum of the free ligand.

The strong, sharp absorption at 1615 cm^{-1} (with shoulder at 1595 cm^{-1}),is most probably due to the asymmetric C=0 stretching frequency of the co-ordinated carboxylate group(s). The strong, sharp absorption at 1420 cm^{-1}, is the most likely candidate to have arisen from the symmetric C=0 stretching frequency of the co-ordinated carboxylate group(s). The separation of 195 cm^{-1}, is greater than for the previous complexes. The position of the asymmetric C=0 stretching frequency at 1615 cm^{-1}, could indicate bridging by the carboxylate group, but the large separation of symmetric and asymmetric C=0 stretching frequencies would best fit the assignment of asymmetric bidentate co-ordination.

The absorptions at 1245 and 960 cm^{-1}, also appear in the spectra obtained from the other complexes, and can presumably be given the same interpretation. The slight displacement of the absorption at 1245 cm^{-1} and its intensity compared with the values obtained for the zinc (1220 cm^{-1}), the cobalt (1220, broad) and the copper (1235 cm^{-1}) complexes is worthy of note.

Iron (II) Complexes

The infra-red spectra of the green and the brown (with golden sheen) complexes, from the iron (II) preparations, are very different.

The infra-red spectrum of the green complex has a strong, broad absorption centred around 3300 cm^{-1}, while the brown complex has only a weak, broad absorption around 3450 cm^{-1}. These absorptions most probably arise from O-H stretching vibrations. The weak, sharp absorption at 3100 cm^{-1}, in the spectrum of the brown complex, probably arises from the aromatic C-H stretching vibrations of the ligand.

The spectrum of the green complex exhibits a sharp, strong absorption at 1600 cm^{-1}, with a bulky complex series of shoulders extending from about 1750 cm^{-1}, culminating in an almost resolved maximum at 1620 cm^{-1}. It is either this feature or the strong, sharp absorption at 1565 cm^{-1}, which can be assigned as the asymmetric C=O stretching frequency.

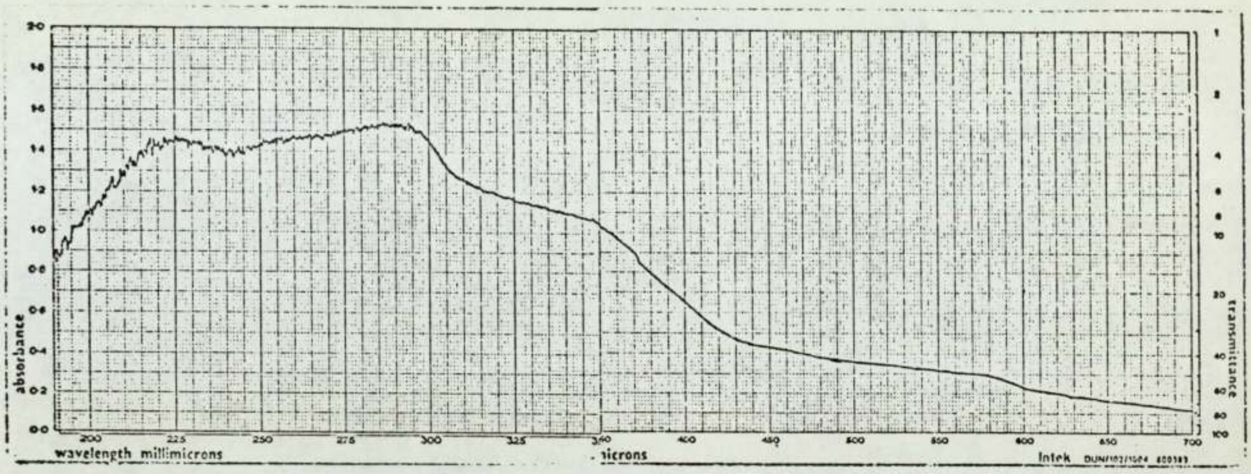
The asymmetric C=O stretching frequency of the brown complex is most probably the strong, broad absorption at 1540 -1560 cm^{-1}, although this could also be assigned to the doublet at 1590 and 1610 cm^{-1}, although this doublet is more probably derived from ligand vibrations.

The symmetric C=O stretching frequency of the brown complex is easily assigned to the strong, sharp absorption at 1415 cm^{-1} (with the shoulder at 1400 cm^{-1}). This assignment is more difficult in the case of the green complex, since the spectrum has two strong, sharp doublets at 1360 and 1405 cm^{-1}, although two different environments for the carboxylate anions, could resolve this problem.

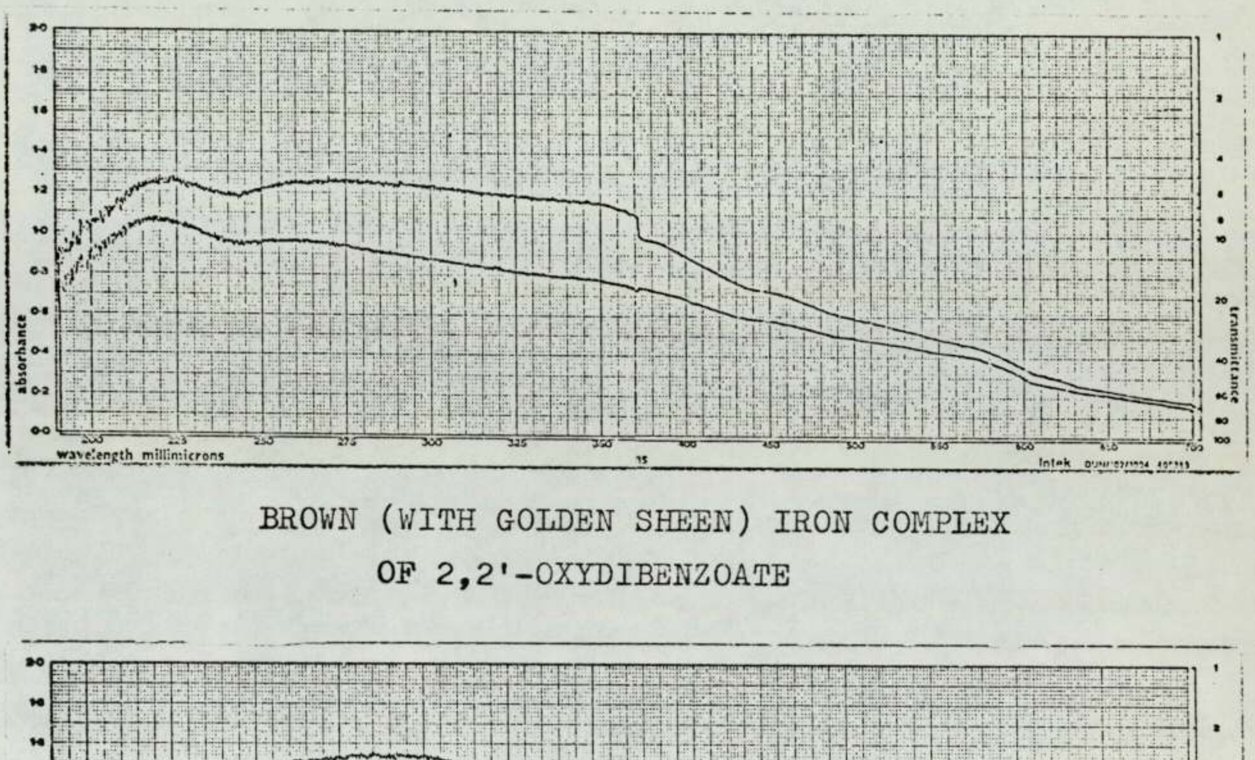
The separation between the asymmetric and symmetric C=O stretching frequencies, seems to be about 125 - 145 cm^{-1} for the brown complex, but could be anywhere in the range 165 - 240 cm^{-1} for the green complex.

The weak, broad absorption observed in the spectrum of the brown complex at 1730 cm^{-1}, could be present in the spectrum of the green complex, but be hidden by the shoulder of the absorption at 1600 cm^{-1}. This feature is most probably

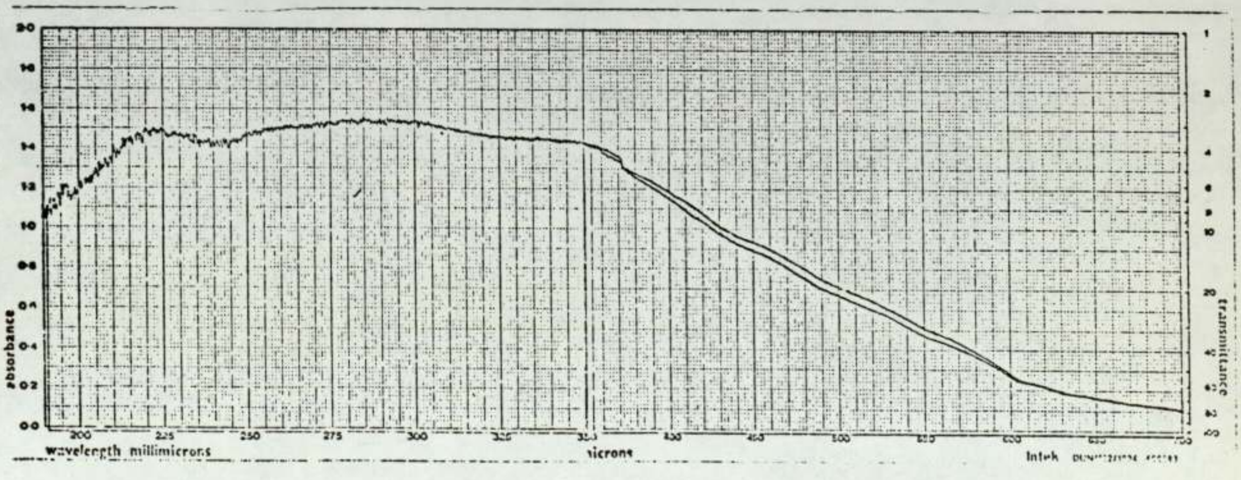
DIFFUSE REFLECTANCE SPECTRA



GREEN IRON (II) COMPLEX OF 2,2'-OXYDIBENZOATE



BROWN (WITH GOLDEN SHEEN) IRON COMPLEX
OF 2,2'-OXYDIBENZOATE



IRON (III) COMPLEX OF 2,2'-OXYDIBENZOATE the result of a O-H deformation frequency of an hydroxyl or a water molecule.

The green complex has a strong, sharp absorption at 1220 cm^{-1} and the same feature is present in the spectrum of the brown complex at about 1240 cm^{-1}, which is slightly less intense than in the spectrum of the green complex, and also possibly a poorly resolved doublet. This absorption could have arisen from the C-O stretching frequency of the ether linkage but C-O or C-H deformation modes are also feasible.

Both complexes exhibit a strong, sharp absorption at about 855 cm^{-1}.

Diffuse Reflectance Spectra

The spectra obtained for the green iron (II) complex and the iron (III) complex are different and characteristic, but give no structural information.

The brown complex with the golden metallic sheen, obtained by drying the green iron (II) complex over P_4O_{10} in vacuo, gives a diffuse reflectance spectrum, similar to that obtained for the iron (III) complex, indicating that the oxidation state is probably +3.

TABLE 14, MÖSSBAUER RESULTS

COMPLEX	OBSERVED MAXIMA		CENTRE OF MAXIMA		CONVERSION FACTORS for 1 channel in mm/sec	CHEMICAL ISOMER SHIFT (δ)	QUADRUPOLE SPLITTING (Δ)
	POSITION	WIDTH	COMPLEX	STANDARD			
	channel number	in channels	channel number	channel number			
GREEN IRON (II)	183 308	14 12	245·5	188·5	0·214	57 channels 1·22 mm/sec	125 channels 2·675 mm/sec.
BROWN WITH GOLDEN SHEEN FROM GREEN IRON (II)	185 253		219	181.5	0·010967	37.5 channels 0·41 mm/sec	68 channels 0·745 mm/sec.
IRON (III)	190 242	40 40	216	182	0·01184	34 channels 0·40 mm/sec.	52 channels 0·616 mm/sec.

^{57}Fe Mössbauer Spectra

The results of the Mössbauer experiments are summerised in Table 14(page 145).

The green iron (II) complex gave a chemical isomer shift of 1.22 mm/second and a quadrupole splitting of 2.675 mm/second. While the iron (III) complex gave a chemical isomer shift of 0.40 mm/second and a quadrupole splitting of 0.616 mm/second. The chemical shifts are related to a stainless steel standard and the results are typical for iron (II) and iron (III).

The brown complex with a golden sheen, obtained by drying the green iron (II) complex over P_4O_{10} in vacuo, gave a chemical shift of 0.41 mm/second and a quadrupole splitting of 0.745 mm/second. Thus, indicating that this complex contains iron in the +3 oxidation state.

Table 15, Results for the Brown (with Golden Sheen) Iron Complex of 2,2'-Oxydibenzoate

MAGNETIC SUSCEPTIBILITY AT CURRENT (IN AMPÉRES)												χ_m	χ'_m	μ.
5	5½	6	6½	7	7½	8	8½	9	9½	10	AVERAGE			
											χ	$\chi . 346{\cdot}5$	$\chi_m + 156$	T= 292·15°K
12·44	12·51	12·62	12·48	$12{\cdot}43_5$	12·44	12·53	12·53	12·44	$12{\cdot}47_5$	12·40	12·50	4331	4487	3·25
13·15	12·94	13·11	12·74	13·05	12·99	13·05	13·19	13·08	13·13	$13{\cdot}09_5$	13·05	4522	4678	3·32
12·66	12·63	12·76	12·62	12·56	12·55	12·61	12·60	$12{\cdot}68_5$	12·88	12·67	12·66	4387	4543	3·27
12·28	12·27	12·34	12·32	12·29	$12{\cdot}31_5$	12·27	12·34	12·25	12·33	12·30	12·30	4262	4418	3·23

Table 16, Results for the Iron (III) Complex of 2,2'-Oxydibenzoate

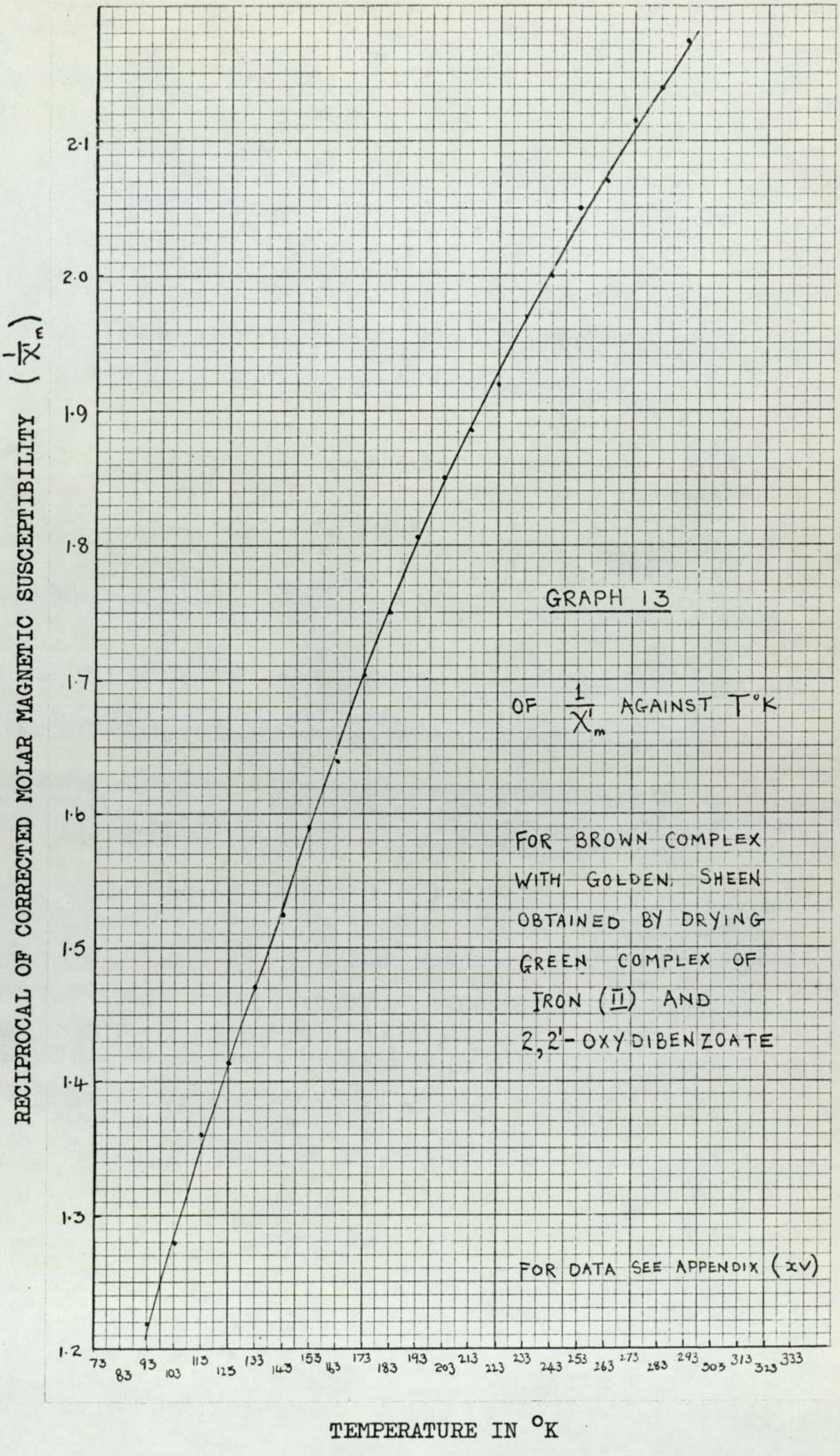
MAGNETIC SUSCEPTIBILITY AT CURRENT (IN AMPÈRES)												χ_m	χ'_m	μ.
5	5½	6	6½	7	7½	8	8½	9	9½	10	AVERAGE			
											χ	χ.328·5	χ'_m + 130	T= 292·15°K
10·20	10·20	10·36	10·36	$10{\cdot}37_5$	10·37	10·39	10·41	10·38	10·37	10·37	10·34	3397.	3527	2·88
$10{\cdot}43_5$	10·42	10·53	10·36	10·44	10·38	10·41	10·39	10·35	10·39	10·39	10·41	3420	3550	2·89
11·72	11·79	11·79	11·70	11·74	11·75	11·72	11·73	11·66	$11{\cdot}77_5$	11·74	11·74	3857	3987	3·06
12·36	12·07	12·10	12·03	$11{\cdot}99_5$	11·99	12·02	11·98	11·96	11·97	12·02	12·05	3958	4088	3·10

Magnetic Susceptibility Measurements

Measurement of the magnetic susceptibility of the brown iron (II) complex at different field strengths, showed no significant variation, indicating that ferromagnetic interactions are most probably absent.

The magnetic susceptibility measurements for the brown complex with the golden sheen, averaged out to give 4487, 4678, 4543 and 4418 x 10^{-6} c.g.s. (χ'_m) per gram-atom of iron, with the appropriate diamagnetic correction having been made, as can be seen from Table 15. The effective magnetic moments, calculated from $\mu_{eff} = 2.84\sqrt{\chi'_m.T}$ were 3.25, 3.32, 3.27 and 3.23 Bohr magnetons. These values are too large, for the brown complex to be spin-paired, with one unpaired electron, since complexes of this type usually have experimental moments of 2.0 to 2.5 Bohr magnetons (1.73 Bohr magnetons in theory). The spin-free complexes, having 5 unpaired electrons, usually have magnetic moments in the range 5.7 to 6.0 Bohr magnetons (5.92 Bohr magnetons in theory). Thus, the brown complex with the golden sheen, has an abnormally low magnetic moment, indicating that spin-pairing is occuring, of the antiferromagnetic type, because it is not field dependent.

The iron (III) complex also gave reasonably constant values for the magnetic susceptibility, at the various magnetic fields used, as can be seen from Table 16. These results averaged out to give, for the diamagnetic corrected, susceptibilities of 3527, 3550, 3987 and 4088 c.g.s., per gram-atom of iron. These values yielded effective magnetic moments, calculated from the above formula, of 2.88, 2.89, 3.06 and 3.10 Bohr magnetons. Indicating that the iron (III) complex, has spin-spin interactions, of the antiferromagnetic type, because of the field independence of the results.

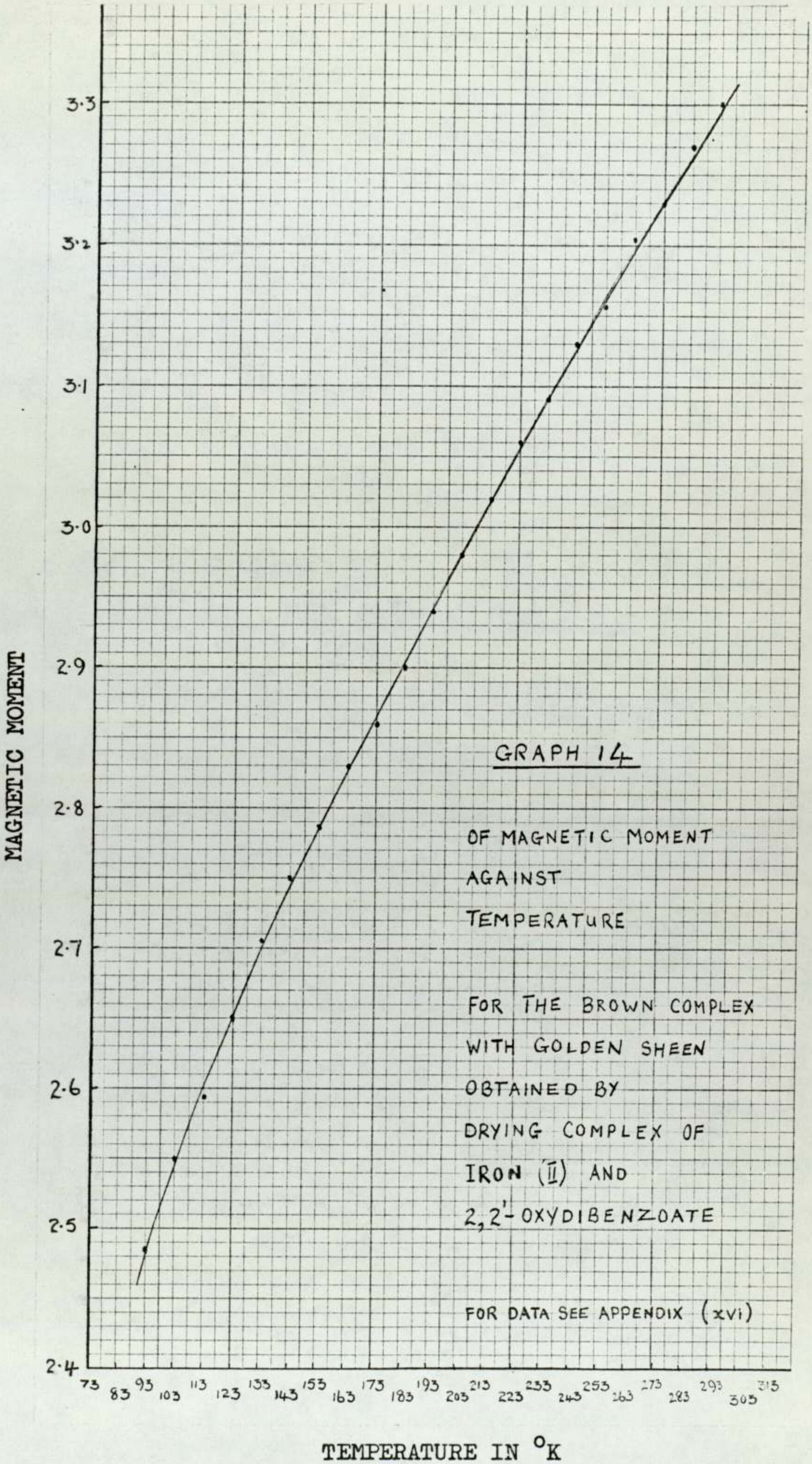


GRAPH 13

OF $\frac{1}{\chi'_m}$ AGAINST T°K

FOR BROWN COMPLEX
WITH GOLDEN SHEEN
OBTAINED BY DRYING
GREEN COMPLEX OF
IRON (II) AND
2,2'-OXYDIBENZOATE

FOR DATA SEE APPENDIX (XV)



GRAPH 14

OF MAGNETIC MOMENT AGAINST TEMPERATURE

FOR THE BROWN COMPLEX WITH GOLDEN SHEEN OBTAINED BY DRYING COMPLEX OF IRON (II) AND 2,2'-OXYDIBENZOATE

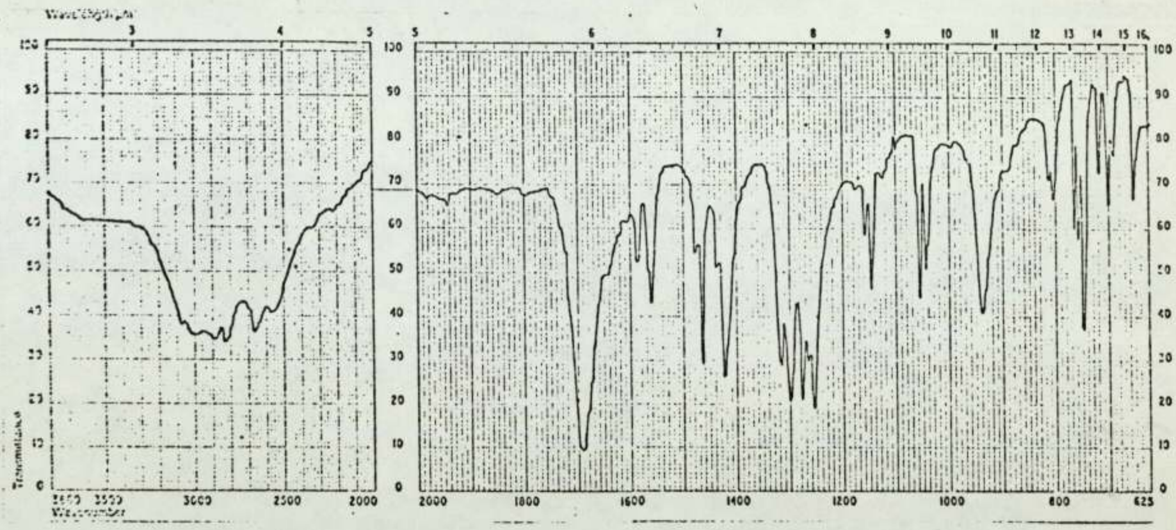
FOR DATA SEE APPENDIX (xvi)

Measurement of the magnetic susceptibility, of the brown complex with the golden sheen, at different temperatures, enabled a plot of $1/\chi'_m$ against temperature (in ^{o}K), to be constructed. This plot was non-linear (as can be seen from graph 13), particularly at higher temperatures, hence deviating from the Curie-Weiss law. The effective magnetic moments decreased in value as the temperature was lowered, falling from about 3.3 Bohr magnetons at room temperature to about 2.5 Bohr magnetons at 93^{o}K, as can be seen from graph 14. These results indicate antiferromagnetic type behaviour, with spin-spin interactions being antiparallel and thus cancelling one another out partially. The empirical formula obtained from the elemental analysis, indicates that this may be achieved by way of a "super exchange" mechanism, through a bridging oxygen atom, hydroxyl or water molecule, although exchange through a carboxylate bridge or even direct metal-metal interactions cannot be eliminated.

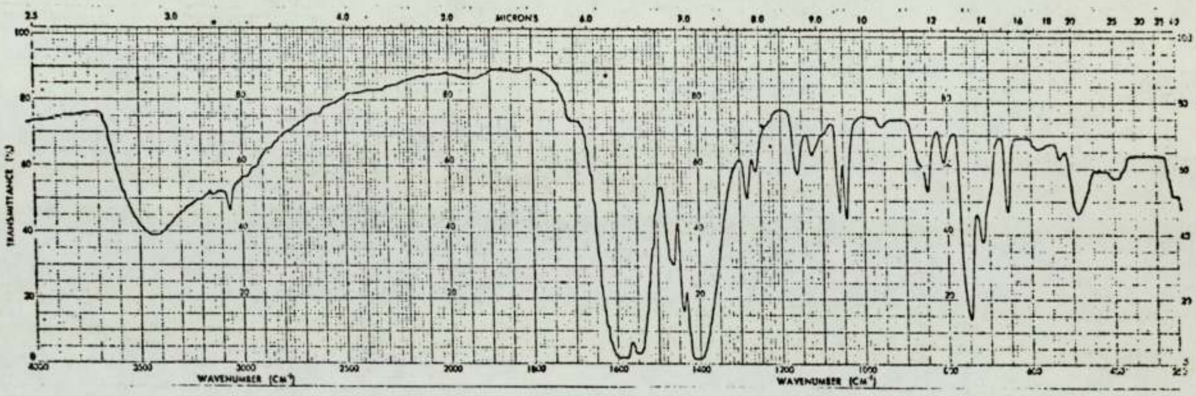
Table 17, Results of the Elemental Analysis of the Zinc Complex of 2,2'-Thiodibenzoate

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L·OH	M·L·$\frac{1}{2}H_2O$	M·L·H_2O	M·L·$1\frac{1}{2}H_2O$	M·L·$2H_2O$	M·O·L ·H_2O	M·L ·H_2O·OH
ZINC	18.0 , 18.6	19.36	18.49	18.43	18.86	18.38	17.93	17.50	17.59	17.54
CARBON	46.38	49.80	47.55	47.41	48.51	47.28	46.11	45.00	45.24	45.12
HYDROGEN	2.78	2.39	2.28	2.56	2.62	2.83	3.04	3.24	2.71	2.98
SULPHUR	7.51	9.50	9.07	9.04	9.25	9.01	8.79	8.58	8.63	8.60

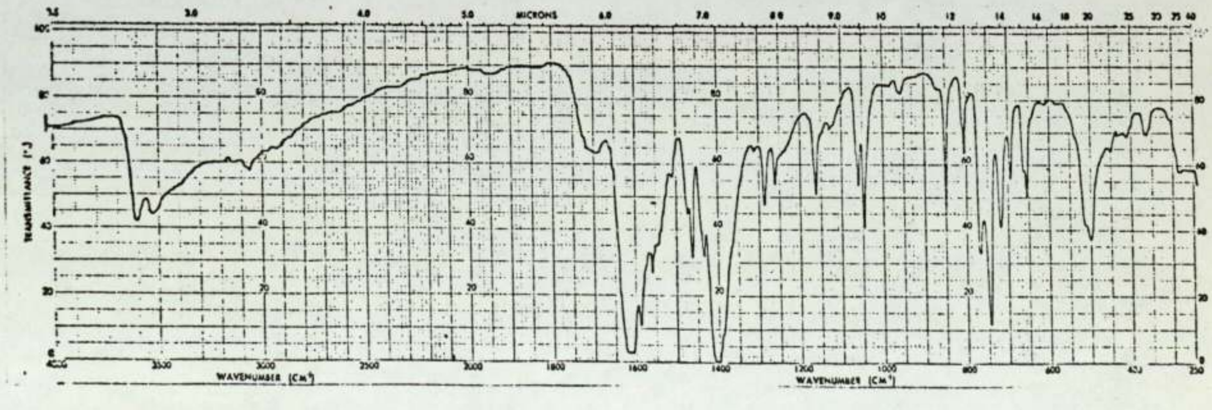
INFRA-RED SPECTRA



2,2'-THIODIBENZOIC ACID



ZINC COMPLEX OF 2,2'-THIODIBENZOATE



COPPER (II) COMPLEX OF 2,2'-THIODIBENZOATE

Complexes of 2,2'-Thiodibenzoic Acid

Zinc Complex of 2,2'-Thiodibenzoic Acid

The results of the elemental analysis for the zinc complex of 2,2'-thiodibenzoic acid (as can be seen from Table 17), confirmed a metal to ligand ratio of one to one, with the less positive presence of one water molecule, although other possible compositions cannot be ruled out.

Infra-red Spectrum

The broad, medium intensity absorption centred around 3400 - 3450 cm^{-1}, most probably arises from an O-H stretching vibration. The sharp absorption imposed upon this band at 3060 cm^{-1}, probably arises from an aromatic C-H stretching vibration of the ligand.

The asymmetric C=O stretching vibration, can either be assigned to the strong, broad absorption at 1575 - 1600 cm^{-1}, or the narrower strong, absorption at 1500 cm^{-1}. An alternative explaination could be that the two carboxylate groups are non-equivalent.

Assuming the strong, broad absorption at about 1400 cm^{-1}, to have arisen from the symmetric C=O stretching vibration. This would give a separation of either 175 - 200 cm^{-1} or 100 cm^{-1}, confirming that should the absorptions arise from separate carboxylate groups the two environments are very different.

The only other feature worthy of note is the strong, sharp absorption (possibly with shoulder) at 750 cm^{-1}, which may be associated with the less intense absorption at 720 cm^{-1}.

Table 18, Results of the Elemental Analysis of the Copper (II) Complex of 2,2'-Thiodibenzoate

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L $\cdot\frac{1}{2}H_2O$	M·L $\cdot H_2O$	M·L $\cdot 1\frac{1}{2}H_2O$	M·L $\cdot 2H_2O$	M·L $\cdot H_2O\cdot OH$	M·O·L $\cdot H_2O$
COPPER	17·96 , 18·45	18·92	18·06	18·01	18·42	17·96	17·51	17·09	17·14	17·08
CARBON	47·57 , 48·78	50·07	47·80	47·66	48·76	45·52	46·34	45·22	45·34	45·47
HYDROGEN	2·92 , 3·24	2·40	2·29	2·57	2·63	2·85	3·06	3·25	2·99	2·73

Copper (II) Complex of 2,2'-Thiodibenzoic Acid

The copper (II) complex of 2,2'-thiodibenzoic acid gave an elemental analysis (as can be seen from Table 18), consistent with a metal to ligand ratio of one to one, with the less certain presence of half a water molecule.

Infra-red Spectrum

The infra-red spectrum of the copper (II) complex is very different from that obtained for the zinc complex in respect of its dominant features, although the weak, sharp features, presumably mostly attributed to the ligand, have much in common, although they tend to be broader in the spectrum of the copper (II) complex and have slight displacements of position and relative intensity.

A sharp, medium intensity absorption at 3610 cm^{-1} and a slightly broader absorption of equal intensity at about 3530 cm^{-1}, are a feature of this spectrum which differ from that obtained for the zinc complex. These absorptions are probably O-H stretching vibrations, two distinct hydroxyl environments being postulated. The possibility exists that the absorption at 3610 cm^{-1}, may be indicative of a bridging hydroxyl group.

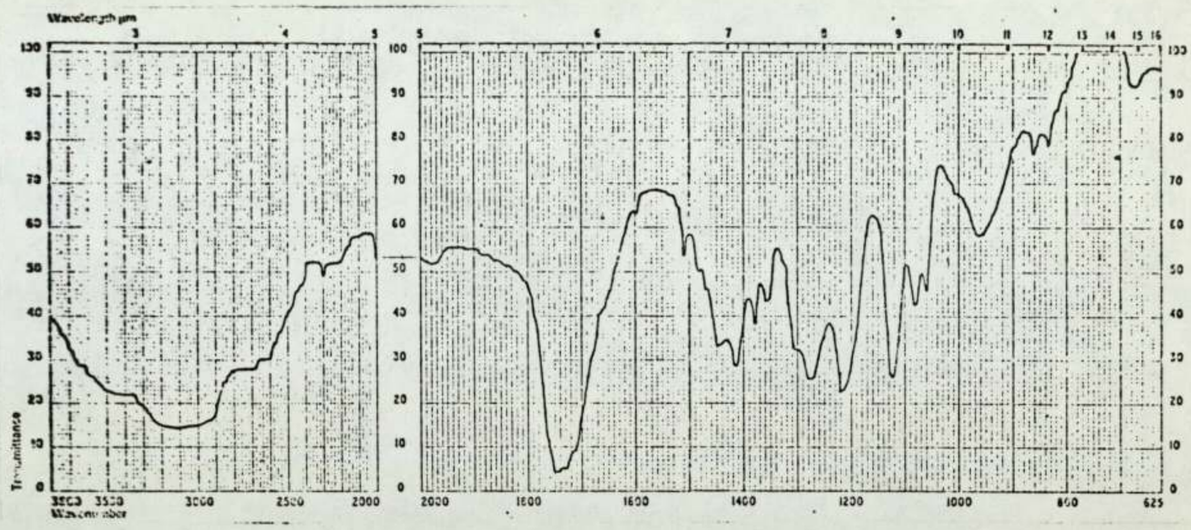
The asymmetric C=O stretching vibration is easily assigned to the strong, sharp absorption found at 1605 - 1625 cm^{-1}. The weak, broad absorption at around 1700 cm^{-1}, is worthy of note since it is most probably the result of an O-H deformation mode.

The symmetric C=O stretching vibration, must be assigned to the absorption at 1400 cm^{-1}, giving a separation of 205 - 225 cm^{-1}. This is large and suggests that the carboxylate anion is engaged in asymmetrical bidentate co-ordination, with one long and one short bond.

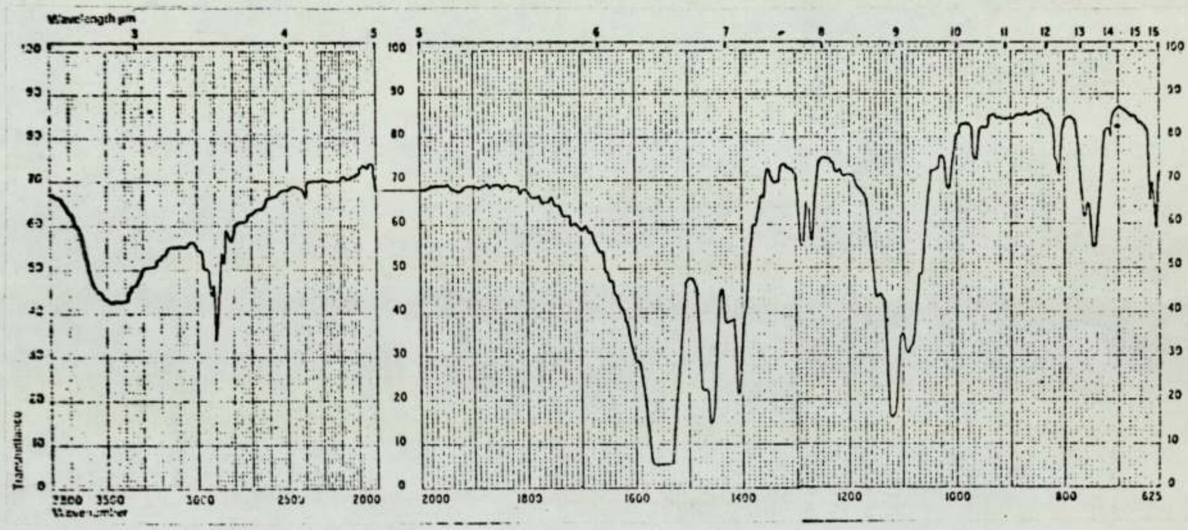
Table 19, Results of the Elemental Analysis of the Zinc and Copper (II) Complexes of 3,3'-Oxydipropionate

ELEMENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED					
		M·L	M·L ·ClO_4	M·L·$\frac{1}{2}H_2O$	M·L·H_2O	M·L·$\frac{1}{2}O_2$	M·L·OH
ZINC	20·7	29·0	20·1				
CARBON	23·31	31·96	22·12				
HYDROGEN	3·04	3·58	2·48				
COPPER	$27{\cdot}3_5$	28·41		27·31	26·63	26·51	26·40
CARBON	30·56	32·22		30·97	29·82	30·07	29·94
HYDROGEN	3·29	$3{\cdot}60_5$		3·90	4·17	3·36	3·77

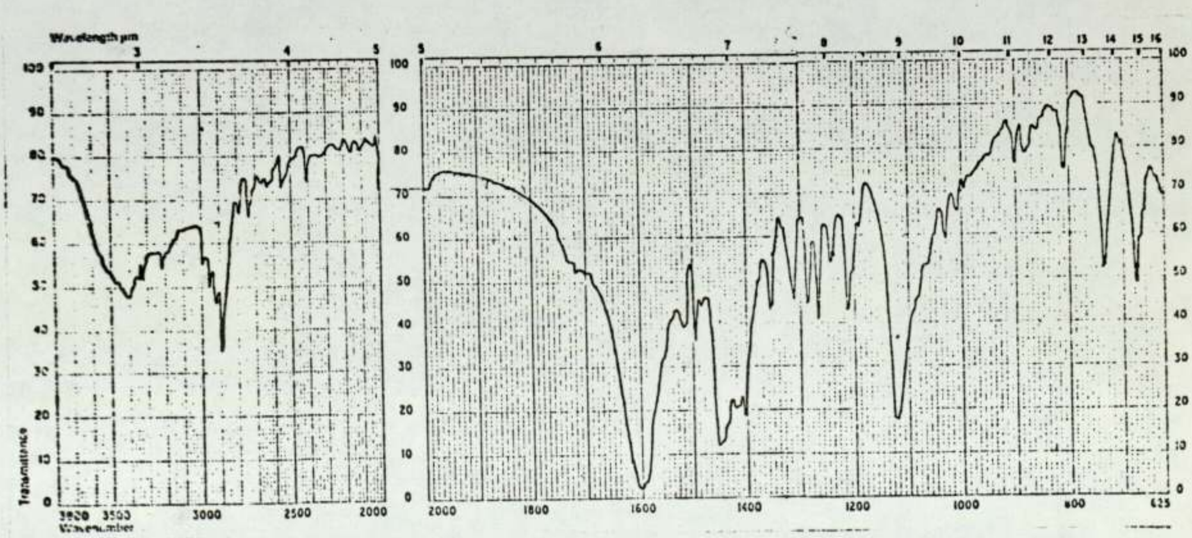
INFRA-RED SPECTRA



3,3'-OXYDIPROPIONIC ACID



ZINC COMPLEX OF 3,3'-OXYDIPROPIONATE



COPPER (II) COMPLEX OF 3,3'-OXYDIPROPIONATE

Complexes of 3,3'-Oxydipropionic Acid

Zinc Complex of 3,3'-Oxydipropionic Acid

Elemental analysis of this complex, showed a metal to ligand ratio of one to one, and as can be seen from Table 19, the data is consistent with the presence of a perchlorate molecule, giving the empirical formula $Zn.L.ClO_4$.

Infra-red Spectrum

The weak, broad absorption at 3400 - 3500 cm^{-1}, in the infra-red spectrum of the zinc complex, must be assigned to the O-H stretching vibration. The sharp, weak absorption at 2900 cm^{-1}, with attendant sharp, weak absorptions most probably arises from aliphatic C-H vibrations.

The asymmetric C=O stretching frequency can be assigned to the strong, broad absorption at 1530 - 1570 cm^{-1}, which exhibits a shoulder at 1600 cm^{-1}.

The symmetric C=O stretshing frequency is more difficult to assign, since two suitable candidates are available. The strong, sharp absorption at 1460 cm^{-1} (with a shoulder at 1470 cm^{-1}), would give a separation of 70 - 110 cm^{-1}, while the strong, sharp absorption at 1410 cm^{-1} would give a separation of 120 - 160 cm^{-1}. One possible explaination of these results, would be the existence of two separate environments for the carboxylate groups.

Copper (II) Complex of 3,3'-Oxydipropionic Acid

Elemental analysis of this complex showed a metal to ligand ratio of one to one, and as can be seen from Table 19, the probable presence of half a water molecule, i.e. $Cu.L.\frac{1}{2}H_2O$.

Infra-red Spectrum

The infra-red spectrum of the copper (II) complex of 3,3'-oxydipropionate, is different from that obtained for the zinc complex.

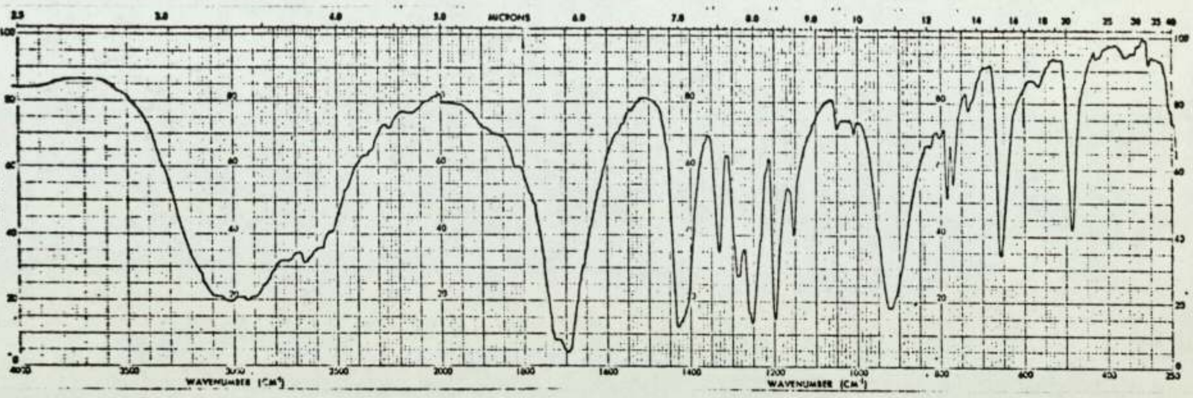
Both spectra have in common the weak, broad absorption at 3400 - 3500 cm^{-1}, which has been postulated as arising from a O-H stretching vibration and the sharp, medium intensity absorption at 2900 cm^{-1}, with attendant weak, sharp absorptions previously thought due to aliphatic C-H stretching vibrations.

The asymmetric C=O stretching frequency, can be assigned to the strong, sharp absorption at 1600 cm^{-1}. While the symmetrical C=O stretching frequency presents some problems, since there are three posible candidates. The sharp, strong absorption at 1400 cm^{-1}, would give a separation of 200 cm^{-1}. The sharp, strong absorption at 1450 cm^{-1}, would give a separation of 150 cm^{-1}. While the sharp, strong doublet at 1415 and 1420 cm^{-1}, gives values of 185 and 180 cm^{-1}.

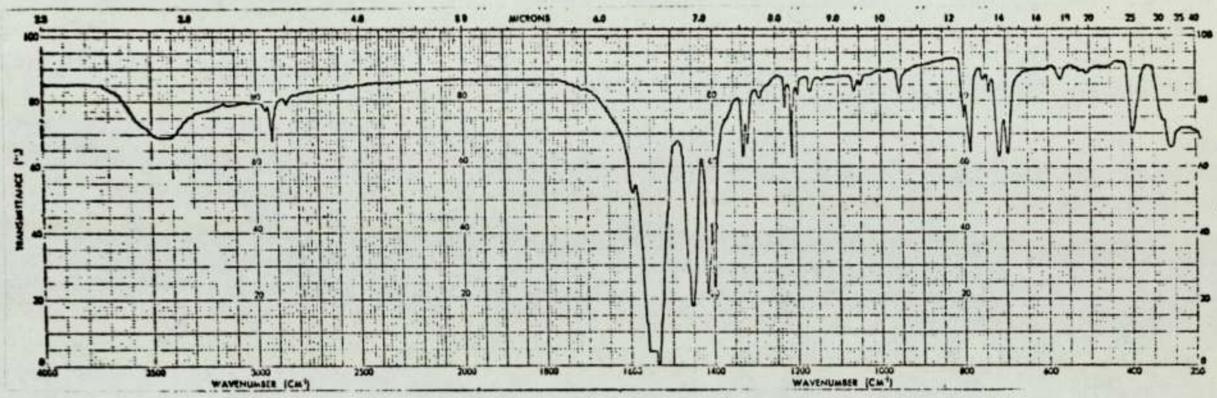
Table 20, Results of the Elemental Analysis for the Zinc Complex of 3,3'-Thiodipropionate

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L $\cdot\frac{1}{2}H_2O$	M·L $\cdot H_2O$	M·L $\cdot 1\frac{1}{2}H_2O$	M·L $\cdot 2H_2O$	M·L $\cdot H_2O\cdot OH$	M·O·L $\cdot H_2O$
ZINC	25·6 , 27·4	27·07	25·38	25·29	26·09	25·19	24·34	23·55	23·64	23·72
CARBON	28·88 , 28·67	29·83	28·76	27·87	27·98	27·76	26·83	25·96	26·06	26·15
HYDROGEN	3·55 , 3·56	3·34	3·13	3·51	3·62	3·88	4·13	4·36	4·01	3·66

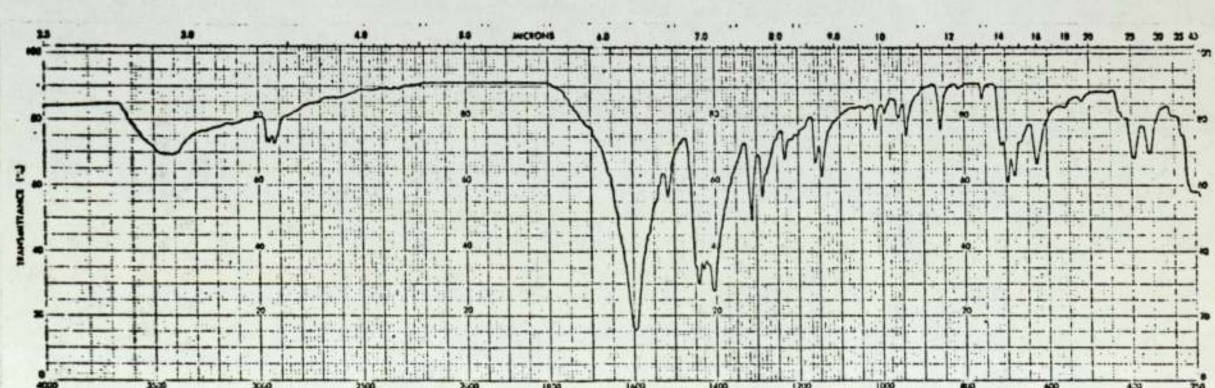
INFRA-RED SPECTRA



3,3'-THIODIPROPIONIC ACID



ZINC COMPLEX OF 3,3'-THIODIPROPIONATE



COPPER (II) COMPLEX OF 3,3'-THIODIPROPIONATE

Complex of 3,3'-Thiodipropionic Acid

Zinc Complex of 3,3'-Thiodipropionic Acid

Elemental analysis of this complex, gave a zinc to ligand ratio of one to one, and as can be seen from Table 20, there is probably half a water molecule also present.

Infra-red Spectrum

The broad, weak absorption at 3400 - 3500 cm^{-1}, is probably the result of an O-H stretching vibration. While the sharp, weak absorption at 3020 cm^{-1}, probably arises from the presence of an aliphatic C-H stretching vibration of the ligand.

The sharp, strong absorption at 1535 cm^{-1}, with shoulders at 1555 and 1565 cm^{-1}, is the most likely candidate to be due to the asymmetric C=O stretching frequenc

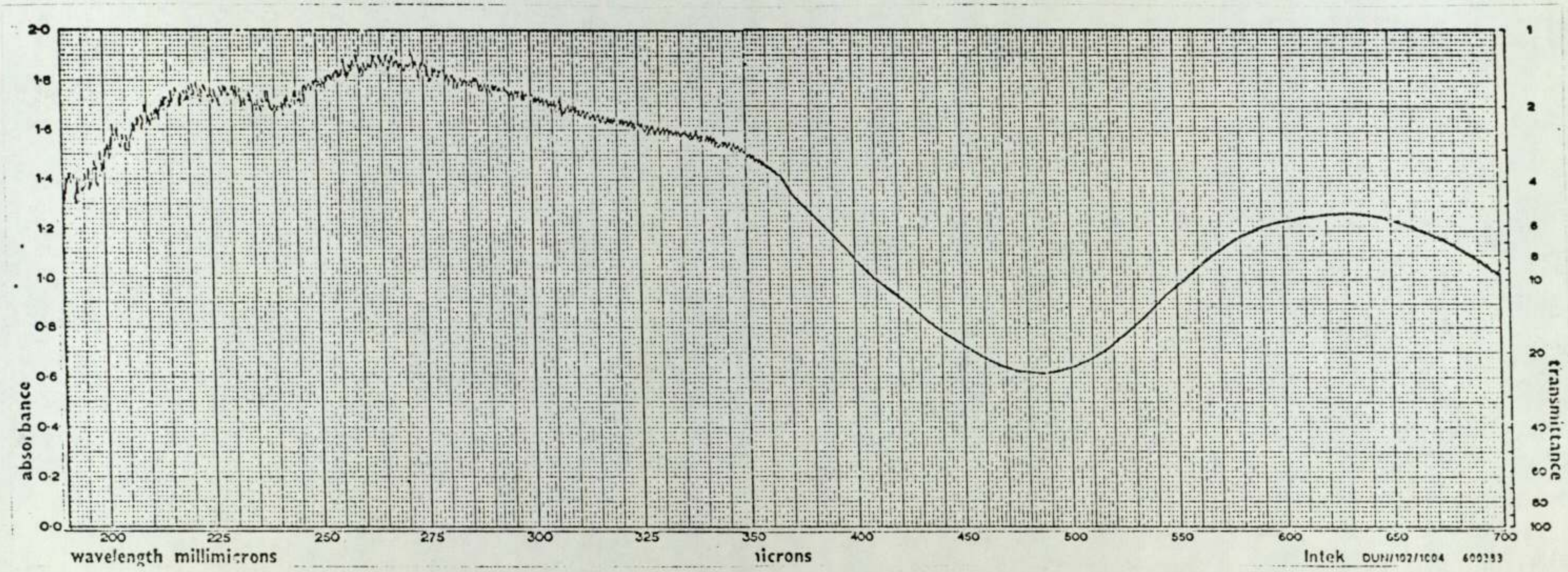
The symmetric C=O stretching frequency is most likely to give rise to the sharp, medium-strong absorption at 1450 cm^{-1} (with shoulder at 1460 cm^{-1}), giving a separation of 85 cm^{-1}.

The very sharp, strong absorptions at 1400, 1410 and 1415 cm^{-1}, are most probably due to ligand vibrations, but should any of these have arisen from a symmetric C=O stretching vibration, then more than one environment for the carboxylate groups could be postulated.

Table 21, Results of the Elemental Analysis for the Copper (II) Complex of 3,3'-Thiodipropionate

ELEMENT PRESENT	PERCENTAGE FOUND	PERCENTAGE CALCULATED								
		M·L	M·O·L	M·L ·OH	M·L ·$\frac{1}{2}H_2O$	M·L ·H_2O	M·L ·$1\frac{1}{2}H_2O$	M·L ·$2H_2O$	M·L ·H_2O·OH	M·O·L ·H_2O
COPPER	25·4, 25·8 (AA) 25·21, 25·62 (Vol.)	26·51	24·85	24·75	25·55	24·66	23·82	23·04	23·13	23·21
CARBON	29·82, 30·12	30·06	28·18	28·07	28·97	27·96	27·02	26·13	26·23	26·33
HYDROGEN	3·15, 3·71	3·36	3·15	3·53	3·65	3·91	4·16	4·39	3·68	4·04

DIFFUSE REFLECTANCE SPECTRUM of the Copper (II) Complex of 3,3'-Thiodipropionate



Copper (II) Complex of 3,3'-Thiodipropionic Acid

The elemental analysis of this complex, indicated a copper to ligand ratio of one to one, and as can be seen from Table 21, the possible presence of half a molecule of water.

Infra-red Spectrum

The infra-red spectrum of the copper complex is similar to the zinc complex in exhibiting a broad, wea absorption at 3400 - 3500 cm^{-1}, presumably having arisen from an O-H stretching vibration. The three sharp, weak absorptions at 2920, 2950 and 2960 cm^{-1} (together with the shoulder at 2910 cm^{-1}), presumably arise from aliphatic C-H stretching vibrations of the ligand.

The asymmetric C=O stretching frequency, is easily assigned to the sharp, strong absorption at 1595 cm^{-1}.

The assignment of the symmetrical C=O stretching frequency is more difficult, but must be a member or members of the sharp, quintet of strong absorptions at 1405, 1420, 1430, 1440 and 1450 cm^{-1}. The most prominent absorptions at 1405 and 1440 cm^{-1}, would give separations of 190 and 155 cm^{-1}.

Both the zinc and copper complexes spectra have a number of sharp, weak absorptions, but there seems to be no common pattern of these, presumably ligand absorptions.

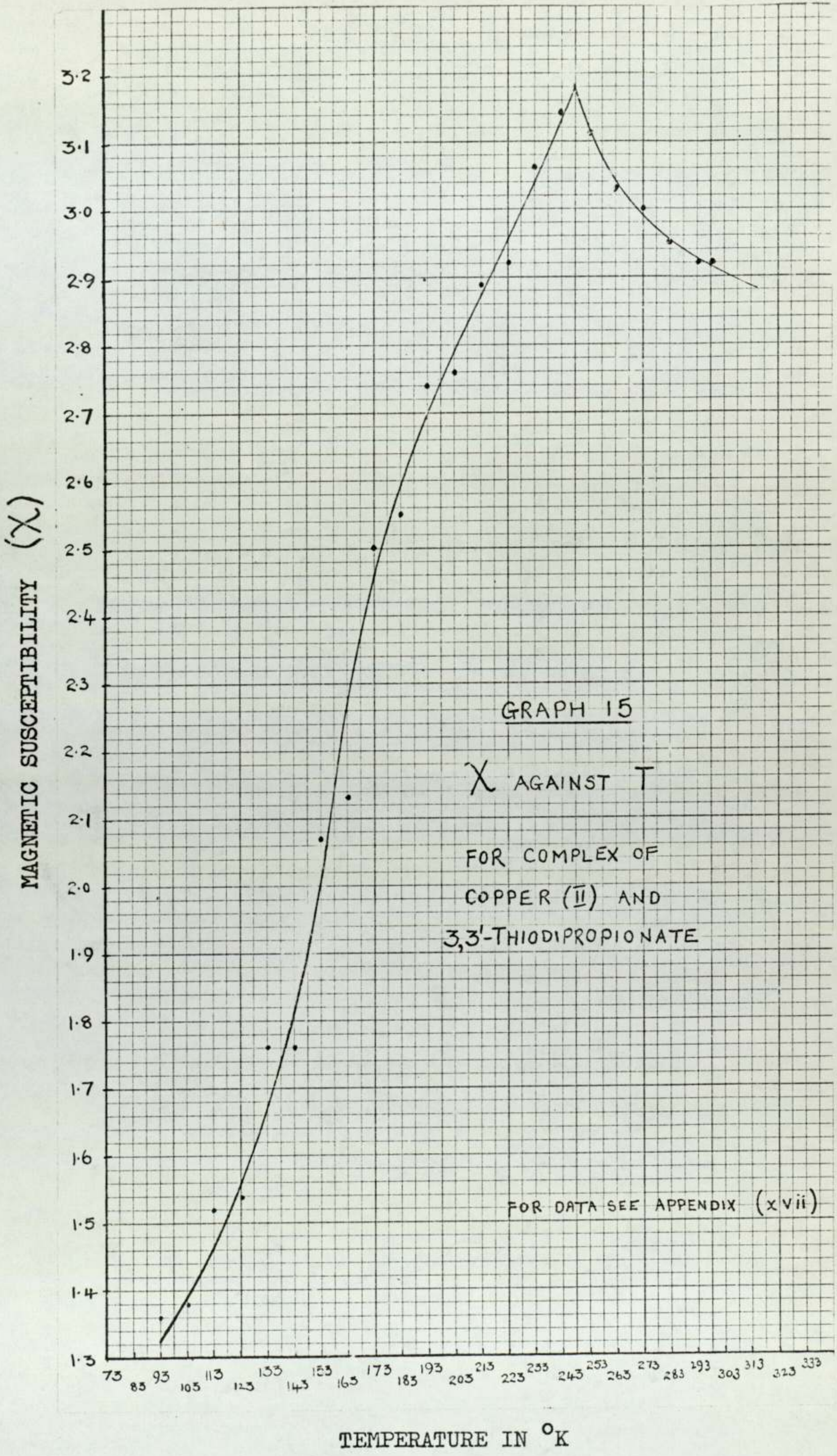
Diffuse Reflectance Spectrum

The diffuse reflectance spectrum of the copper (II) and 3,3'-thiodipropionate complex, is similar to that obtained for copper (II) and 2,2'-oxydibenzoate, with the exception that it exhibits a single very broad, intense absorption at 630 nm (15,850 cm^{-1}).

The absorption at 225 nm (44,450 cm^{-1}) and 260 nm

Table 22, Results for Copper (II) Complex of 3,3'-Thiodipropionate

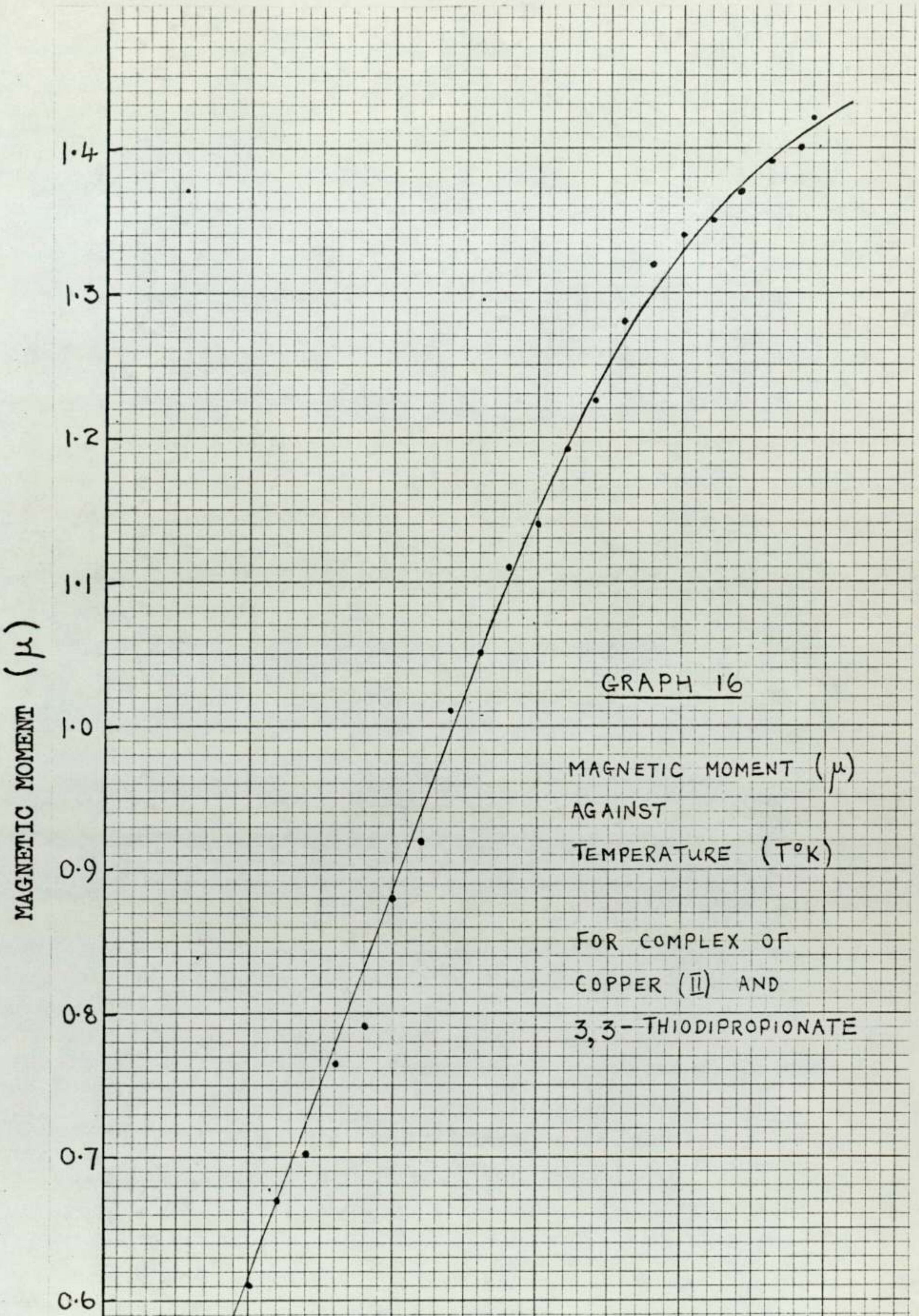
MAGNETIC SUSCEPTIBILITY AT CURRENT (IN AMPÈRES)												χ_m	χ'_m	μ.
5	5½	6	6½	7	7½	8	8½	9	9½	10	AVERAGE			
											χ	$\chi \cdot 248.7$	$\chi_m + 107.2$	T = 292°K
3·16	3·11	3·09	3·05	3·05	3·05	3·05	3·06	3·06	3·04	3·05	3·07	764	871	1·43
3·14	3·00	3·03	3·00	3·01	3·02	3·03	3·03	3·02	3·02	3·04	3·05	759	866	1·43
3·13	3·12	3·12	3·12	3·09	3·11	3·12	3·10	3·10	3·10	3·11	3·11	774	881	1·44
3·20	3·17	3·18	3·15	3·14	3·15	3·15	3·13	3·13	3·13	3·15	3·15	783	890	1·45


GRAPH 15

X AGAINST T

FOR COMPLEX OF
COPPER (II) AND
3,3'-THIODIPROPIONATE

FOR DATA SEE APPENDIX (xvii)


GRAPH 16
MAGNETIC MOMENT (μ)
AGAINST
TEMPERATURE (T°K)
FOR COMPLEX OF
COPPER (II) AND
3, 3-THIODIPROPIONATE
FOR DATA SEE APPENDIX (xviii)
MAGNETIC MOMENT (μ)
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
63
75
83
93
103
113
123
133
143
153
163
173
183
193
203
213
223
233
243
253
263
273
283
293
303
313
323
TEMPERATURE IN °K

(38,500 cm^{-1}), are probably due to electronic transfers between molecular orbitals of the ligand. The absorption which gives rise to the shoulder at about 350 nm (28,600 cm^{-1}), could be due to this cause, or may be a manifestation of a weak δ bond.

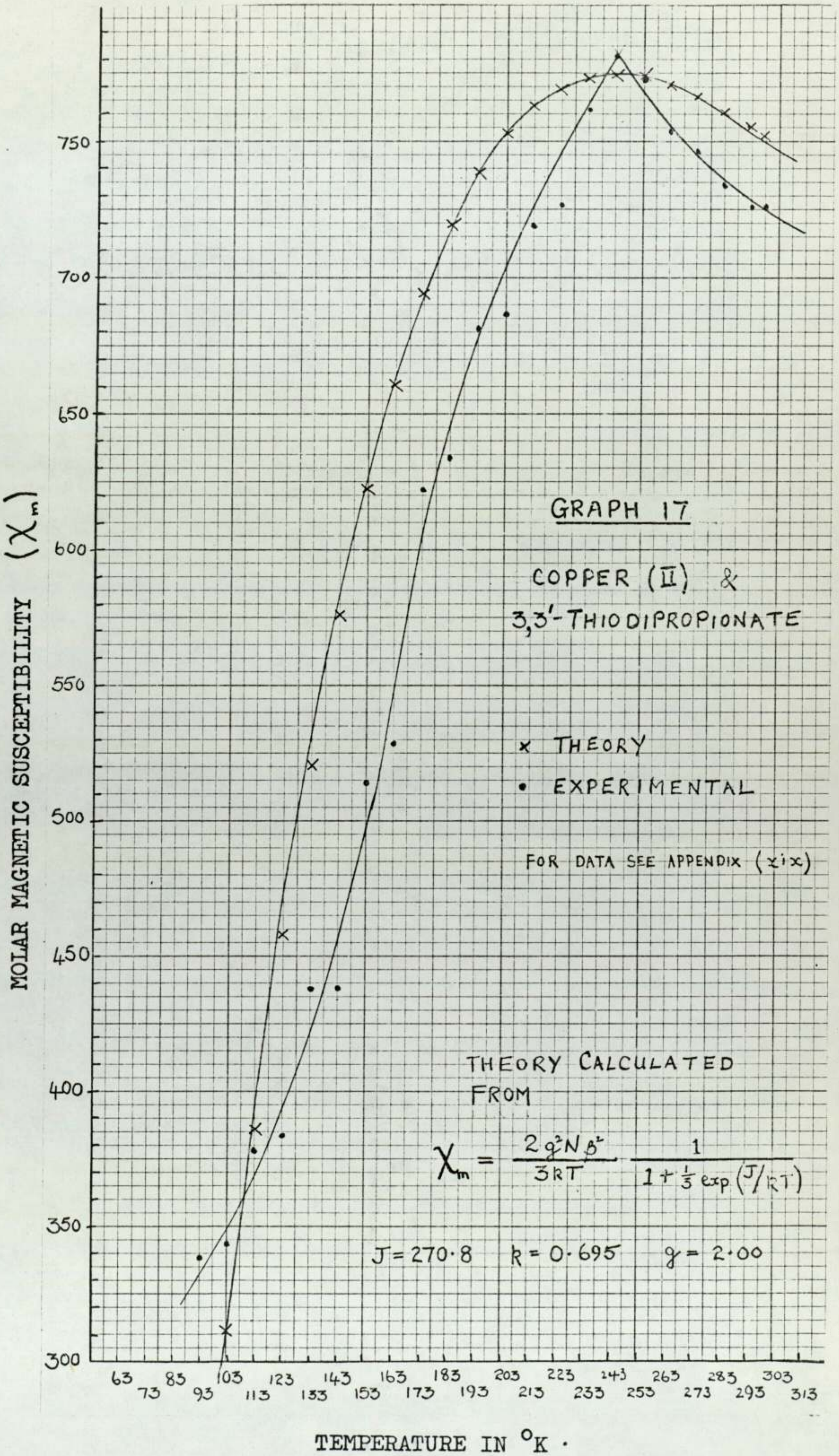
Magnetic Susceptibility Measurements

The value of the magnetic susceptibility when measured at different magnetic field strengths was constant, as can be seen from Table 22. The effective magnetic moment, calculated from, $\mu_{eff} = 2.84 \sqrt{\chi_m . T}$

ranged from 1.43 to 1.45 Bohr magnetons. This value is lower than expected for experimental magnetic moments, which are usually in the range 1.70 to 2.20 Bohr magnetons (1.73 Bohr magnetons in theory).

Measurement of the magnetic susceptibility at different temperatures, showed the magnetic moment to be about 1.40 Bohr magnetons at room temperature, but falling to 0.58 Bohr magnetons at 93°K., as can be seen from graph 16.

A plot of the reciprocal of the molar magnetic susceptibilities, corrected for diamagnetic contributions against temperature, does not give a straight line but a characteristic double curve, displaying a maximum (the Néel point T_n) at 243.5 °K. This is also observed in a plot of magnetic susceptibility (χ) against temperature, as can be seen from graph 15, this being very characteristic of antiferromagnetic behaviour. This indicates that spin-spin interactions are occuring, the moments of the copper (II) ions aligning themselves so that they cancel one another.


GRAPH 17
COPPER (II) &
3,3'-THIODIPROPIONATE
× THEORY
• EXPERIMENTAL
FOR DATA SEE APPENDIX (xix)
THEORY CALCULATED FROM
$\chi_m = \frac{2g^2N\beta^2}{3kT} \frac{1}{1+\frac{1}{3}\exp(J/kT)}$
J = 270·8   k = 0·695   g = 2·00
MOLAR MAGNETIC SUSCEPTIBILITY (χ_m)
300
350
400
450
500
550
600
650
700
750
63
73
83
93
103
113
123
133
143
153
163
173
183
193
203
213
223
233
243
253
263
273
283
293
303
313
TEMPERATURE IN °K ·

For the case of binuclear copper (II) complexes, the molar susceptibility of the dimer can be described by the following equation[69].

$$\chi_m = \frac{2g^2N\beta^2}{3kT} \cdot \frac{1}{1 + \frac{1}{3}\exp(J/kT)} + N\alpha$$

It follows that $\chi_m = N\alpha$ when $T = 0$, and rises to a maximum value at $T_n \simeq 5J/8k$, so that J the exchange energy can be determined directly from the Neel temperature, i.e. $J = 1.6kT_n$. The Curie-Weiss law will not be strictly obeyed until $T \gg T_n$, when $\theta \simeq 0.4T_n$.

Hence, for the complex of copper (II) and 3,3'-thiodipropionate; $J = 1.6 \times 0.695 \times 243.5 = 270.8\ \mathrm{cm}^{-1}$ (389.6 °K)

Assuming a knowledge of $N\alpha$ by using experimental values of χ_m at known temperatures, g and J may be determined from the above equation by solving the simultaneous equations produced when the experimental values of χ_m and T are inserted.

Since time did not permit this work to be done, a simpler approach was employed, the values $N\alpha = 60 \times 10^{-6}$, $J = 270.8$ and $g = 2.0$, were substituted into the equations, the χ_m values calculated and compared with those obtained experimentally. The results, as can be seen from graph have a reasonable degree of correlation.

These results lend weight to the arguement that the complex of copper (II) and 3,3'-thiodipropionate could be binuclear and so exhibit intramolecular antiferromagnetism. The possibility of intermolecular antiferromagnetic behaviour could be eliminated by two procedures. Dissolution by surrounding the complex species with solvent molecules and thus, separating the interacting ions, should destroy the interactions. The main difficulties with this method are that;

(i) the substance in question may be insoluble or considerably changed by dissolution and,

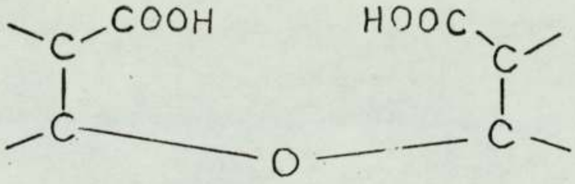
(ii) the experimental errors in measuring χ_m, particularly if the solution were very dilute, may be greater than the effect being observed.

The second method is dilution with a solid, diamagnetic, isomorphous compound. This is really the same as the solution technique and presents the difficulties of finding a suitable host material and of measuring a probably very small susceptibility.

Conclusion

The postulated brightening agents in alkaline zinc electroplating, the bimolecular ethers, could not be isolated and so it was decided to explore the co-ordination chemistry of model compounds with zinc. The hope being that any information acquired could be extrapolated to the bimolecular ethers to give some clues about the mechanism of the brightening action.

It was decided to concentrate on the structural unit;



The main questions to be answered seemed to be, the mode of co-ordination of the carboxylate groups and more interestingly the co-ordinating ability of the ether oxygen, which gives the possibility of one isomer of the bimolecular ethers acting as a terdentate ligand, with the ability to bind zinc ions firmly.

Two compounds were thought to be the best models for the bimolecular ethers and of these 2,2'-oxydibenzoic acid was synthersised first, because difficulty was encountered with the purification of 3,3'-oxydipropionic acid. Consequently, most of the work has involved the former compound.

It was intended originally to restrict the work to the preparation and identification of the zinc complexes of the model compounds, but since elemental analysis proved unable to distinguish unambiguously between all possible formulae and the infra-red spectra did not give enough structural information, it was decided to prepare complexes of other first row transition metals in order that other physical techniques could be employed.

COMPLEX	STRUCTURE	INFRA-RED ASSIGNMENTS (cm^{-1})				^{57}Fe MÖSSBAUER DATA		OTHER DATA
		OH STRETCHING (& DEFMTN)	ASYMM. OCO STRETCHING	SYMM. OCO STRETCHING	SEPARATION	CHEMICAL ISOMER SHIFT (δ)	QUADRUPOLE SPLITTING (Δ)	
ZINC	$Zn.L.1\frac{1}{2}H_2O$	m, b AROUND 3250	1560 (shdr. 1545)	1400	160			
BLUE COBALT	$Co\cdot L\cdot H_2O$	m, b AROUND 3400	1565 (shdr. 1545)	1410	155			$\mu = 4{\cdot}88$ ($\mu = 4{\cdot}67$ purple)
GREEN COPPER	$Cu\cdot L\cdot H_2O$	m, b AROUND 3400	1560 (shdr. 1545)	1410	150	in mm. per sec.		$\mu = 1{\cdot}58$ & $1{\cdot}65_5$ at room temp. falling to 1·50 at 90°K. ($\mu = 1{\cdot}47_5$ blue) Plot of $1/\chi'_m$ against temp. linear, $\theta = 20°K$
IRON (III)	$Fe\cdot O\cdot L$ $Fe\cdot L\cdot OH$	m, b AROUND 3400 - 3500 (w, b 1725)	1615	1420	195	0·40	0·616	$\mu = 2{\cdot}98$
GREEN IRON (II)	$Fe\cdot L\cdot xH_2O$?	s, b AROUND 3300	Complex 1625 to 1565	1405 (poss. 1360)	220 (265) to 160 (205)	1·22	2·675	
BROWN (GOLDEN SHEEN) IRON	$Fe\cdot L\cdot H_2O\cdot OH$ $Fe\cdot O\cdot L\cdot H_2O$	m, b AROUND 3450 (w, s 1730)	1560 to 1540	1415	145 to 125	0·41	0·745	$\mu = 3{\cdot}27$ & $3{\cdot}30$ at room temp., falling to 2·5 at 90°K A plot of $1/\chi'_m$ against temp., was non-linear

The zinc complex of 2,2'-oxydibenzoate (L) was easily prepared and elemental analysis suggested the empirical formula $Zn.L.\frac{1}{2}H_2O$. The infra-red spectrum contributed the information, that the separation of the asymmetric (1560 cm^{-1}) and symmetric (1400 cm^{-1}) OCO stretching frequencies was 160 cm^{-1}, and so the carboxylate anion was most probably engaged in asymmetric bidentate co-ordination.

The inability of zinc-2,2'-oxydibenzoate to dissolve in water or any of the common solvents, indicates that this is probably a polymeric species, with the carboxylate groups of the ligand attached to different zinc atoms.

The cobalt (II) and copper (II) complexes of 2,2'-oxydibenzoate were then prepared so that other physical techniques could be employed.

the complexes obtained initially, formed slowly and had a crystalline appearance, which was retained when they were dried, but in both cases a colour change was observed. Attention was concentrated on the desiccated materials and for both elemental analysis indicated the most probable empirical formula to be $M.L.H_2O$, were M is cobalt or copper and L is 2,2'-oxydibenzoate.

The infra-red spectra of these complexes are almost identical, both having much in common with the spectrum of zinc-2,2'-oxydibenzoate. The main difference being that, the spectra of cobalt and copper, -2,2'-oxydibenzoate have broader absorptions, which are possibly poorly resolved doublets.

The doublet around 1600 cm^{-1}, is most probably due to a ligand vibration and so the asymmmetric OCO stretching vibration is best assigned to the absorption at 1565 cm^{-1} (with shoulder at 1545 cm^{-1}) in the spectrum of cobalt -2,2'-oxy dibenzoate and to the absorption at 1560 cm^{-1} (with shoulder at 1545 cm^{-1}) in the spectrum of copper-2,2'-oxydibenzoate. The symmetric OCO stretching vibration can best be assigned to the absorption at 1410 cm^{-1}, and this may be a poorly resolved doublet like the one found in the spectrum of zinc-2,2'-oxydibenzoate.

The separation of the asymmetric and symmetric OCO stretching frequencies are consequently 155 cm^{-1} (& 135 cm^{-1}) for cobalt-2,2'-oxydibenzoate and 150 cm^{-1} (& 135 cm^{-1}) for copper-2,2'-oxydibenzoate, which according to Curtis[58] indicates that the carboxylate groups are engaged in asymmetric bidentate co-ordination. The existance of two absorptions arising from the asymmetric OCO stretching vibrations suggests that two environments must be postulated for the carboxylate groups.

The shape and position of the absorptions thought due to the O-H stretching vibrations are the same in the spectra of cobalt and copper complexes but are different to the absorption in the spectrum of the zinc complex, presumably due to the extra $\frac{1}{2}H_2O$ present in the empirical formula of this complex.

The question that still remains unanswered is that concerning the co-ordinating ability of the ether oxygen. The only feature that may be connected is the absorption at 1220 cm^{-1} in the spectrum of zinc-2,2'-oxydibenzoate, the absorption at 1235 cm^{-1} in the spectrum of copper-2,2'-oxydibenzoate and the broad absorption at 1220-1240 cm^{-1} in the spectrum of cobalt-2,2'-oxydibenzoate. This feature is also present in the spectrum of the free acid at 1245 cm^{-1} but could also be the result of other ligand vibrations.

The magnetic moment, determined at room temperature, was found to be 4.9 B.M., for the blue cobalt complex, but only 4.7 B.M., for the purple cobalt complex which precipitated initially. Similarly the magnetic moment, determined at room temperature, was found to be 1.65 B.M., for the green copper complex, but only 1.5 B.M., for the blue copper complex which formed initially.

The magnetic moment of the green copper complex fell as the temperature was lowered, being about 1.5 B.M., at 90 K. A plot of the reciprocal value of the corrected molar magnetic susceptibility $(1/\chi_m)$ against temperature was linear intersecting the temperature axis at -20 K. Since the magnetic susceptibility did not vary when different strength magnetic fields were used the material must be exhibiting antiferromagnetic behaviour. Thus implying that there is interaction between the copper ions of the complex, resulting in spin-spin pairing.

This and the inability of all the complexes to dissolve in water or other common solvents, leads to the conclusion that these are polymeric species, which have the two carboxylate groups of a single ligand molecule attached to different metal atoms. The alternative postulation to explain the antiferromagnetic interactions would have to involve bridging between metal ions of water molecules.

The preparation of the iron(II) and iron(III) complexes was an attempt to provide more structural information by the use of Mössbauer spectroscopy, but succeeded in only further complicating the issue.

The iron(III) complex precipitated immediately like the zinc complex, but they must have different structures, because the presence of an hydroxyl anion or a μ-oxa bridge must be postulated to maintain electrical neutrality. This is confirmed by elemental analysis which suggests the empirical formula Fe.L.OH or less probably $Fe.O_{\frac{1}{2}}.L$.

The infra-red spectrum of the iron(III) complex, as expected, is different to the spectra of the zinc, cobalt and copper complexes. The presence of a weak, broad absorption around 3400-3500 cm^{-1}, is comparable to those observed in the spectra of the cobalt and copper complexes, but one unique feature is the broad, weak absorption at 1725 cm^{-1}.

The assignment of the absorption at 1615 cm^{-1} as the asymmetric OCO stretching vibration and the resultant separation of 195 cm^{-1}, between this and the symmetrical OCO stretching vibration at 1420 cm^{-1}, suggests that the carboxylate groups are bridging two iron atoms, while showing asymmetric bidentate co-ordination.

The iron(II) complex was similar to the cobalt and copper complexes in as much as the green crystals formed slowly. These however, on drying in a vacuum desiccator (or oven) changed to a dark brown colour and had a golden sheen on one face.

The infra-red spectrum of the brown iron complex with the golden sheen was similar to the spectrum of the copper complex and to a lesser extent the cobalt complex. The asymmetric OCO stretching vibration was assigned to the absorption at 1560 cm^{-1} (almost a doublet with absorption at 1540 cm^{-1}) and the symmetric OCO stretching vibration to the absorption at 1415 cm^{-1}, giving a separation of 145 cm^{-1} (and 125 cm^{-1}). Thus indicating two environments for the carboxylate groups, both being engaged in asymmetric bidentate co-ordination.

The infra-red spectrum of the green iron(II) complex, exhibited many differences when compared to the other spectra already considered.

The metallic sheen on the dark brown crystals obtained by desiccating the green iron(II) complex was thought to indicate the presence of metal to metal interactions. Elemental analysis suggested that the empirical formula of the brown complex is probably $Fe.L.OH.H_2O$ although $Fe.O_{\frac{1}{2}}.L.H_2O$ is also possible. This interpretation is vindicated by the evidence of the diffuse reflectance spectra and Mössbauer spectra of the three iron complexes which showed that the brown complex contained iron in the +3 oxidation state.

The magnetic moment of the brown complex has been determined by two different Gouy balances to be 3.30 B.M., at room temperature, falling to about 2.50 B.M., at 90 K. A plot of the reciprocal of the corrected molar magnetic susceptibility ($1/\chi_m$) against temperature was non-linear, which in combination with the unusual magnetic moments (which are high for low spin and low for high spin) indicates antiferromagnetic coupling between the iron atoms of the complex.

The magnetic moment of the iron(III) complex was 3.0 B.M., at room temperature and while this is comparable to that obtained for the brown iron complex, the infra-red spectra of these complexes suggest different structures. The differences in the quadrupole splitting obtained from the Mössbauer spectra also reflects this difference.

Work to date has been concentrated on the desiccated complexes, however, the colour changes observed suggest that the cobalt, copper and iron(II) complexes obtained initially, could be different structurally to the complexes studied. Investigation of the complexes obtained initially, which only requires the development of less intensive drying techniques, may give information regarding the charges observed and so lead to a better outstanding of the structures of these complexes and TGA may be an appropriate technique to apply.

COMPLEX		STRUCTURE	INFRA-RED ASSIGNMENTS (cm^{-1})				OTHER DATA
			OH STRETCHING (& DEFMTN)	ASYMM. OCO STRETCHING	SYMM. OCO STRETCHING	SEPARATION	
2,2'-THIODIBENZOATE	ZINC	$Zn \cdot L \cdot H_2O$ $Zn \cdot L \cdot 1\frac{1}{2}H_2O$	3430	1600 - 1575 1550	1405	195 - 170 145	
	COPPER (II)	$Cu \cdot L \cdot H_2O$	3610 3530	1625 - 1605 1590 1560	1400 (shdr. 1410)	225 - 205 190 160	
3,3'-OXYDIPROPIONATE	ZINC	$Zn \cdot L \cdot ClO_4$	3450	1570 - 1530 (shdr. 1600)	1460 (shdr. 1470) 1410 ?	110 - 70 160 - 120	Complex adsptn. at 1090, 1120, 1115 due to Perchlorate ?
	COPPER (II)	$Cu \cdot L \cdot \frac{1}{2}H_2O$	3400	1600 (shdr. 1590)	1450	150	
3,3'-THIODIPROPIONATE	ZINC	$Zn \cdot L \cdot \frac{1}{2}H_2O$	3450	1535 (shdrs. 1555 1565)	1400 1415 1450	135 120 85	
	COPPER (II)	$Cu \cdot L$ $Cu \cdot L \cdot \frac{1}{2}H_2O$	3450	1595	1405 1420 1430 1440 1450	190 175 165 155 145	μ = 1·40 & 1·44 at room temp. falling to 0·58 at 90°K. A plot of χ against temp. exhibited Antiferromagnetic behaviour.

Complexes of 2,2'-Thiodibenzoic Acid

2,2'-Thiodibenzoic acid was synthersised and the zinc and copper(II) complexes prepared in order that a comparison could be made with the appropriate complexes of 2,2-oxydibenzoic acid.

Zinc complex

Elemental analysis indicated that the empirical formula of this complex could be $Zn.L.H_2O$ or $Zn.L.1\frac{1}{2}H_2O$, the latter being that found for zinc-2,2'-oxydibenzoate.

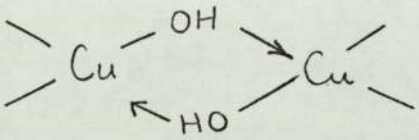
The infra-red spectra of these two complexes are similar in the region 3600 to 2000 cm^{-1}, but below this they have little in common, the prime difference being that the absorptions in the spectrum of zinc-2,2'-thiodibenzoate are broader.

In the spectrum of zinc-2,2-thiodibenzoate the asymmetric OCO stretching frequency has been assigned to the broad, strong absorption at 1600-1575 cm^{-1}, while for zinc-2,2'-oxydibenzoate this was much lower at 1560 cm^{-1}. The symmetric OCO stretching frequencies are much closer being assigned to the absorption at 1405 cm^{-1} in the spectrum of zinc-2,2'-thiodibenzoate and 1400 cm^{-1} for zinc-2,2'-oxydibenzoate. This gives a separation of the asymmetric and symmetric stretching frequencies of 195-170 cm^{-1} for zinc-2,2'-thiodibenzoate compared to 160 cm^{-1} for zinc-2,2'-oxydibenzoate, suggesting that they are both acting as asymmetric bidentate ligands, with one C-O bond longer than the other and that this bond is longer for zinc-2,2'-thiodibenzoate.

Copper complex of 2,2'-Thiodibenzoate

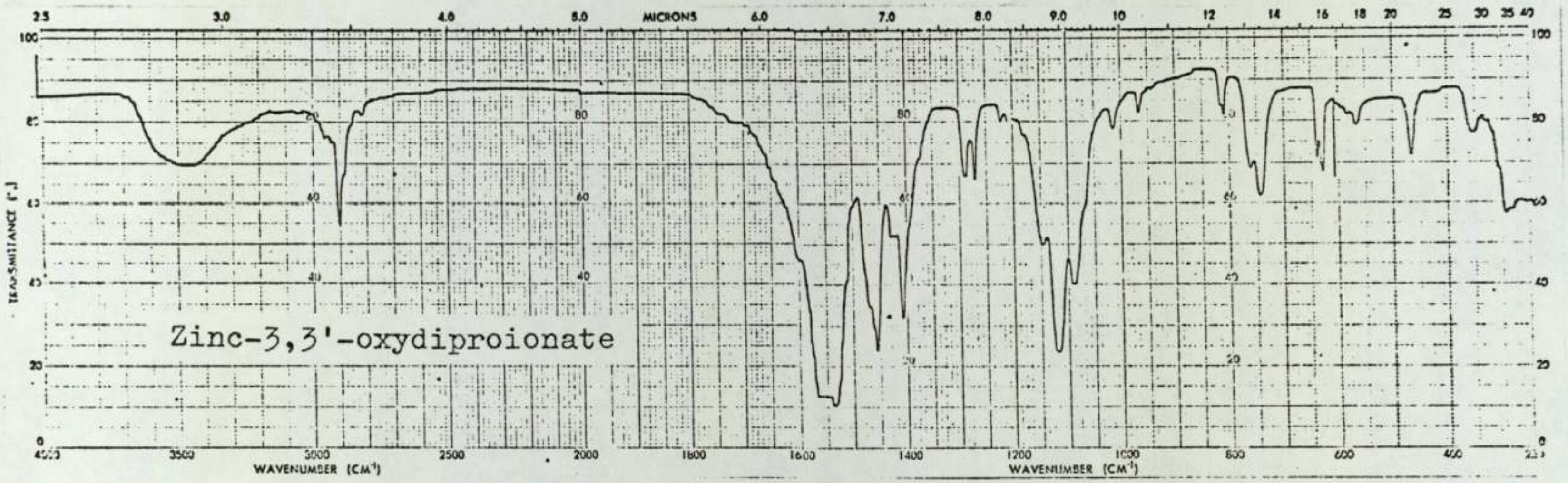
This complex appears to have the same empirical formula as the copper complex of 2,2'-oxydibenzoate namely $Cu.L.H_2O$.

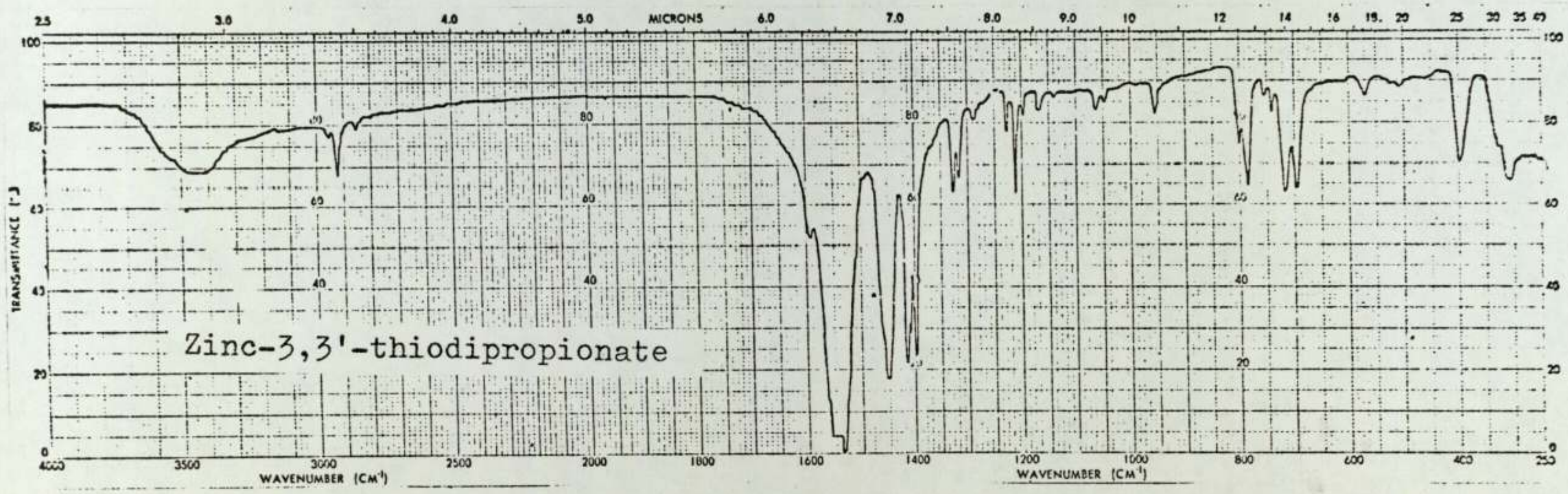
However, the infra-red spectra of these complexes are very different. The infra-red spectrum of the copper complex of 2,2'-oxydibenzoate has a single broad absorption around 3400 cm^{-1}, while the spectrum of the copper complex of 2,2'-thiodibenzoate has two sharp absorptions at 3610 and 3530 cm^{-1}. The latter is readily assigned since the O-H stretching vibrations of a free hydroxyl group are usually found in the range 3560 to 3500 cm^{-1}. The absorption at 3610 cm^{-1} is more difficult to assign but is possibly due to hydroxyl bridging between two copper atoms.



The asymmetric OCO stretching frequency of the carboxylate group in the infra-red spectrum of the coppper complex of 2,2'-thiodibenzoate has been assigned to the very sharp, strong absorption at 1625-1605 cm^{-1}, compared to 1560 cm^{-1} in the spectrum of the copper complex of 2,2'-oxydibenzoate. The assignment made for the symmetric OCO stretching frequency was only slightly higher for copper-2,2'-thiodibenzoate, being at 1410 cm^{-1}, compared with 1400 cm^{-1} in the spectrum of copper-2,2'-oxydibenzoate.

The high frequency of 1625-1605 cm^{-1} observed in the spectrum of copper-2,2'-thiodibenzoate can best be explained by postulating carboxylate bridging between copper atoms.


Zinc-3,3'-oxydiproionate


Zinc-3,3'-thiodipropionate

Complexes of 3,3'-Oxydipropionic Acid and 3,3'-Thiodipropionic Acid

3,3'-Oxydipropionic acid is probably a better choice as a model compound for the proposed bimolecular ether than 2,2'-oxydibenzoic acid, since it is plausible to suppose that contributions from the electron density of the aromatic rings of the latter compound make the bond order of the carbon to ether oxygen bonds intermediate between single and double, as in the case of diphenyl ether[83]. This would have the effect of making the C-O-C bond angle increase and possibly inhibit co-ordination.

The difficulties encountered during the preparation of 3,3'-oxydipropionic acid has resulted in very little work on the complexes of this compound.

Since 3,3'-thiodipropionic acid was readily available little attention was paid initially to its complexes, because it was assumed they would have been thoroughly studied. As data accumulated about complexes of the other model compounds, the complexes of 3,3'-thiodipropionate assumed more importance, since it was hoped that a knowledge of its co-ordination chemistry could help to resolve the problems encountered with the complexes of the other model compounds. A search of the literature however, revealed that very little was known about its co-ordinating ability, the majority of available knowledge being based on data derived from potentiometric studies. The only description of a solid complex being obtained from U.S. patent 3 697 488, which used zinc complexes of 3,3'-thiodipropionic acid but does not reveal much detail.

Zinc complexes

Elemental analysis of zinc-3,3'-oxydipropionate indicated that the most probable empirical formula was $Zn.L.ClO_4$, but the discrepancies involved suggests that further work is necessary. Should the above empirical formula be correct, then for electrical neutrality, the ligand must be in the form $HOOC.CH_2.CH_2.O.CH_2.CH_2.COO^-$. No perchlorate analysis was undertaken, but possible evidence for its existance may be the absorptions in the region 1150-1050 cm^{-1} in the infra-red spectrum, which are more complex than those observed in the spectra of the copper complex or free acid of 3,3'-oxydi-propionate.

The empirical formula for zinc-3,3'-thiodipropionate appeared to be $Zn.L.\frac{1}{2}H_2O$ and consequently appears similar to the zinc complexes of 2,2'-oxydibenzoate and 2,2'-thiodibenzoate.

The infra-red spectra of zinc-3,3'-oxydipropionate and zinc-3,3'-thiodipropionate, apart from the region 1150-1050 cm^{-1}, are similar, especially in the region 3800 to 1800 cm^{-1}, were the main feature is a weak, broad absorption around 3450 cm^{-1}.

The asymmetric OCO stretching vibration has been assigned to the strong absorption at 1560-1530 cm^{-1}, (which has a superimposed sharp absorption at 1535 cm^{-1}) in the spectrum of zinc-3,3'-thiodipropionate. While the corresponding feature in the spectrum of zinc-3,3'-oxydipropionate has a broader absorption from 1570-1530 cm^{-1} (again with a superimposed sharp absorption at 1535 cm^{-1}).

Both spectra have a weak absorption at about 1600 cm^{-1}, possibly suggesting the presence of another environment for a carboxylate anion.

The symmetric OCO stretching vibration was thought best assigned to the sharp, strong absorption at 1450 cm^{-1} (with a shoulder at 1460 cm^{-1}) in the spectrum of zinc-3,3'-thiodi-propionate and the sharp, strong absorption at 1455 cm^{-1} (with shoulders at 1460 and 1470 cm^{-1}) in the spectrum of zinc-3,3'-oxydipropionate.

This would give in both cases a separation between the asymmetric and symmetric OCO stretching frequencies of 110-70 cm^{-1}, which according to Curtis[58] suggests unidentate co-ordination, since the separation is rather low for symmetrical bidentate co-ordination. However, both the absorptions thought due to the asymmetric and symmetric OCO stretching vibrations have undergone displacements. While in the example used by Curtis[58] for unidentate co-ordination i.e., nickel acetate tetrahydrate the absorptions recorded are 1520 and 1413 cm^{-1} (a separation of 107 cm^{-1}). Consequently it would seem more appropriate to suggest symmetrical bidentate co-ordination, because in the example i.e., zinc acetate dihydrate, the absorptions recorded are 1550 and 1430 cm^{-1} (a separation of 120 cm^{-1}).

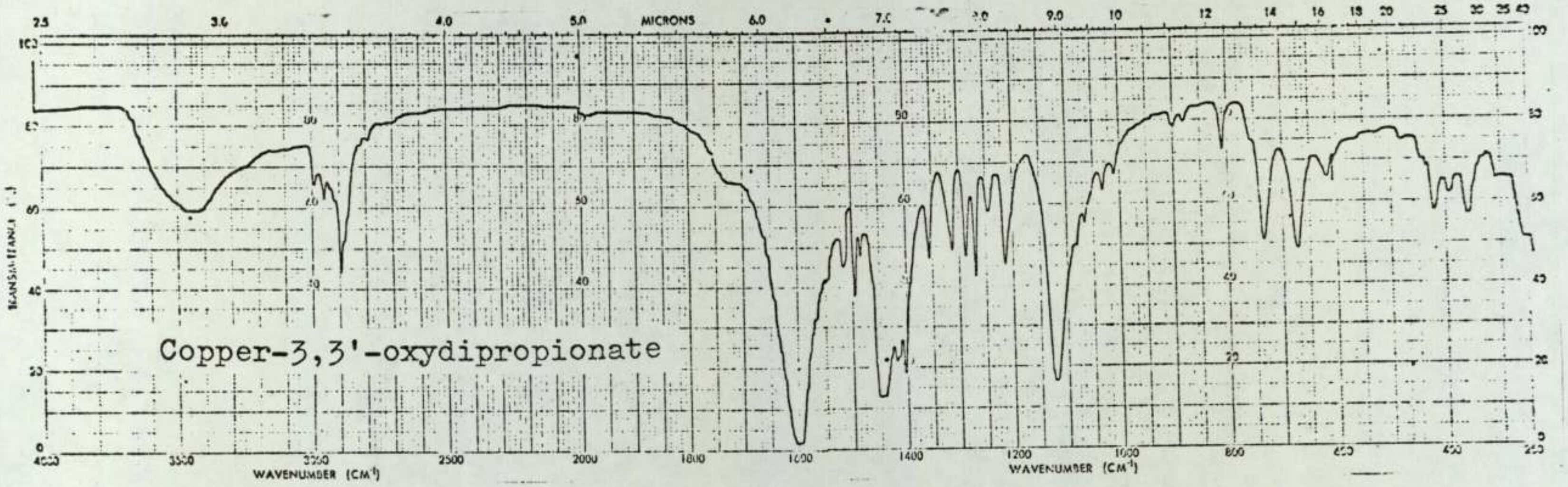
The most probable explanation is the existance of both unidentate and symmetrical bidentate co-ordination which is in accord with the postulation of two environments for the carboxylate groups.

The absorptions at 1400 and 1415 cm^{-1} in the spectrum of zinc-3,3'-thiodipropionate and 1410 cm^{-1} (with shoulder at 1420 and 1430 cm^{-1}) in the spectrum of zinc-3,3'-oxydipropionate are most probably ligand vibrations, although the possibility exists that they could arise from the symmetric OCO stretching vibrations of a carboxylate group.

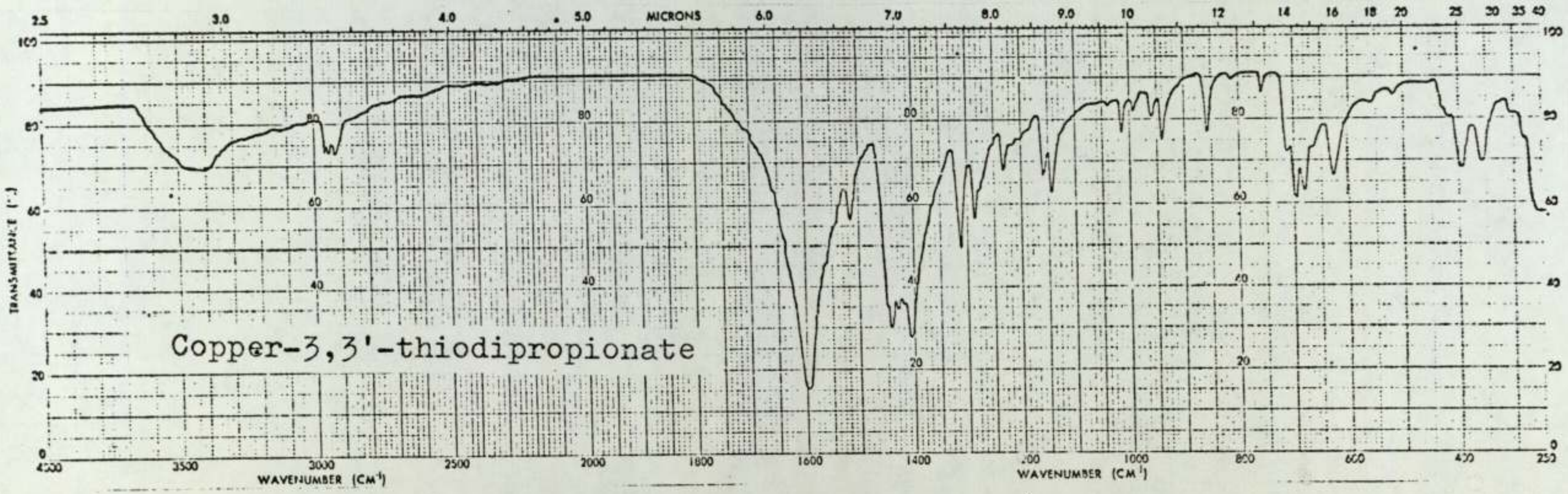
Copper complexes

Elemental analysis suggested that the empirical formula for copper-3,3'-thiodipropionate could be either Cu.L or $Cu.L.\frac{1}{2}H_2O$, the latter being that found for copper-3,3'-oxy-dipropionate.

The infra-red spectra of both complexes contained the now familiar broad, weak absorption around 3400 cm^{-1}, although



Copper-3,3'-oxydipropionate



Copper-3,3'-thiodipropionate

this feature appeared sharper in the spectrum of copper-3,3'-oxydipropionate. Both spectra have an overall similarity in the region 1800-1300 cm^{-1}. Both also have a sharp, strong absorption at 1600 cm^{-1}, although this is broader for copper-3,3'-oxydipropionate, possibly due to this being a poorly resolved doublet, and the most obvious candidate to have arisen from the asymmetric OCO stretching vibrations.

The assignment of the symmetric OCO stretching frequency is more difficult, since there are four possible candidates. Discounting the absorptions at 1400 and 1420 cm^{-1}, as arising from ligand vibrations, this leaves the absorption at 1450 cm^{-1} (with shoulder at 1460 cm^{-1}) in the spectrum of copper-3,3'-oxydipropionate and the absorptions at 1440 and 1430 cm^{-1} in the spectrum of copper-3,3'-thiodipropionate. This suggests the possibility of more than one environment for the carboxylate anions, but these would appear to be different to that encountered in the complexes of 2,2'-oxydibenzoate and 2,2'-thiodibenzoate, because in these complexes it is the asymmetric OCO stretching frequency which has two or more absorptions assigned.

According to Curtis[58] the occurrence of the asymmetric OCO stretching frequency at 1600 cm^{-1}, suggests that the carboxylate responsible is bridging two different copper atoms.

The plot of magnetic susceptibility against temperature for copper-3,3'-thiodipropionate was interesting because its characteristic shape and the fall of the magnetic moment from 1.4 B.M., at room temperature to 0.6 B.M., at 90 K, showed that the complex was exhibiting antiferromagnetic behaviour indicating that there was interaction between the copper ions resulting in spin-spin pairing.

The experimental curve shows some degree of fit to a curve based on the equation;

$$\chi_m = \frac{2g^2N\beta^2}{3kT} \cdot \frac{1}{1 + \frac{1}{3}\exp\left(J/kT\right)}$$

derived for dimeric copper acetate, the discrepancy in the fit arising from either errors introduced in the derivation of the above equation or the possibility that the copper-3,3'-thiodipropionate is not a dimer, but a trimer or higher agglomerate. One possible approach toward future work would thus appear to be the derivation of alternative expressions in the hope that eventually a perfect fit could be achieved.

Time did not permit any magnetic susceptibility measurements to be made on copper-3,3'-oxydipropionate, but this would be a convenient start to any future work on this complex.

3,3'-Oxydipropionate and 3,3'-thiodipropionate are interesting ligands and it is perhaps worth exploring the cobalt and iron complexes if they can be prepared, since they could hopefully give structural information and elucidate the co-ordinating ability of the ether oxygen and thioether sulphur atoms.

APPENDIX (i)

GROWTH OF MAXIMUM AT ABOUT 360 nm.

WAVELENGTH IN NANOMETRES.	ALKALINE ZINCATE ELECTROLYTE + 0·5 gl^{-1} 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE		0·5 gl^{-1} 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE & 100 gl^{-1} SODIUM HYDROXIDE	
	INITIALLY	AFTER 25 hours	INITIALLY	AFTER 25 hours.
230	1·14	1·16	1·20	1·24$_5$
240	0·76	1·03	0·81	0·94$_5$
250	0·74$_5$	1·28	0·79	1·33
260	0·92	1·52	0·97	1·57
270	0·87$_5$	1·27	0·91	1·27
280	0·40	0·76$_5$	0·42	0·81
290	0·15$_5$	0·44$_5$	0·16$_5$	0·47
300	0·09$_5$	0·33$_5$	0·10$_5$	0·35
310	0·07$_5$	0·25$_5$	0·08$_5$	0·27
320	0·06	0·20	0·07	0·22
330	0·05	0·17	0·06$_5$	0·19$_5$
340	0·04$_5$	0·20	0·05$_5$	0·23
350	0·04	0·25	0·05	0·26
360	0·03$_5$	0·30	0·045	0·32
370	0·03	0·32	0·04	0·34
380	0·03	0·29	0·03$_5$	0·30$_5$
390	0·02$_5$	0·19$_5$	0·03$_5$	0·22
400	0·02$_5$	0·07$_5$	0·03	0·09

APPENDIX (ii): DATA FOR GRAPH 1.

SOLUTION COMPOSITION; 0·05 grams ($0{\cdot}5\,gL^{-1}$) 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE, 10·0 grams ($100\,gL^{-1}$) SODIUM HYDROXIDE & 100 cm^3 WATER

TIME IN HOURS	OPTICAL DENSITY AT WAVELENGTH INDICATED							
	330	340	350	360	370	380	390	400
0	$0{\cdot}18_5$	$0{\cdot}15_5$	$0{\cdot}12_3$	$0{\cdot}10_5$	0·09	$0{\cdot}07_8$	0·063	0·05
1	0·22	$0{\cdot}20_5$	0·2	$0{\cdot}19_8$	$0{\cdot}18_2$	0·15	$0{\cdot}10_4$	0·06
2	0·34	0·34	0·35	$0{\cdot}35_5$	$0{\cdot}33_4$	0·28	0·2	0·13
3	0·39	0·4	0·43	0·44	0·42	$0{\cdot}34_3$	0·24	$0{\cdot}15_5$
5	0·46	0·51	0·57	0·61	$0{\cdot}57_5$	0·47	0·31	$0{\cdot}17_6$
6	$0{\cdot}50_5$	$0{\cdot}56_5$	0·64	$0{\cdot}68_5$	0·66	0·54	0·35	$0{\cdot}20_2$
7½	0·59	$0{\cdot}67_5$	$0{\cdot}77_5$	$0{\cdot}81_5$	0·79	$0{\cdot}64_5$	0·42	$0{\cdot}23_5$
29	1·16	1·41	1·7	1·8	1·72	1·42	0·9	0·44

APPENDIX (iii) DATA FOR GRAPH 2.

TIME IN MINUTES	OPTICAL DENSITY AT TEMPERATURE STATED			
	20°C	25°C	30°C	35°C
2	0·16	0·21	0·3	0·6
3	0·2	0·29	0·41	0·7
4	0·24	0·37	0·49	0·8
5	0·27	0·42	0·6	0·88
6	0·31	0·49	0·67	0·97
7	0·34	0·57	0·77	1·06
8	0·38	0·61	0·86	1·16
9	0·41	0·69	0·93	1·25
10	0·45	0·75	1·03	1·34
11	0·48	0·81	1·08	1·4
12	0·51	0·87	1·15	1·48
13	0·54	0·93	1·22	——
14	0·57	0·98	1·28	——
15	0·6	1·02	1·34	——

APPENDIX (iv) DATA FOR GRAPH 3.

EFFECT ON MAXIMUM AT 360 nm. OF VARYING SODIUM HYDROXIDE CONCENTRATION WITH 1-BENZYL-3-CARBOXYPYRIDINIUM CONSTANT AT $2\,gl^{-1}$

TIME IN MINUTES	OPTICAL DENSITY AT 360 nm. FOR NaOH conc. STATED				
	1 g	3 g	5 g	7 g	10 g
5	0·015	0·03	0·07$_5$	0·14$_5$	0·34
7½				0·18	0·44$_5$
10	0·015	0·05	0·11	0·21$_5$	0·56
12½				0·24	0·66
15	0·017$_5$	0·06	0·13$_5$	0·27	0·76
17½				0·29$_5$	0·88
20	0·017$_5$	0·07	0·17	0·33	0·98
22½				0·35$_5$	1·06
25	0·017$_5$	0·08	0·19$_5$	0·38	1·16
27½				0·40	1·25
30	0·02	0·09	0·21$_5$	0·43$_5$	1·34
32½				0·46	1·42.
35	0·02	0·10	0·23$_5$	0·48$_5$	
40	0·022$_5$	0·11	0·25$_5$	0·53	
45	0·022$_5$	0·12	0·27	0·58	
50	0·025	0·13	0·29	0·62$_5$	
55	0·025	0·14	0·31	0·67	
60	0·03	0·15	0·32	0·72	

APPENDIX (v) DATA FOR GRAPH 4

TIME IN MINUTES	OPTICAL DENSITY AT 360 nm. FOR 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE CONC. STATED					TIME IN MINUTES
	0·05 g	0·1 g	0·2 g		0·5 g	
5	0·1	0·115	0·27		0·1	2
10	0·12	0·15	0·45		0·3	3
15	0·13	0·22	0·6		0·5	4
20	0·145	0·27	0·75		0·72	5
25	0·15	0·32	0·89		0·92	6
30	0·16	0·36	1·02		1·06	7
35	0·17	0·40	1·14		1·20	8
40	0·18	0·44	1·25		1·36	9
45	0·18	0·47	1·36		1·48	10
50	0·19	0·5	1·43			
55	0·19	0·53	——			
60	0·20	0·55	——			

APPENDIX (vi) DATA FOR GRAPH 5.

SODIUM HYDROXIDE CONCENTRATION			INITIAL REACTION RATE	
GRAMS	MOLES	$\log_{10}$	OPTICAL DENSITY UNITS PER SECOND	$\log_{10}$
1	0·025	$-1{\cdot}60_2$	$5{\cdot}50 \times 10^{-6}$	$-5{\cdot}26$
3	0·075	$-1{\cdot}12_5$	$4{\cdot}47 \times 10^{-5}$	$-4{\cdot}35$
5	0·125	$-0{\cdot}90_3$	$1{\cdot}00 \times 10^{-4}$	$-4{\cdot}00$
7	0·175	$-0{\cdot}75_7$	$1{\cdot}97_2 \times 10^{-4}$	$-3{\cdot}70_5$
10	0·25	$-0{\cdot}602$	$7{\cdot}17 \times 10^{-4}$	$-3{\cdot}14_{45}$

APPENDIX (vii) DATA FOR GRAPH 6

1-BENZYL-3-CARBOXYPYRIDINIUM CONCENTRATION			INITIAL REACTION RATE	
GRAMS	MOLES	$\log_{10}$	OPTICAL DENSITY UNITS PER SECOND	$\log_{10}$
0·5	1×10^{-2}	$-3{\cdot}00$	$3{\cdot}57 \times 10^{-2}$	$-2{\cdot}45$
0·2	4×10^{-3}	$-3{\cdot}40$	$5{\cdot}73_3 \times 10^{-3}$	$-3{\cdot}24_2$
0·1	2×10^{-4}	$-3{\cdot}70$	$1{\cdot}72 \times 10^{-3}$	$-3{\cdot}76_{45}$
0·05	1×10^{-4}	$-4{\cdot}0$	$4{\cdot}72 \times 10^{-4}$	$-4{\cdot}32_6$

APPENDIX (viii) DATA FOR GRAPH 7

CHANGES IN OPTICAL DENSITY OF MAXIMUM AT 360 nm. WITH TIME, FOR SOLUTION COMPRISING
$4\,gl^{-1}$ 1-PROPYL-3-CARBOXYPYRIDINIUM BROMIDE & $100\,gl^{-1}$ SODIUM HYDROXIDE

WAVELENGTH IN NANOMETRES	OPTICAL DENSITY AT TIME (IN HOURS) STATED							
	0	$1\frac{1}{2}$	4	6	22	25	30	48
320	$0{\cdot}08_5$	0·13	0·25	$0{\cdot}32_7$	0·80	0·86	1·02	1·60
330	$0{\cdot}05_5$	$0{\cdot}09_5$	$0{\cdot}21_2$	0·27	0·57	0·62	0·67	0·96
340	$0{\cdot}04_5$	$0{\cdot}09_4$	$0{\cdot}21_8$	$0{\cdot}30_5$	0·67	0·72	0·76	0·94
350	$0{\cdot}03_7$	0·10	$0{\cdot}23_8$	0·34	0·80	$0{\cdot}85_5$	0·88	1·05
360	$0{\cdot}03_3$	$0{\cdot}10_1$	$0{\cdot}24_8$	$0{\cdot}35_7$	0·88	$0{\cdot}92_5$	0·99	1·20
370	$0{\cdot}03_1$	$0{\cdot}09_4$	$0{\cdot}22_4$	$0{\cdot}32_8$	0·84	0·89	$0{\cdot}95_5$	$1{\cdot}23_5$
380	$0{\cdot}02_4$	$0{\cdot}07_2$	$0{\cdot}17_5$	$0{\cdot}25_1$	0·67	0·70	0·77	1·06
390	0·015	$0{\cdot}04_2$	$0{\cdot}10_8$	$0{\cdot}15_2$	$0{\cdot}41_7$	0·43	0·46	0·68
400	0·008	$0{\cdot}01_5$	0·05	$0{\cdot}06_5$	0·17	$0{\cdot}17_3$	0·19	$0{\cdot}28_5$

APPENDIX (ix), DATA FOR GRAPH 8

OPTICAL DENSITY AT 360 nm., WITH TIME FOR CONCENTRATION OF PYRIDINIUM DERIVATIVE STATED

TIME IN MINUTES	1-BENZYL-3-CARBOXY PYRIDINIUM CHLORIDE	1-PROPYL-3-CARBOXYPYRIDINIUM BROMIDE	
	1·0 gl^{-1}	4·0 gl^{-1}	10·0 gl^{-1}
5	0·11	0·02	0·04
10	0·17	0·02$_5$	0·08
15	0·22	0·03	0·12$_5$
20	0·27	0·03$_5$	0·16
25	0·31	0·04	0·19
30	0·34$_5$	0·04$_5$	0·22
35	0·39$_5$	0·05	0·24
40	0·43	0·05$_5$	0·26
45	0·45	0·06	0·29
50	0·49	0·06$_5$	0·30
55	0·52	0·07	0·32
60	0·54$_5$	0·07$_5$	0·33

APPENDIX (x) DATA FOR GRAPH 9

$5\ gl^{-1}$ 1-BENZYL-4-CARBOXYPYRIDINIUM CHLORIDE & $100\ gl^{-1}$ SODIUM HYDROXIDE.

WAVELENGTH IN NANOMETRES		330	340	350	360	370	380	390	400
TIME IN HOURS	0	0·83	$0·35_5$	$0·15_5$	0·08	0·05	0·04	0·03	$0·02_5$
	17	0·85	0·36	0·16	0·08	$0·05_5$	$0·04_5$	0·03	$0·02_5$
	41	0·9	0·39	0·17	0·09	$0·06_5$	0·05	$0·03_5$	0·03

APPENDIX (xi) DATA FOR GRAPH 10

$5\ gl^{-1}$ 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE & $100\ gl^{-1}$ SODIUM HYDROXIDE.

WAVELENGTH IN NANOMETRES	OPTICAL DENSITY AT TIME (IN HOURS) INDICATED					
	zero	3	5	6	7	25
510		$0·30_5$	0·42	$0·47_5$	0·54	0·83
520		$0·20_5$	$0·30_5$	0·35	0·41	0·69
530		0·14	0·21	0·26	$0·31_5$	0·57
540		$0·10_5$	0·17	$0·21_5$	$0·26_5$	0·48
550		$0·09_5$	0·16	0·20	0·25	$0·40_5$
560		0·11	0·17	0·21	0·26	0·34
570		$0·13_5$	0·19	0·23	$0·27_5$	0·28
580		0·15	$0·20_5$	$0·23_5$	0·28	0·22
590		0·13	0·16	0·17	0·20	0·18
600		$0·09_5$	$0·10_5$	0·11	0·12	$0·12_5$

APPENDIX (xii)

GROWTH OF MAXIMUM AT ABOUT 360 nm.
IN THE PRESENCE AND ABSENCE OF ZINC.

TIME IN MINUTES	$2gl^{-1}$ 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE + $100gl^{-1}$ NaOH		TIME IN MINUTES	$2gl^{-1}$ 1-BENZYL-3-CARBOXYPYRIDINIUM CHLORIDE + $100gl^{-1}$ NaOH	
	With Zn^{2+}	Without Zn^{2+}		With Zn^{2+}	Without Zn^{2+}
2	0·18	0·17	16	$0{\cdot}63_5$	0·65
3	$0{\cdot}20_5$	$0{\cdot}20_5$	17	$0{\cdot}66_5$	0·67
4	$0{\cdot}24_5$	0·24	18	$0{\cdot}69_5$	0·70
5	$0{\cdot}27_5$	$0{\cdot}26_5$	19	0·72	$0{\cdot}72_5$
6	$0{\cdot}31_5$	$0{\cdot}31_5$	20	0·75	0·75
7	0·34	0·35	21	$0{\cdot}77_5$	0·77
8	0·38	0·39	22	$0{\cdot}80_5$	0·80
9	0·41	$0{\cdot}42_5$	23	$0{\cdot}83_5$	0·82
10	0·45	0·46	24	$0{\cdot}86_5$	0·85
11	0·48	0·49	25	0·89	0·88
12	0·51	$0{\cdot}52_5$	26	$0{\cdot}91_5$	0·91
13	$0{\cdot}54_5$	0·56	27	$0{\cdot}94_5$	$0{\cdot}95_5$
14	$0{\cdot}57_5$	0·59	28	0·97	0·97
15	$0{\cdot}60_5$	$0{\cdot}61_5$	29	1·00	$0{\cdot}98_5$

Data for Graphs 11 & 12

$\alpha = 0.02575$ $\beta = 0.44$ $\delta = 2.15$ milligrams $\omega = 0.5758$ grams.

TEMPERATURE IN °K	WT. IN GRAMS OF GOUY TUBE AND SAMPLE NO FIELD	WT. IN GRAMS OF GOUY TUBE AND SAMPLE WITH FIELD	WT. GAIN F IN MILLIGRAMS	F + δ IN MILLIGRAMS	$\chi \cdot 10^{-6} = \frac{\alpha + (F+\delta)\beta}{\omega}$
293	7.2972_5	7.2986_5	1.4	3.55	2.76
283	7.2972	7.2987_5	1.55	3.7	2.87
273	7.2970	7.2987	1.7	3.85	2.99
263	7.2969	7.2987_5	1.85	4.0	3.10
253	7.2967_5	7.2988	2.05	4.2	3.25
243	7.2966_5	7.2989	2.25	4.4	3.41
233	7.2965	7.2989_5	2.45	4.6	3.56
223	7.2963_5	7.2990	2.65	4.8	3.71
213	7.2961_5	7.2990_5	2.9	5.05	3.90
203	7.2959_5	7.2990_5	3.1	5.3	4.10
193	7.2957	7.2991_5	3.45	5.6	4.32
183	7.2955	7.2992_5	3.75	5.9	4.55
173	7.2952	7.2993	4.1	6.25	4.82
163	7.2949	7.2994	4.5	6.65	5.13
153	7.2944	7.2993	4.9	7.05	5.43
143	7.2940_5	7.2994_5	5.4	7.55	5.81
133	7.2936	7.2995_5	5.95	8.1	6.23
123	7.2931	7.2996_5	6.55	8.7	6.69
113	7.2924	7.2997	7.3	9.45	7.27
103	7.2917_5	7.2998	8.05	10.2	7.84
93	7.2909	7.2999	9.0	11.15	8.57

Data for Graphs 11 & 12

TEMPERATURE IN °K	$\chi \cdot 10^{-6}$	$\chi \cdot 336{\cdot}75$ $\chi_m \cdot 10^{-6}$	$\chi_m + 135{\cdot}41$ $\cdot\, \chi'_m \cdot 10^{-6}$	$\frac{1}{\chi'_m} \cdot 10^2$	μ $= 2{\cdot}84\sqrt{\chi'_m \cdot T}$
293	2·76	927	1062	$9{\cdot}41_5$	$1{\cdot}58_5$
283	2·87	964	1099	9·1	$1{\cdot}58_4$
273	2·99	1003	1138	8·79	$1{\cdot}58_4$
263	3·10	1041	1176	8·5	1·58
253	3·25	1093	1228	8·14	$1{\cdot}58_5$
243	3·41	1144	1279	7·82	$1{\cdot}58_4$
233	3·56	1195	1331	7·52	$1{\cdot}58_2$
223	3·71	1247	1382	$7{\cdot}23_5$	$1{\cdot}57_7$
213	3·90	1311	1446	$6{\cdot}91_5$	$1{\cdot}57_7$
203	4·10	1375	1510	6·62	$1{\cdot}57_3$
193	4·32	1452	1587	6·30	$1{\cdot}57_{25}$
183	4·55	1529	1664	6·01	$1{\cdot}56_8$
173	4·82	1619	1754	5·70	$1{\cdot}56_5$
163	5·13	1721	1857	5·39	$1{\cdot}56_3$
153	5·43	1824	1959	5·10	$1{\cdot}55_6$
143	5·81	1952	2088	4·79	$1{\cdot}55_{25}$
133	6·23	2093	2229	4·49	$1{\cdot}54_7$
123	6·69	2247	2383	4·20	$1{\cdot}53_8$
113	7·27	2440	2575	3·88	$1{\cdot}53_3$
103	7·84	2632	2768	3·61	$1{\cdot}51_8$
93	8·57	2876	3011	3·32	$1{\cdot}50_4$

Data for Graphs 13 & 14

$\alpha = 0.02575$ $\beta = 0.44$ $\delta = 2.15$ milligrams $\omega = 0.8234$ grams

TEMPERATURE IN °K.	WT. IN GRAMS OF GOUY TUBE & SAMPLE FIELD OFF	WT IN GRAMS OF GOUY TUBE & SAMPLE FIELD ON	WEIGHT GAIN F IN MILLIGRAMS	$F+\delta$ IN MILLIGRAMS	$\chi \cdot 10^{-6} = \frac{\alpha+(F+\delta)\beta}{\omega}$
293	7.5398	7.5618	22.0	24.15	12.94
283	7.5398	7.5622	22.4	24.55	13.15
273	7.5397	7.5624	22.7	24.85	13.31
263	7.5395	7.5628	23.3	25.45	13.63
253	7.5394	7.5629	23.5	25.65	13.74
243	7.5392_5	7.5634	24.1_5	26.30	14.09
233	7.5391	7.5637	24.6	26.75	14.33
223	7.5389	7.5642	25.3	27.45	14.70
213	7.5388	7.5646	25.8	27.95	14.97
203	7.5386	7.5650	26.4	28.55	15.29
193	7.5384	7.5655	27.1	29.25	15.66
183	7.5381	7.5661	28.0	30.15	16.14
173	7.5378	7.5667	28.9	31.05	16.62
163	7.5375	7.5676	30.1	32.25	17.26_5
153	7.5371	7.5682	31.1	33.25	17.80
143	7.5368	7.5694	32.6	34.75	18.60
133	7.5363	7.5703	34.0	36.15	19.35
123	7.5360	7.5714	35.4	37.55	20.10
113	7.5356	7.5726	37.0	39.15	20.95
103	7.5349	7.5742	39.3	41.45	22.18
93	7.5341_5	7.5757	41.5_5	43.70	23.38

Data for Graphs 13 & 14

TEMPERATURE IN °K	MAGNETIC SUSCEPTIBILITY $\chi \cdot 10^{-6}$	$\chi \,.\, 346$ $\chi_m \cdot 10^{-6}$	$\chi_m + 122{\cdot}61$ $\chi'_m \cdot 10^{-6}$	$\frac{1}{\chi'_m} \cdot 10^{2}$	μ $= 2{\cdot}84\sqrt{\chi'_m \cdot T}$
293	12·94	4477	4599	$2{\cdot}17_4$	3·30
283	13·15	4550	4672	2·14	3·27
273	13·31	4605	4728	$2{\cdot}11_5$	3·23
263	13·63	4716	4838	2·07	$3{\cdot}20_5$
253	13·74	4754	4876	2·05	$3{\cdot}15_6$
243	14·09	4875	4997	2·00	3·13
233	14·33	4958	5080	1·97	3·09
223	14·70	5086	5208	1·92	3·06
213	14·97	5180	5302	$1{\cdot}88_6$	3·02
203	15·29	5290	5412	1·85	2·98
193	15·66	5418	5540	$1{\cdot}80_5$	2·94
183	16·14	5584	5706	1·75	2·90
173	16·62	5750	5872	$1{\cdot}70_3$	2·86
163	$17{\cdot}26_5$	5974	6096	1·64	2·83
153	17·80	6159	6281	1·59	$2{\cdot}78_6$
143	18·60	6436	6558	$1{\cdot}52_5$	2·75
133	19·35	6695	6817	1·47	$2{\cdot}70_6$
123	20·10	6955	7077	$1{\cdot}41_3$	2·65
113	20·95	7249	7371	1·36	$2{\cdot}59_4$
103	22·18	7674	7796	1·28	2·55
93	23·38	8089	8211	1·22	$2{\cdot}48_4$

Data for Graphs 15 & 16

α = 0·02575 β = 0·44 δ = 2·15 milligrams ω = 0·8292 grams

TEMPERATURE IN °K	WT. IN GRAMS OF Gouy TUBE + SAMPLE FIELD OFF	WT. IN GRAMS OF Gouy TUBE + SAMPLE FIELD ON	WT. GAIN F IN MILLIGRAMS	F + δ IN MILLIGRAMS.	MAGNETIC SUSCEPTIBILITY $\chi \cdot 10^{-6}$
298	7·5511	7·5544	3·3	5·45	2·92
293	7·5510	7·5543	3·3	5·45	2·92
283	7·5509	7·5542$_5$	3·35	5·50	2·95
273	7·5508$_5$	7·5543	3·45	5·60	3·00
263	7·5507	7·5542	3·50	5·65	3·03
253	7·5505	7·5541$_5$	3·65	5·8	3·11
243	7·5504	7·5541	3·70	5·85	3·14
233	7·5502	7·5537$_5$	3·55	5·70	3·06
223	7·5500	7·5533	3·3	5·45	2·92
213	7·5497	7·5529$_5$	3·25	5·40	2·89
203	7·5496	7·5526	3·0	5·15	2·76
193	7·5492$_5$	7·5522	2·95	5·10	2·74
183	7·5491	7·5517	2·6	4·75	2·55
173	7·5487	7·5512	2·5	4·65	2·50
163	7·5486	7·5504	1·8	3·95	2·13
153	7·5482	7·5499	1·7	3·85	2·07
143	7·5479	7·5490	1·1	3·25	1·76
133	7·5473$_5$	7·5484$_5$	1·1	3·25	1·76
123	7·5467$_5$	7·5474$_5$	0·7	2·85	1·54
113	7·5463	7·5469$_5$	0·65	2·80	1·52
103	7·5453	7·5457	0·4	2·55	1·38
93	7·5441	7·5444$_5$	0·35	2·50	1·36

Data for Graphs 15 & 16

TEMPERATURE IN °K	$\chi \cdot 10^{-6}$	$\chi . 248{\cdot}74$ $\chi_m \cdot 10^{-6}$	$\chi_m + 107{\cdot}18$ $\chi'_m \cdot 10^{-6}$	$\frac{1}{\chi'_m} \cdot 10^2$	$\mu = 2{\cdot}84\sqrt{\chi'_m \cdot T}$
298	2·92	726	834	1·20	1·42
293	2·92	726	834	1·20	1·40
283	2·95	734	841	1·19	1·39
273	3·00	746	853	1·17	1·37
263	3·03	754	861	1·16	1·35
253	3·11	774	881	$1{\cdot}13_5$	1·34
243	3·14	781	888	1·13	1·32
233	3·06	761	868	1·15	1·28
223	2·92	726	834	1·20	$1{\cdot}22_5$
213	2·89	719	826	1·21	1·19
203	2·76	687	794	1·26	1·14
193	2·74	682	789	1·27	1·11
183	2·55	634	742	1·35	1·05
173	2·50	622	729	1·37	1·01
163	2·13	530	637	1·57	0·92
153	2·07	515	622	1·61	0·88
143	1·76	438	545	$1{\cdot}83_5$	0·79
133	1·76	438	545	$1{\cdot}83_5$	$0{\cdot}76_5$
123	1·54	383	490	2·04	0·70
113	1·52	378	485	2·06	0·67
103	1·38	343	450	2·22	0·61
93	1·36	338	446	$2{\cdot}24_5$	0·58

Data for Graph 17

TEMPERATURE IN °K	$\chi_m \cdot 10^{-6}$ EXPERIMENTAL	$\chi_m \cdot 10^{-6}$ CALCULATED
298	726·3	751·5
293	726·3	754·9
283	733·8	761·2
273	746·2	766·5
263	753·7	770·7
253	773·6	773·5
243	781·0	774·5
233	761·1	773·4
223	726·3	769·8
213	718·9	763·1
203	686·5	752·9
193	681·5	738·3
183	634·3	718·8
173	621·9	693·6
163	529·8	661·7
153	514·9	622·5
143	437·8	575·5
133	437·8	520·1
123	383·1	456·8
113	378·1	386·5
103	343·3	311·4
93	338·3	243·9

RESULTS OF MAGNETIC SUSCEPTIBILITY MEASUREMENTS AT VARIOUS CURRENTS (MAGNETIC FIELDS)

Calculated from $\chi = \frac{\alpha + (F+\delta)\beta}{w}$

Where,

α & β are constants for the Gouy tube

F is the weight increase (in milligrams)

δ is the diamagnetic correction for the Gouy tube

w is the weight of the sample (in grams)

Blue Copper(II) & 2,2'-Oxydibenzoate

wt. tube = 4.3841g   wt. sample = 0.5384g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	4·9225				
5	4·9247	2·2	2·65	0·475	2·38
5½	4·9249	2·4	2·9	0·4144	2·28
6	4·9252	2·7	3·25	0·3735	2·30
6½	4·9255	3·0	3·6	0·34	2·32
7	4·9257	3·2	3·85	0·315	2·30
7½	4·9259	3·4	4·1	0·295	2·29
8	4·9261	3·6	4·35	0·278	2·29
8½	4·9263	3·8	4·6	0·263	2·29
9	4·9265	4·0	4·8	0·25	2·27
9½	4·9267	4·2	5·1	0·24	2·32
10	4·9268	4·3	5·25	0·231	2·30

wt. tube = 4.3841g   wt. sample = 0.5474g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	4·9315				
5	4·9336	2·1	2·55	0·475	2·26
5½	4·9339	2·4	2·9	0·4144	2·24
6	4·9342	2·7	3·25	0·3735	2·26
6½	4·9344	2·9	3·5	0·34	2·22
7	4·9347	3·2	3·85	0·315	2·26
7½	4·9349	3·4	4·1	0·295	2·26
8	4·9351$_5$	3·65	4·4	0·278	2·28
8½	4·9353	3·8	4·6	0·263	2·26
9	4·9355$_5$	4·05	4·9	0·25	2·28
9½	4·9357	4·2	5·1	0·24	2·28
10	4·9359	4·4	5·35	0·231	2·30

Green Copper(II) & 2,2'-Oxydibenzoate

wt. tube = 4.3190g   wt. sample = 0.5399g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	$F+\delta$ (mg.)	β	χ
0	4·8589				
5	4·8616	2·7	3·15	0·475	2·82
5½	4·8620	3·1	3·6	0·4144	2·81
6	4·8623	3·4	3·95	0·3735	2·78
6½	4·8626	3·7	4·3	0·34	2·75
7	4·8629	4·0	4·65	0·315	2·76
7½	4·8631	4·2	4·9	0·295	2·72
8	4·8634	4·5	5·25	0·278	2·75
8½	4·8636	4·7	5·5	0·263	2·73
9	$4·8638_5$	4·95	5·8	0·25	2·73
9½	$4·8640_5$	5·15	6·05	0·24	2·74
10	$4·8642_5$	5·35	6·3	0·231	2·74

wt. tube = 4.3190g   wt. sample = 0.5071_5g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	$F+\delta$ (mg)	β	χ
0	$4·8261_5$				
5	4·8287	2·55	3·0	0·475	2·86
5½	4·8291	2·95	3·45	0·4144	2·87
6	4·8294	3·25	3·8	0·3735	2·85
6½	4·8297	3·55	4·15	0·34	2·83
7	4·8301	3·95	4·6	0·315	2·91
7½	$4·8303_5$	4·2	4·9	0·295	2·90
8	4·8306	4·45	5·2	0·278	2·90
8½	4·8308	4·65	5·45	0·263	2·88
9	4·8310	4·85	5·7	0·25	2·86
9½	4·8312	5·05	5·95	0·24	$2·86_5$
10	4·8314	5·25	6·2	0·231	2·87

Purple Cobalt(II) & 2,2'-Oxydibenzoate

wt. tube = 4.3842g wt. sample = 0.8472g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·2314				
5	5·2770	45·6	46·1	0·475	25·88
5½	5·2834	52·0	52·5	0·4144	25·71
6	5·2895	58·1	58·7	0·3735	25·91
6½	5·2950	63·6	64·2	0·34	25·79
7	5·2998	68·4	69·1	0·315	25·72
7½	5·3046	73·2	73·9	0·295	25·76
8	5·3094	78·0	78·8	0·278	25·89
8½	5·3136	82·2	83·0	0·263	25·79
9	5·3175	86·1	87·0	0·25	25·70
9½	5·3215	90·1	91·0	0·24	25·81
10	5·3246	93·2	94·2	0·231	25·71

wt. tube = 4.3842g wt. sample = 0.8531g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·2373				
5	5·2836	46·3	46·8	0·475	26·08
5½	5·2904	53·1	53·6	0·4144	26·06
6	5·2965	59·2	59·8	0·3735	26·21
6½	5·3019	64·6	65·2	0·34	26·01
7	5·3067	69·4	70·1	0·315	25·91
7½	5·3115	74·2	74·9	0·295	25·93
8	5·3161	78·8	79·6	0·278	25·97
8½	5·3207	83·4	84·2	0·263	25·99
9	5·3248	87·5	88·3	0·25	25·91
9½	5·3285	91·2	92·1	0·24	25·94
10	5·3320	94·7	95·7	0·231	25·94

Blue Cobalt & 2,2'-Oxydibenzoate

wt. tube = 4.3842g wt. sample = 0.7911g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·1753				
5	5·2251	49·8	50·25	0·475	30·20
5 ½	5·2322	56·9	57·4	0·4144	30·10
6	5·2386	63·3	63·85	0·3735	30·18
6 ½	5·2448	69·5	70·1	0·34	30·16
7	5·2503	75·0	75·65	0·315	30·15
7 ½	5·2554	80·1	80·8	0·295	30·16
8	5·2604	85·1	85·85	0·278	30·20
8 ½	5·2649	89·6	90·4	0·263	30·08
9	5·2694	94·1	94·95	0·25	30·04
9 ½	5·2736	98·4	99·2	0·24	30·13
10	5·2767	101·4	102·35	0·231	29·92

wt. tube = 4.3842g wt. sample = 0.8930g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·2772				
5	5·3315	54·3	54·75	0·475	29·15
5 ½	5·3389	61·7	62·2	0·4144	28·89
6	5·3460	68·8	69·35	0·3735	29·03
6 ½	5·3523	75·1	75·7	0·34	28·85
7	5·3583	81·1	81·75	0·315	28·86
7 ½	5·3641	86·9	87·6	0·295	28·97
8	5·3692	92·0	92·75	0·278	28·90
8 ½	5·3741	96·9	97·7	0·263	28·80
9	5·3791	101·9	102·75	0·25	28·79
9 ½	5·3838	106·6	107·5	0·24	28·92
10	5·3872	110·0	110·95	0·231	28·73

Blue Cobalt(II) & 2,2'-Oxydibenzoate

wt. tube = 4.3842g wt. sample = 0.7914g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg.)	β	χ
0	5·1756				
5	5·2250	49·4	49·85	0·475	29·95
5 ½	5·2323	56·7	57·2	0·4144	29·98
6	5·2381	62·5	63·05	0·3735	29·79
6 ½	5·2446	69·0	69·6	0·34	29·93
7	5·2498	74·2	74·85	0·315	29·82
7 ½	5·2551	79·5	80·2	0·295	29·93
8	5·2591	83·5	84·25	0·278	29·63
8 ½	5·2640	88·4	89·2	0·263	29·67
9	5·2682	92·6	93·45	0·25	29·55
9½	5·2730	97·4	98·3	0·24	29·84
10	5·2773	101·7	102·65	0·231	29·99

wt. tube = 4.3842g wt. sample = 0.7961g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·1803				
5	5·2309	50·6	51·05	0·475	30·49
5 ½	5·2380	57·7	58·2	0·4144	30·33
6	5·2451	64·8	65·35	0·3735	30·69
6 ½	5·2511	70·8	71·4	0·34	30·53
7	5·2563	76·0	76·65	0·315	30·36
7 ½	5·2616	81·3	82·0	0·295	30·42
8	5·2668	86·5	87·25	0·278	30·50
8 ½	5·2717	91·4	92·2	0·263	30·49
9	5·2758	95·5	96·35	0·25	30·29
9 ½	5·2803	100·0	100·9	0·24	30·45
10	5·2839	103·6	104·55	0·231	30·37

Iron(III) & 2,2'-Oxydibenzoate

wt. tube = 4.4524_5g wt. sample = 0.3710_5g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	4·8235				
5	$4{\cdot}8321_5$	8·65	9·1	0·475	11·72
5½	4·8335	10·00	10·5	0·4144	11·79
6	4·8346	11·1	11·65	0·3735	11·79
6½	4·8356	12·1	12·7	0·34	11·70
7	4·8366	13·1	13·75	0·315	11·74
7½	4·8375	14·0	14·7	0·295	11·75
8	4·8383	14·8	15·55	0·278	11·72
8½	$4{\cdot}8391_5$	15·65	16·45	0·263	11·73
9	$4{\cdot}8398_5$	16·35	17·2	0·25	11·66
9½	4·8407	17·2	18·1	0·24	$11{\cdot}77_5$
10	4·8413	17·8	18·75	0·231	11·74

wt. tube = 4.4524_5g wt. sample = 0.3697_5g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	4·8222				
5	$4{\cdot}8312_5$	9·05	9·6	0·475	12·36
5½	$4{\cdot}8324_5$	10·25	10·75	0·4144	12·07
6	4·8336	11·4	11·95	0·3735	12·10
6½	$4{\cdot}8346_5$	12·45	13·05	0·34	12·03
7	4·8356	13·4	14·05	0·315	$11{\cdot}99_5$
7½	4·8365	14·3	15·0	0·295	11·99
8	4·8374	15·2	15·95	0·278	12·02
8½	4·8382	16·0	16·8	0·263	11·98
9	4·8390	16·8	17·65	0·25	11·96
9½	4·8397	17·5	18·4	0·24	11·97
10	$4{\cdot}8404_5$	18·25	19·2	0·231	12·02

Iron(III) & 2,2'-Oxydibenzoate

wt. tube = 4.4522g   wt. sample = 0.3865g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	4·8387				
5	4·8465	7·8	8·25	0·475	10·20
5½	$4·8476_5$	8·95	9·45	0·4144	10·20
6	4·8488	10·1	10·65	0·3735	10·36
6½	4·8498	11·1	11·7	0·34	10·36
7	4·8507	12·0	12·65	0·315	$10·37_5$
7½	4·8515	12·8	13·5	0·295	10·37
8	4·8523	13·6	14·35	0·278	10·39
8½	4·8531	14·4	15·2	0·263	10·41
9	4·8538	15·1	15·95	0·25	10·38
9½	4·8544	15·7	16·6	0·24	10·37
10	4·8550	16·3	17·25	0·231	10·37

wt. tube = 4.4522g   wt. sample = 0.3961_5g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	$4·8483_5$				
5	$4·8565_5$	8·2	8·65	0·475	$10·43_5$
5½	$4·8577_5$	9·4	9·9	0·4144	10·42
6	4·8589	10·55	11·1	0·3735	10·53
6½	$4·8597_5$	11·4	12·0	0·34	10·36
7	$4·8607_5$	12·4	13·05	0·315	10·44
7½	4·8615	13·15	13·85	0·295	10·38
8	$4·8623_5$	14·0	14·75	0·278	10·41
8½	4·8631	14·75	15·55	0·263	10·39
9	4·8638	15·45	16·3	0·25	10·35
9½	4·8645	16·15	17·05	0·24	10·39
10	4·8651	16·75	17·7	0·231	10·39

Brown crystals with Golden Sheen from $(NH_4)_2.SO_4.FeSO_4$ & 2,2'-Oxydibenzoate

wt. tube = 4.6803g   wt. sample = 0.5240g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·2043				
5	5·2181	13·8	14·05	0·47	12·66
5½	5·2198	15·5	15·75	0·4185	12·63
6	5·2215	17·2	17·42$_5$	0·382	12·76
6½	5·2227$_5$	18·45	18·67$_5$	0·3525	12·62
7	5·2242	19·9	20·12$_5$	0·3256	12·56
7½	5·2255	21·2	21·4	0·306	12·55
8	5·2269$_5$	22·65	22·85	0·288	12·61
8½	5·2280	23·7	23·9	0·275	12·60
9	5·2295	25·2	25·37$_5$	0·2608	12·68$_5$
9½	5·2308$_5$	26·55	26·72$_5$	0·2514	12·88
10	5·2315	27·2	27·37$_5$	0·2415	12·67

wt. tube = 4.6803g   wt. sample = 0.9130g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·5933				
5	5·6168$_5$	23·53	23·8	0·47	12·28
5½	5·6197$_5$	26·45	26·7	0·4185	12·27
6	5·6225	29·2	29·42$_5$	0·382	12·34
6½	5·6249	31·6	31·82$_5$	0·3525	12·32
7	5·6274$_5$	34·15	34·37$_5$	0·3256	12·29
7½	5·6297$_5$	36·45	36·65	0·306	12·31$_5$
8	5·6319	38·6	38·8	0·288	12·27
8½	5·6339$_5$	40·65	40·85	0·275	12·34
9	5·6359	42·6	42·77$_5$	0·2608	12·25
9½	5·6378	44·5	44·67$_5$	0·2514	12·33
10	5·6395	46·2	46·37$_5$	0·2415	12·30

Brown crystals with Golden Sheen from $(NH_4)_2.SO_4.FeSO_4$ & 2,2'-Oxydibenzoate

wt. tube = 5.2160g   wt. sample = 0.9166g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg.)	β	χ
0	6·1326				
5	6·1561	23·5	23·7	0·48	12·44
5½	6·1591	26·5	26·7	0·4285	12·51
6	6·1623	29·7	29·9	0·386	12·62
6½	6·16475	32·15	32·32$_5$	0·353	12·48
7	6·1673	34·7	34·87$_5$	0·326	12·43$_5$
7½	6·1696	37·0	37·17$_5$	0·306	12·44
8	6·1719$_5$	39·35	39·5	0·29	12·53
8½	6·1741	41·5	41·65	0·275	12·53
9	6·1762	43·6	43·75	0·26	12·44
9½	6·1781	45·5	45·62$_5$	0·25	12·47$_5$
10	6·1797	47·1	47·22$_5$	0·24	12·40

wt. tube = 5.2160g   wt. sample = 0.3153g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	F+δ (mg)	β	χ
0	5·5313				
5	5·5548	23·5	23·75	0·47	13·15
5½	5·5573	26·0	26·25	0·4185	12·94
6	5·5602	28·9	29·12$_5$	0·382	13·11
6½	5·5627$_5$	30·45	30·67$_5$	0·3525	12·74
7	5·5651	33·8	34·02$_5$	0·3256	13·05
7½	5·5674	36·1	36·3	0·306	12·99
8	5·5695$_5$	38·25	38·45	0·288	13·05
8½	5·5718	40·5	40·7	0·275	13·19
9	5·5737	42·4	42·57$_5$	0·2608	13·08
9½	5·5754$_5$	44·15	44·32$_5$	0·2514	13·13
10	5·5771$_5$	45·85	46·02$_5$	0·2415	13·09$_5$

Copper(II) & 3,3'-Thiodipropionate

wt. tube = 4.3188_5g   wt. sample = 0.9169

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	$F+\delta$ (mg)	β	χ
0	5.2357_5				
5	5.2414_5	5.7	6.15	0.475	3.16
5 ½	5.2422	6.45	6.95	0.4144	3.11
6	5.2428_5	7.1	7.65	0.3735	3.09
6 ½	5.2434_5	7.7	8.3	0.34	3.05
7	5.2440_5	8.3	8.95	0.315	3.05
7 ½	5.2446	8.85	9.55	0.295	3.04_5
8	5.2451_5	9.4	10.15	0.278	3.05
8 ½	5.2457	9.95	10.75	0.263	3.06
9	5.2461_5	10.4	11.25	0.25	3.04
9 ½	5.2465_5	10.8	11.7	0.24	3.03_5
10	5.2470	11.25	12.2	0.231	3.05

wt. tube = 4.3188_5g   wt. sample = 0.9594_5g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	$F+\delta$ (mg)	β	χ
0	5.2783				
5	5.2842_5	5.95	6.4	0.475	3.14
5 ½	5.2848	6.5	7.0	0.4144	3.0
6	5.2856	7.3	7.85	0.3735	3.03
6 ½	5.2862_5	7.95	8.55	0.34	3.0
7	5.2869	8.6	9.25	0.315	3.01
7 ½	5.2875	9.2	9.9	0.295	3.02
8	5.2881	9.8	10.55	0.278	3.03
8 ½	5.2886_5	10.35	11.15	0.263	3.03
9	5.2891_5	10.85	11.7	0.25	3.02
9 ½	5.2896	11.3	12.2	0.24	3.02
10	5.2901	11.8	12.75	0.231	3.04

Copper(II) & 3,3'-Thiodipropionate

wt. tube = 4.4522_5g wt. sample = 0.9714g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	$F+\delta$ (mg)	β	χ'
0	5.4236_5				
5	5.4295_5	5.9	6.35	0.475	3.13
5 ½	5.4304	6.75	7.25	0.4144	3.12
6	5.4311_5	7.5	8.05	0.3735	3.12
6 ½	5.4319	8.25	8.85	0.34	3.12
7	5.4324_5	8.8	9.45	0.315	3.09
7 ½	5.4331	9.45	10.15	0.295	3.11
8	5.4337	10.05	10.8	0.278	3.12
8 ½	5.4342	10.55	11.35	0.263	3.10
9	5.4347_5	11.1	11.95	0.25	3.10
9 ½	5.4352	11.55	12.45	0.24	3.10
10	5.4356_5	12.0	12.95	0.231	3.11

wt. tube = 4.4522_5g wt. sample = 0.9354_5g

CURRENT IN AMPERES	WT. OF TUBE & SAMPLE FIELD ON	WT. GAIN F (mg)	$F+\delta$ (mg)	β	χ
0	5.3877				
5	5.3935	5.8	6.25	0.475	3.20
5 ½	5.3943	6.6	7.1	0.4144	3.17
6	5.3950_5	7.35	7.9	0.3735	3.18
6 ½	5.3957	8.0	8.6	0.34	3.15
7	5.3963	8.6	9.25	0.315	3.14
7 ½	5.3969	9.2	9.9	0.295	3.15
8	5.3974_5	9.75	10.5	0.278	3.15
8 ½	5.3979_5	10.25	11.05	0.263	3.13
9	5.3984_5	10.75	11.6	0.25	3.13
9 ½	5.3989	11.2	12.1	0.24	3.13
10	5.3993_5	11.65	12.6	0.231	3.14

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